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РЕФЕРАТ

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Об'єкт дослідження – супрамолекулярні сполуки на прикладі комплексів "гість-хазяїн" при використанні у якості молекул "хазяїнів" – кисень і азот вмістних краун-етерів різної будови, а у якості молекул "гостей" – органічних і неорганічних сполук.

Мета роботи – дослідження синтезу і фізико-хімічне тестування та аналіз нових оригінальних супрамолекулярних сполук (комплексів "гість-хазяїн") при використанні як порожнинні молекули "хазяїнів" – кисень і азот вмістних краун-етерів різної будівлі, а як молекул "гостей" – органічних і неорганічних сполук, у тому числі біологічноактивних сполук, а також лабільних рівноважних розчинів кислот.

Метод дослідження – розробка методики й синтез названих супрамолекулярних сполук у виді монокристалів і здійснення рентгеноструктурного дослідження для отриманих продуктів.

Експериментально доведена можливість зв'язування порожнинами краун-етерів тетраметру синильної кислоти, флуоро-кислот ніобію та танталу. Проведено розробку методики і здійснення синтезу "контейнера" цих кислот. Проведено також розробку методики і синтез комплексів 3-нітро-1,2,4-триазолу, 1Н-імідазол-4,5-дікарбонитрила, 3-нітро-1,2,4-триазолу, 1Н-тетразолу та пірімідин-2,4-дітіону з широким колом краун-етерів. Здійснений синтез комплексів тетрафлуороборату з діазакраун-етером. Закінчено роботи з виділення кремнефлуороводневої кислоти в індивідуальному виді. Розглянуто структурні аспекти взаємодії кремнефлуороводневої кислоти з краун-етерами. Здійснено розробку методики і синтез ряду оригінальних кристалічних супрамолекулярних сполук краун-етерів з органічними молекулами, у тому числі з об'єктами утримуючими фізіологічно активні фрагменти – зокрема комплексів 1,5-дібензо-18-кран-6 з похідними пірімідину, рубіановою кислотою, похідними 1,2,4-триазолу та пірімідин-2,4-дітіону. Проведено обговорення результатів рентгеноструктурних досліджень перерахованих комплексів і сполук включення. Зроблено висновки щодо особливостей синтезу нових супрамолекулярних речовин, істотності тих чи інших не валентних взаємодій, які

необхідно враховувати при моделюванні біохімічних і природних взаємодій, а також створення лабораторних методик.

Результати НДР використані у матеріалах конференцій, статтях у провідних наукових виданнях.

Ключові слова: кристалічні супрамолекулярні сполуки, комплекси "гість-хазяїн", краун-етері

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ВСТУП

Молекупярна хімія контролює ковалентні зв'язки. Супрамолекупярна хімія - "хімія за межами молекули". Її ціль - досягнення контролю над міжмолекулярними нековалентними взаємодіями. Супрамолекупярна хімія має справу з більш складними утвореннями, чим окремі молекул, - супрамолекупярними ансамблями утримуваними разом міжмолекулярними єднальними взаємодіями. Це - найвищою мірою міждисциплінарна галузь знання, що поєднує науку і технологію, що перекидає мости від хімії до біології. Результати супрамолекулярних досліджень неодмінно використовується як хімічна база при моделюванні молекулярних і міжмолекулярних взаємодій природних молекул, а взагалі і в навколишньому середовище, а також у спрямованому синтезі супрамолекулярних ансамблів.

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- Лен Ж-М. Супрамолекулярна хімія: Концепції і перспективи. Новосибірськ: Наука, 1998. 334 с. (мова - російська)

Лен Ж-М. є лауреатом Нобелівської премії і головним координатором сучасних супрамолекулярних досліджень у Європі й Америці.]

Об'єктами дослідження супрамолекулярної хімії є великі порожнинні молекули і їх комплекси з катіонами, аніонами та нейтральними молекулами, порівняно невеликого розміру. В останні десятиліття синтезовані і достатньо добре вивчені такі надзвичайно цікаві макрогетероциклічні сполуки як краун-етери, криптанди, кавитанди, каліксарени, аннулени, циклофани, катенани, ротаксани. Особливе місце при цьому в хімії макроциклів із ряду причин займають краун-етери, криптанди і їхні гетероаналоги. Такі сполуки здатні утворювати стабільні комплекси з іонами металів, нейтральними органічними сполуками і водою, солюбілюзовати їх в органічні розчинники, або переносити іони через природні і штучні мембрани.

Методами дослідження супрамолекулярної хімії є такі сучасні фізико-хімічні методи досліджень як ПМР, ІЧ, УФ, мас-спектрометрія, рентгеноструктурний аналіз і ін., що забезпечує надійність і однозначну інтерпретацію отриманих результатів.

Однак, далеко не всі закономірності таких взаємодій ретельно вивчені і доведені. Тому дослідження в цьому напрямку є досить актуальними.

Метою даного дослідження є синтез і фізико-хімічне тестування нових оригінальних супрамолекулярних сполук (комплексів "гість-хазяїн") при використанні як порожнинні молекули "хазяїнів" – кисень і азот вмістних краун-етерів різної будівлі, а як молекул "гостей" – органічних і неорганічних сполук, у тому числі порівнянних за розміром і функціональною структурою з краун-етерами, перед-біологічних сполук, а також лабільних рівноважних розчинів кислот. Результати цих досліджень можуть бути прийняті до уваги як хімічна основа при моделюванні молекулярних і міжмолекулярних взаємодій природних молекул, а також у спрямованому синтезі інших супрамолекулярних ансамблів. Отримані результати цієї роботи будуть апробовані на міжнародних конференціях, нарадах, симпозіумах і опубліковані в міжнародних журналах.

Задачі дослідження включають аналіз відомих літературних даних і розробку методів синтезу перерахованих вище об'єктів, перетворення їх у монокристали, здійснення рентгеноструктурних досліджень архітектури отриманих супрамолекулярних ансамблів у співавторстві з усілякими інтернаціональними науковими командами, аналіз і узгодження отриманих результатів відносно відомих феноменів включення, накопичення конструктивних висновків.

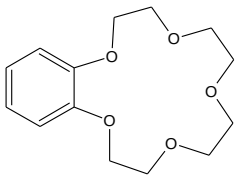
Термін виконання теми “Супрамолекулярна хімія на основі краун-етерів” з 01.01.2003 р. до 31.12.2006 р.

1 КОМПЛЕКСИ КРАУН-ЕТЕРІВ ТА ДІАМІНОМАЛЕОДІНІТРИЛА

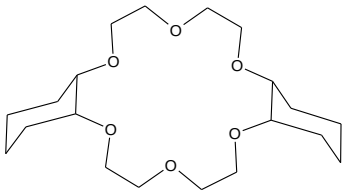
1,2-діаміномалеодінітрил [тетраметр синильної кислоти – $(HCN)_4$] прийнято розглядати як одну з ключових структур хімічної еволюції на шляху перетворення ціаністого водню в амінокислоти і гетероцикли.

Метою роботи було визначення можливості синтезу кристалічних молекулярних комплексів краун-етерів з 1,2-діаміномалеодінітрилом і виявлення вибірковісті у взаємодіях цих партнерів комплексоутворення.

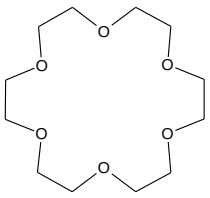
Встановлено, що при мимовільному випарі розчинників з розчинів краун-етерів – бензо-15-краун-5 (Bz15c5), 18-краун-6 (18c6), бензо-18-краун-6 (Bz18c6), суміші ціс-сін-ціс і ціс-анті-ціс ізомерів діциклогексано-18-краун-6 (A-DCH6 та B-DCH6) з 1,2-диаминомалеодінітрилом (DAMN) утворяться кристалічні молекулярні комплекси: [Bz15c5 · DAMN] - (I), [18c6 · DAMN] - (II), [Bz18c6 · DAMN] - (III), [B-DCH6 · DAMN] - (IV) відповідно.



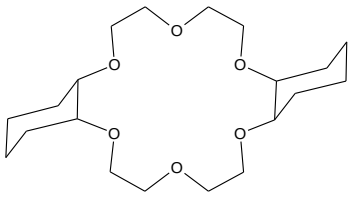
Bz15c5



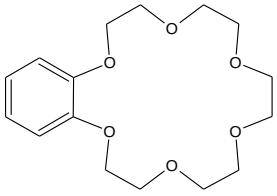
A-DCH6



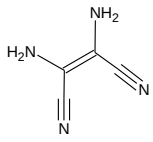
18c6



B-DCH6



Bz18c6



DAMN

Відзначимо, що при взаємодії 1,2-діаміномалеодінітрила із сумішшю ціс-сін-ціс та ціс-анті-ціс ізомерів діциклогексано-18-краун-6 комплекс утвориться селективно лише з ціс-анті-ціс ізомером, що має еквівалентно просторово екрановані сторони порожнини макроциклічного кільця. Описані взаємодії можуть бути враховані як складова частина при моделюванні молекулярних взаємодій природних молекул.

Отримані комплекси можуть становити інтерес як контейнери високорекційноздатного 1,2-діаміномалеодінітрила.

Як приклад, на рис. 1.1, приводимо структуру комплексу бензо-15-краун-5 з 1,2-діаміномалеодінітрилом – [Bz15c5 · DAMN]:

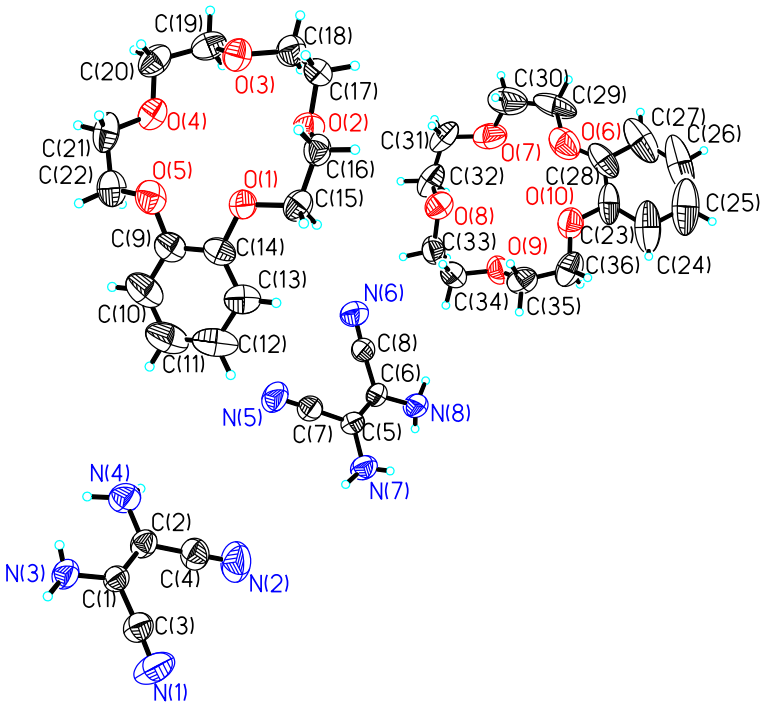


Рис 1.1 Структура комплексу бензо-15-краун-5 з 1,2-діаміномалеодінітрилом – [Bz15c5 · DAMN]

2 ВЗАЄМОДІЯ МОЛЕКУЛ "ХАЗЯЇНІВ"

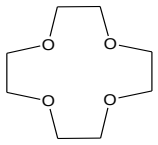
2.1 Селективна взаємодІя молекул "хазяїнів": краун-етерів з похідними трифенілметану

Пошук селективних взаємодій нейтральних молекул, що приводять до утворення молекулярних комплексів моделюючих широко розповсюджені процеси в біологічних системах є одна з пріоритетних задач хімії "гість-хазяїн". Вичерпним керівництвом [Comprehensive supramolecular chemistry / Editors J-M. Lehn, J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Wogtle. Oxford – New York – Tokyo: Pergamon, 1996, Vol. 1-11.] як краун-етери, так і похідні трифенілметану віднесені до молекул "хазяїв", здатним зв'язувати менші по розмірі "гостьові" молекули у комплекси.

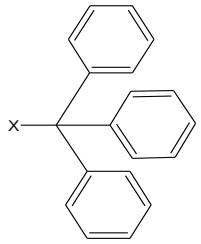
Ціль роботи – визначення можливості синтезу кристалічних молекулярних комплексів краун-етерів з похідними трифенілметану і виявлення селективності у взаємодіях цих партнерів комплексоутворення.

Встановлено, що при мимовільному випарі розчинників з розчинів малого "коронанду" – 1,4,7,10-тетраоксациклододекану (12с4) із трифенілметанолом (Іа), 1,1,1-трифенілметіламіном (Іб) і трифенилметантіолом (Ів) утворяться кристалічні молекулярні комплекси – [12с4·2$(C_6H_5)_3COH$] - (III), [12с4·2$(C_6H_5)_3CNH_2$] - (IV), [12с4·2 $(C_6H_5)_3CSH$] - (V) відповідно.

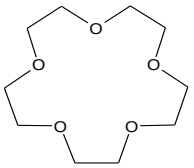
Виявлено також, що в цих же умовах при використанні суміші краун-етерів: 12с4, 15с5 та18с6 похідні трифенілметану (Іа,б) селективно утворять кристалічні комплекси лише з 12с4 - (III, IV). Введення в ароматичну частину молекули трифенілметанолу Н-донорної сульфамідної групи істотно змінює результат комплексоутворення.



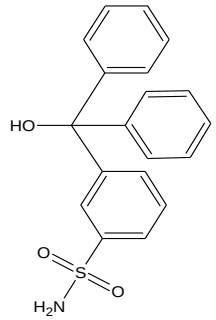
12к4



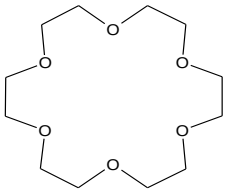
I а-в



15к5



II



18к6

Так при взаємодії 3-(гідроксидіфенілметіл)бензол сульфаміду (II) з названою сумішшю краун-етерів селективно виділяється кристалічний комплекс складу

$$[18к6 \cdot 2\ m\text{-}H_2NSO_2C_6H_4(C_6H_5)_2COH] – (VI).$$

Раніше у взаємодії нейтральних молекул з перерахованими краун-етерами селективності відзначено не було. Навпроти, N-(фенилсульфоніл)бензол сульфамід

$$– \ HN(SO_2C_6H_5)_2 –$$

дає кристалічні молекулярні комплекси як з 12с4, так і з 18с6.

Таким чином, вперше описані селективні взаємодії краун-етерів з об'ємними похідними трифенілметану кристалічних молекулярних комплексів, що приводять до утворення, (III, IV, VI) і що може бути враховане як складова частина при моделюванні молекулярних взаємодій порівняно великих природних молекул, а також являтися хімічною основою поділу сумішей краун-етерів. Як приклад, на рис. 2.1 приводимо структуру комплексу $[18к6 \cdot 2\ m\text{-}H_2NSO_2C_6H_4(C_6H_5)_2COH]$ – (VI):

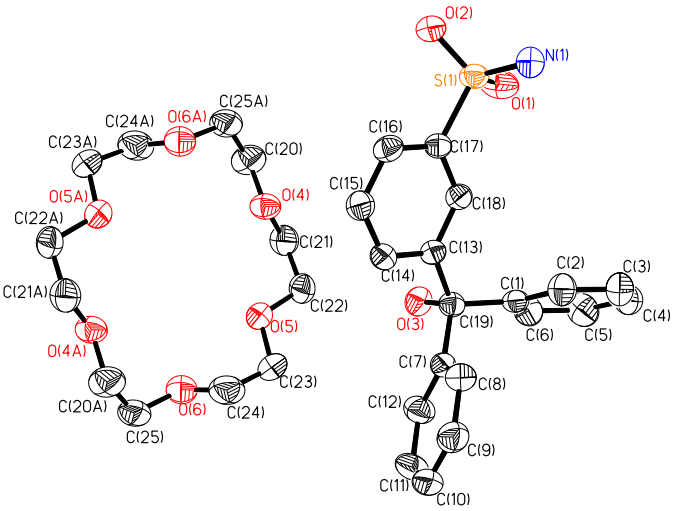


Рис. 2.1 Структура комплексу [18к6 · 2 *m*-$H_2NSO_2C_6H_4(C_6H_5)_2COH$] – (VI)

Відзначимо також, що вперше отримано кристалічний молекулярний комплекс краун-етера з меркаптаном (тіолом) та описана його структура - (V) – (рис. 2.2).

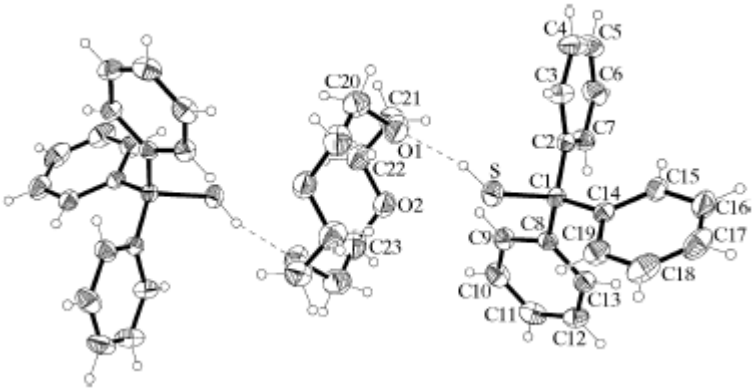


Рис. 2.2 Структура супрамолекулярного комплекса [12с4 • 2 $(C_6H_5)_3CSH$] - (V).

2.2 Комплекс діфенілтіосечовини з краун-етером

Як краун-етери, так і дІфенілсечовини [Comprehensive supramolecular chemistry / Editors J-M. Lehn, J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Wogtle. Oxford – New York – Tokyo: Pergamon, 1996, Vol. 1-11.] віднесені до молекул "хазяїв", здатних зв'язувати менші за розміром "гостьові" молекули у комплекси.

Взаємодією зазначених компонентів отриманий кристалічний молекулярний комплекс (рис. 2.3).

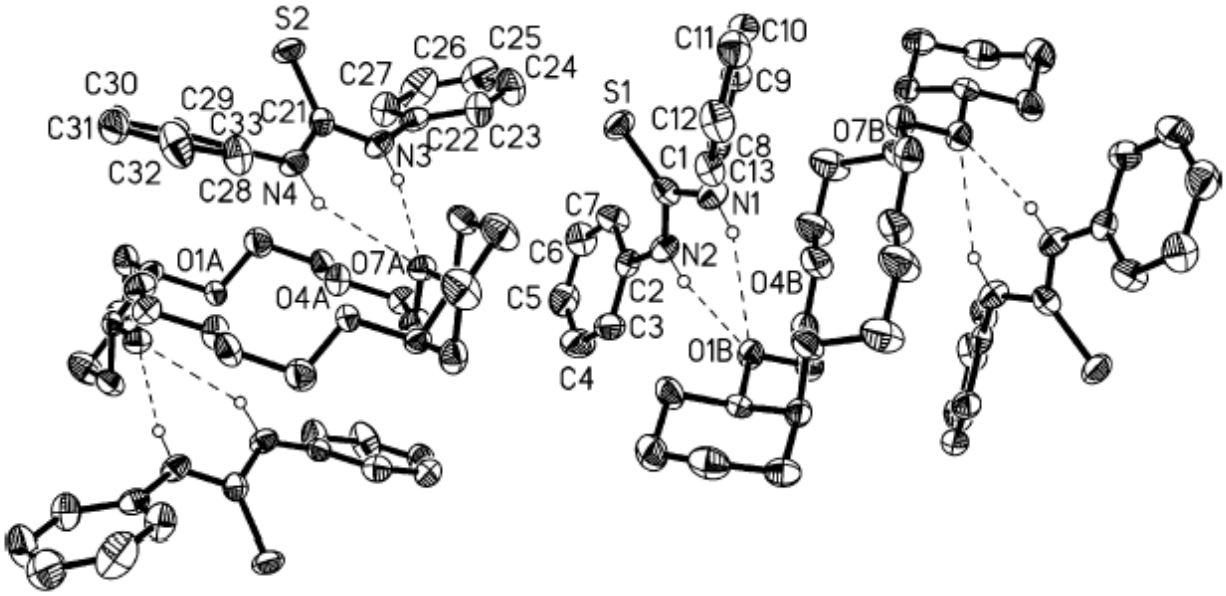


Рис. 2.3 Структура комплексу краун-етера та дІфенілтіосечовини

3 КОМПЛЕКСИ КРАУН-ЕТЕРІВ З 5- ТА 6-ЧЛЕННИМИ ГЕТЕРОЦИКЛАМИ

3.1 Комплекси краун-етерів з 3-нітро-1,2,4-триазолом та пірімідин-2,4-дітіоном

Взаємодією краун-етерів з 3-нітро-1,2,4-триазолом та пірімідин-2,4-дітіоном, що мають по одному протону при двох протонодонорних атомах, розділених валентним зв'язком, отримані кристалічні молекулярні комплекси "хазяїн-гість".

Неодмінною умовою утворення кристалічних молекулярних комплексів "хазяїн-гість" краун-етерів ("хазяїнів") з нейтральними "гостьовими" молекулами є присутність в "гості" протонодонорних центрів при одному С, N або О-атомах, (в частковості H_2N-, H_2NSO_2-, H_2NCS-, H_2NHNCO-, H_3N^+-, H_3C-, CH_3O-, H_2C= груп або молекул води), забезпечуючих стабілізацію компонент комплексу водневими зв'язками. У скріпленні, як правило, бере участь пара протонів донорного центру "гістя", причому стабільність комплексів падає у ланцюгу: $OH_2 > NH_2 > CH_2$. Відомі також нечисленні приклади утворення кристалічних комплексів " хазяїн-гість" при участі лише найефективніших 18-членних краун-етерів (Ib) і (V)] з "гостьовими" молекулами, зв'язуючі протони яких розташованих при сусідніх α-протонодонорних атомах, поодинці при кожному, розділених валентним зв'язком (малєїновий ангідрид, 2-тіоурацил).

Метою роботи було визначення можливості синтезу кристалічних молекулярних комплексів краун-етерів різної будови з "гостьовими" молекулами, що мають по одному протону при двох протонодонорних атомах, розділених валентним зв'язком.

Визначено, що при мимовільному випаровуванні розчинників з розчинів краун-етерів (I-V) з 3-нитро-1,2,4-триазолом (VI) і пірімідин-2,4-дітіоном (VII) утворюються кристалічні молекулярні комплекси (рис. 3.1.).

Утворення стійких кристалічних молекулярних комплексів нейтральних органічних молекул (VI, VII) з краун-етерами, що мають різний розмір макроциклічної порожнини - сполуки (Ia, Ib), ароматичні і аліфатічні заступники при ній - сполуки (II, III) і (IV, V) відповідно, а також різно просторово екрановані сторони порожнини макроциклічного кільця - сполуки (IV, V), дозволяє вважати, що факти скріплення краун-етерів в сполуки "хазяін-гість" молекулами яки мають по одному протону при двох протонодонорних атомах, розділених валентним зв'язком, носять невипадковий

характер, що може бути враховано при моделюванні молекулярних взаємодій природних молекул, а також спрямованому синтезі комплексів "хазяін-гість" краун-етерів і протонодонорних молекул.

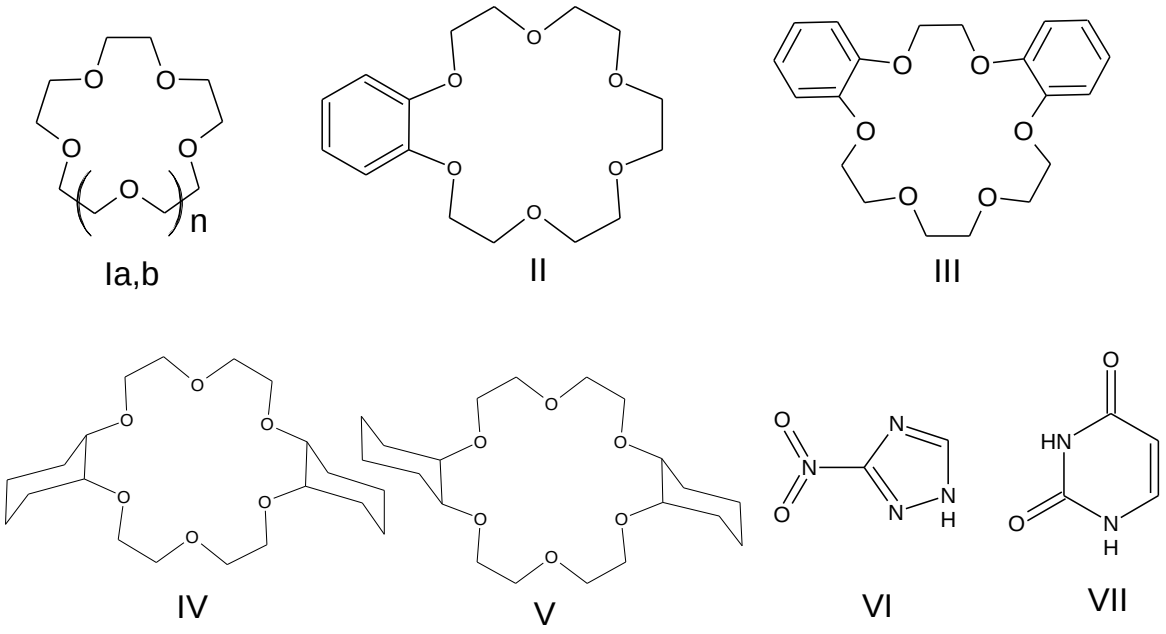


Рис. 3.1 Структура краун-етерів ("хазяїнів") та нейтральних "гостьових" молекул

3.2 Взаємодія краун-етерів з пя'тичленими гетероциклами: 1Н-імідазол-4,5-дікарбонітрилом, 3-нітро-1,2,4-триазолом і 1Н-тетразолом

Взаємодією 1Н-імідазол-4,5-дікарбонитрила, 3-нітро-1,2,4-триазола і 1Н-тетразола, що містять по одному протоні при двох сусідніх протонодонорных атомах розділених одним ковалентним зв'язком, із краун-етерами показана можливість одержання незаряджених кристалічних супрамолекулярних ансамблів за рахунок протонодонорных властивостей ароматичних гетероциклів (рис. 3.2).

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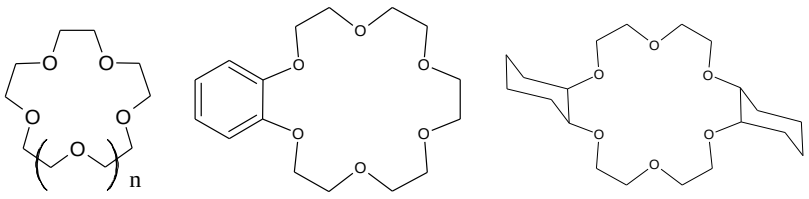
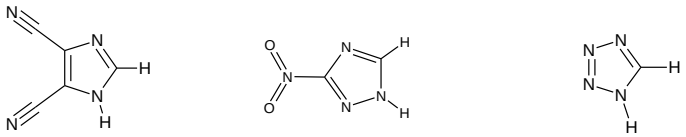


1a,b **2** **3**



4 **5** **6**

1a, n = 1, **b** n = 2

Рис. 3.2 Структура краун-етерів ("хазяїнів") та гетероциклічних "гостьових" молекул

3.3 Супрамолекулярні комплекси 2,4-дітіоурацилу з краун-етерами

Відомо що 2,4-дітіоурацил існує у 6 таутомерних формах (рис. 3.3).

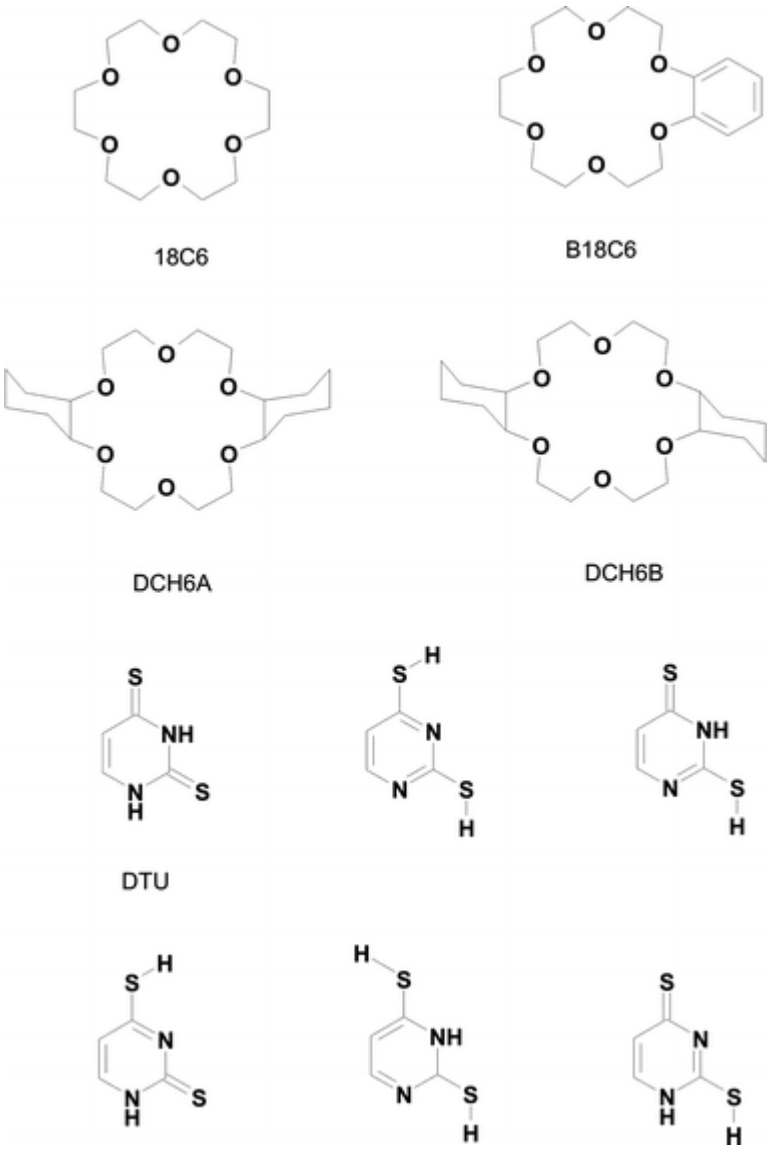


Рис. 3.3 Таутомерні форми 2,4-дітіоурацилу та використані краун-етері

Краун-етери селективно зв'язують у комплекси лише одну таутомерну форму 2,4-дітіоурацилу – DTU, першу (рис. 3.4).

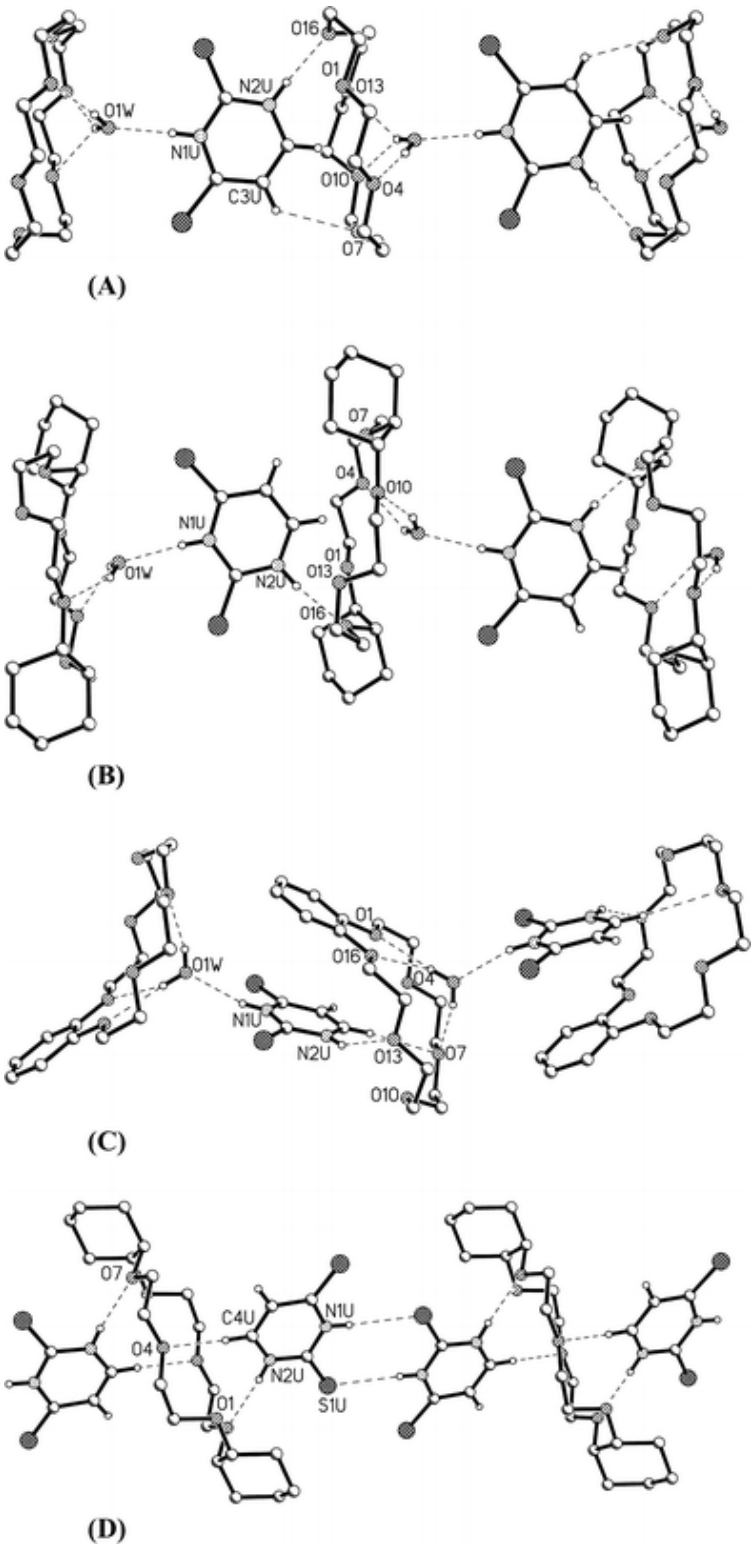


Рис. 3.4 Будова комплексів 2,4-дітіоурацилу та краун-етерів

4 КОМПЛЕКСИ КРАУН-ЕТЕРІВ ІЗ НЕЙТРАЛЬНИМИ МОЛЕКУЛАМИ РІЗНОЇ БУДОВИ

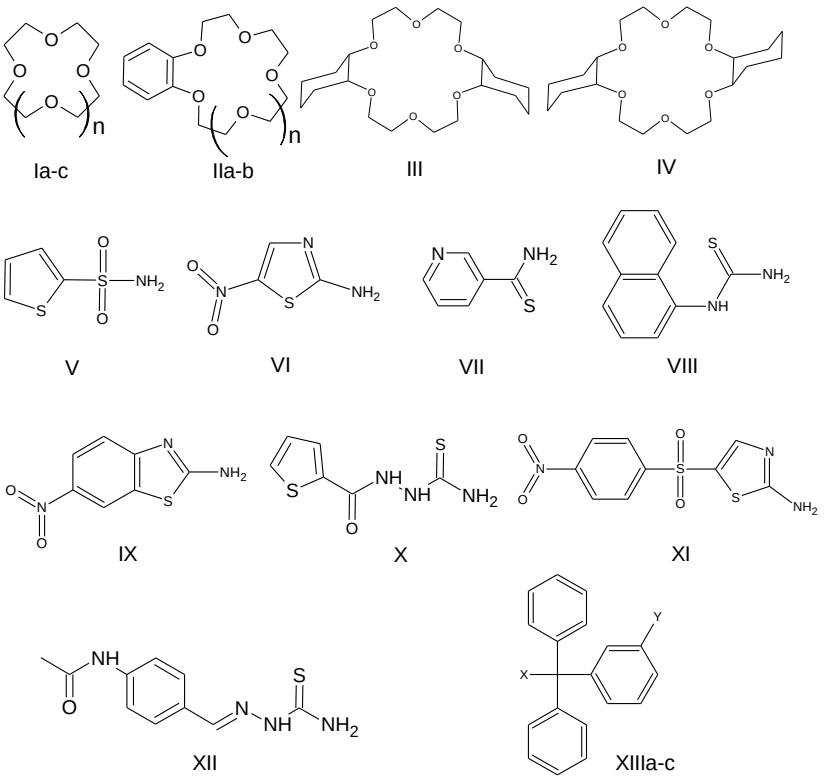
4.1 Комплекси краун-етерів із HN-протонодонорними молекулами

Неодмінною умовою утворення кристалічних молекулярних комплексів "хазяїн-гість" краун-етерів ("хазяїнів") з нейтральними "гостьовими" молекулами є присутність в "гості" протонодонорних центрів при одному C, N або O-атомах, (в частковості H_2N-, H_2NSO_2-, H_2NCS-, H_2NHNCO-, H_3N^+-, H_3C-, CH_3O-, H_2C= груп або молекул води), забезпечуючих стабілізацію компонент комплексу водневими зв'язками. У скріпленні, як правило, бере участь пара протонів донорного центру "гістя", причому стабільність комплексів падає у ланцюгу: OH_2 > NH_2 > CH_2. Відомі також нечисленні приклади утворення кристалічних комплексів " хазяїн-гість" при участі лише найефективного 18-краун-6. Умовою утворення кристалічних молекулярних комплексів є також порівнянно малій розмір „гостьової” компоненти.

Метою роботи було визначення можливості синтезу кристалічних молекулярних комплексів краун-етерів різної будови з "гостьовими" молекулами порівнянно великого розміру.

Взаємодією краун-етерів з "гістьовими" молекулами порівняно великого розміру отримані кристалічні молекулярні комплекси "хазяїн-гість" (рис. 4.1).

Це може бути враховано при моделюванні молекулярних взаємодій природних молекул, а також спрямованому синтезі комплексів "хазяін-гість" краун-етерів та HN-протонодонорних молекул.



I, n = 1 (a), n = 2 (b), n = 3 (c); II, n = 1 (a), n = 2 (b); XIII, X = NH_2, Y = H (a), X = $NH_3^+SCN^-$, Y = H (b), X = OH. Y = SO_2NH_2 (c)

Рис. 4.1 Компоненти комплексів краун-етерів ("хазяїнів") та нейтральних "гостьових" молекул

4.2 Комплекси включення 1,5-дібензо-18-кран-6 з органічними молекулами

Синтезовано комплекси включення 1,5-дібензо-18-кран-6 з дітіодімочевиною, дітіооксамидом і іншими потенційно фізіологічно активними нейтральними молекулами, дані про які представлені на рис. 4.2.

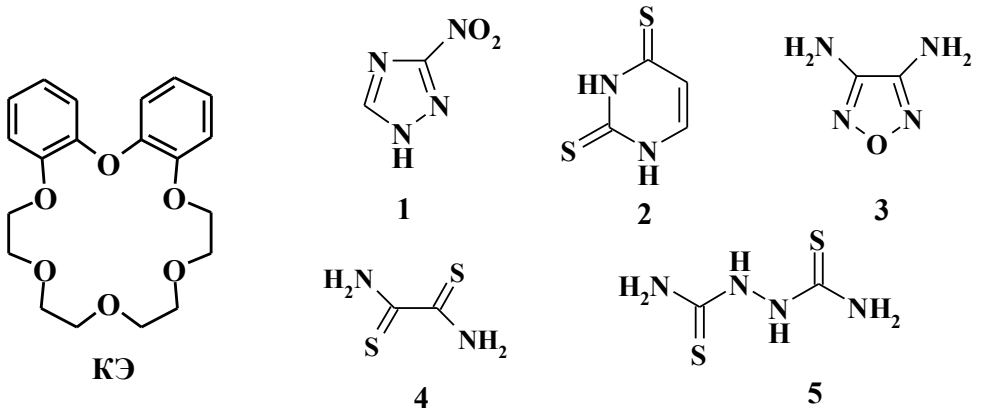


Рис. 4.2 Данні про компоненти комплексів 1,5-дібензо-18-кран-6

Структура комплексів представлена на рис. 4.3.

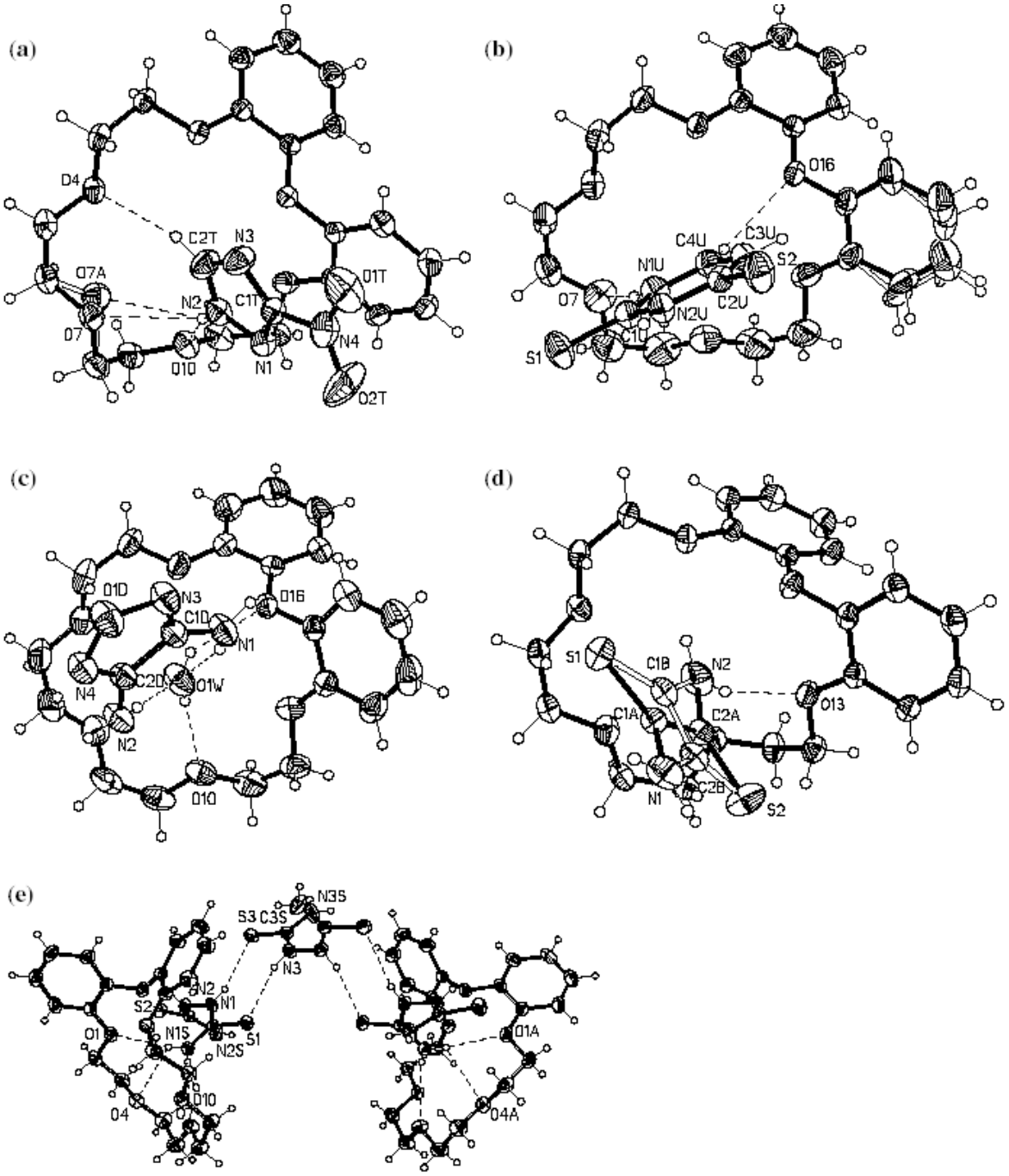


Рис. 4.3 Данні про структуру комплексів 1,5-дібензо-18-краун-6

4.3 Комплекси 18-краун-етерів з нітрозованим гіпотіазідом

Отримані також комплекси 18-краун-етерів з нітрозованим гіпотіазідом. Гіпотіазид є лікарським препаратом. На рис. 4.4 представлено структури цих похідних.

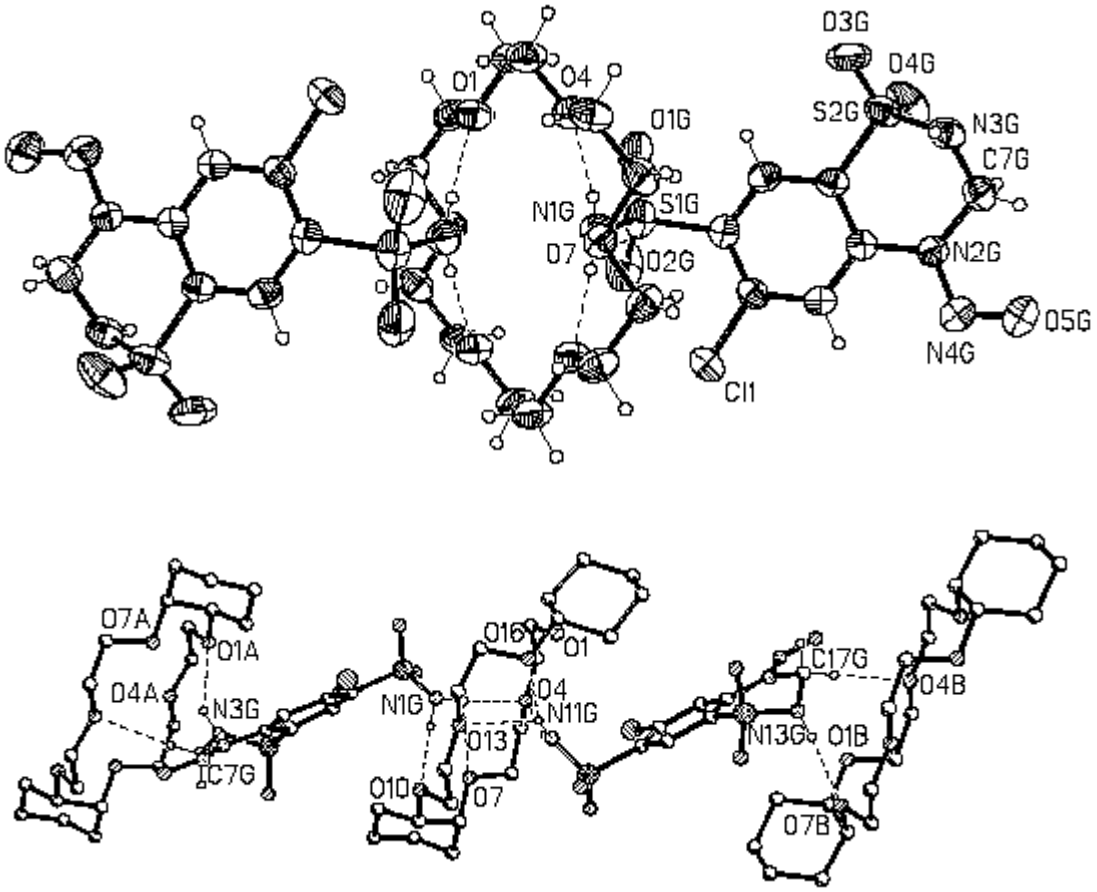


Рис. 4.4 Молекулярна структура 18-краун-етерів з нітрозованим гіпотіазідом

4.4 Комплекси включення N,N’-дібензіл-4,13-діаза-18-кран-6 з дітіосечовиною (рубіанова кислота) та 4-нітробензолсульфамідом

Синтезовано комплекси включення N,N’-дібензіл-4,13-діаза-18-кран-6 з дітіосечовиною (рубіанова кислота), 4-нітробензолсульфамідом і іншими потенційно фізіологічно активними нейтральними молекулами. Дані про комплекси представлені на рис. 4.5.

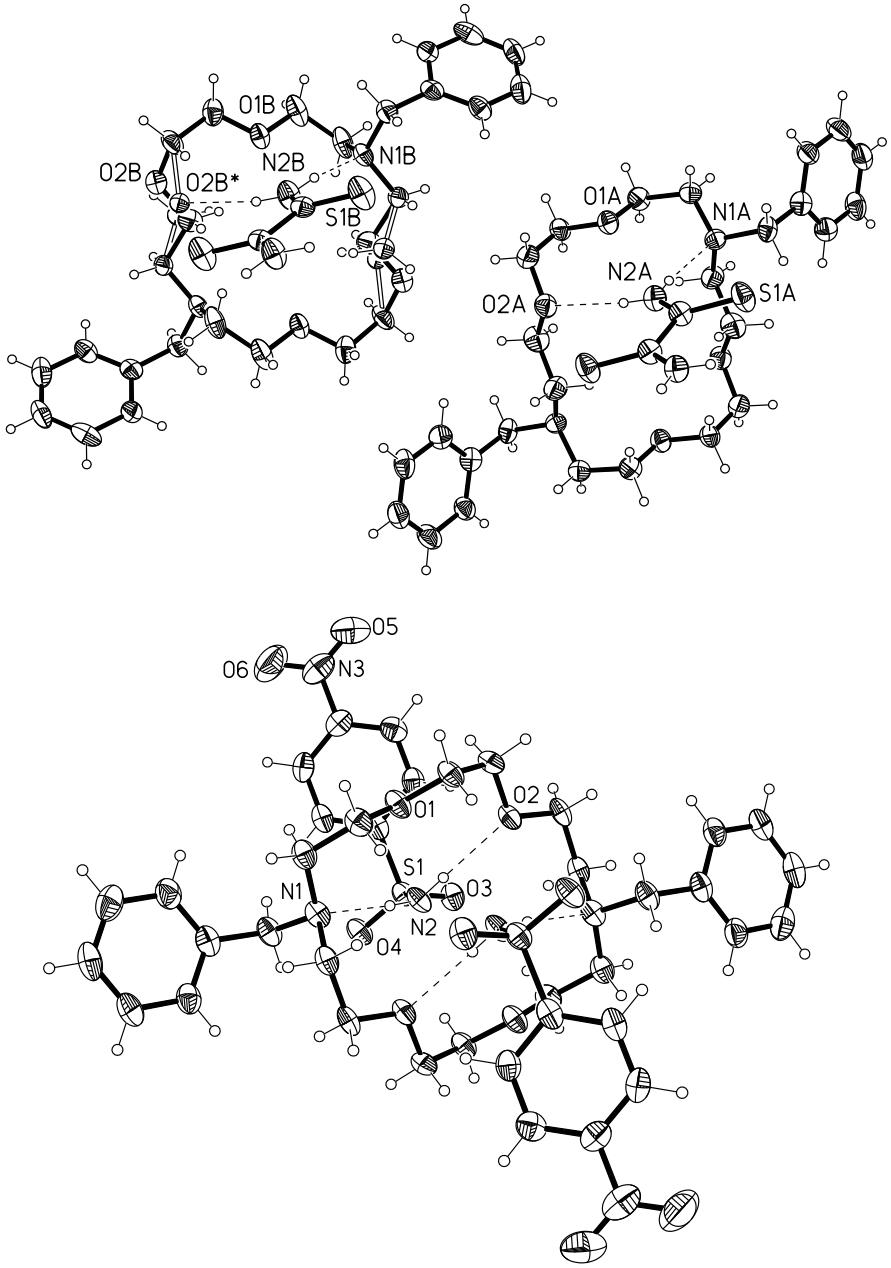


Рис. 4.5 Данні про комплекси N,N’-дібензіл-4,13-діаза-18-краун-6 з дітіосечовиною та 4-нітробензолсульфамідом

4.5 Комплекси гетерокаліксарена з піколіном

Отримано також комплекс гетерокаліксарена з піколіном. Речовина утворить 2 поліморфні структури. На рис. 4.6 представлено структури цих поліморфних об’єктів.

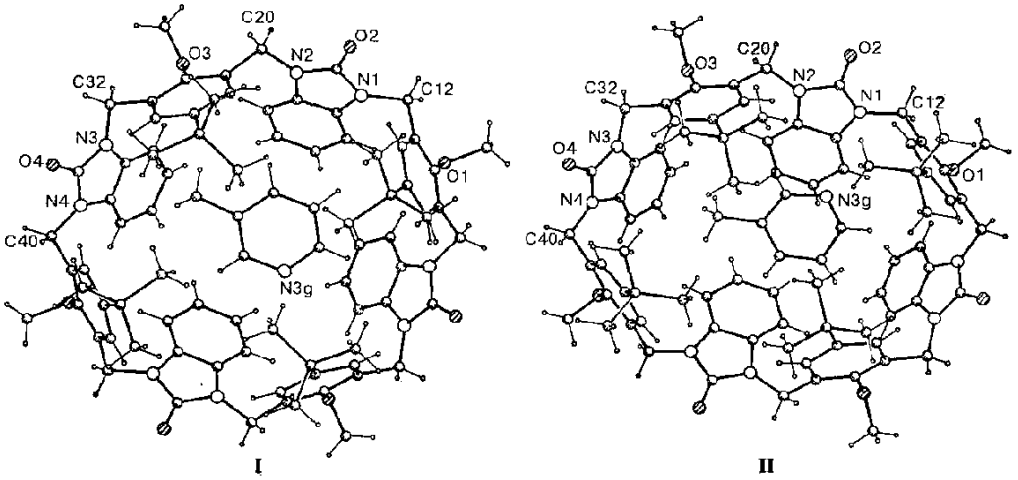


Рис. 4.6. Молекулярні структури гетерокаліксарена з піколіном

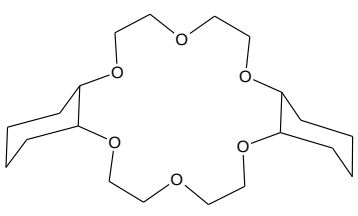
5 СУПРАМОЛЕКУЛЯРНІ СПОЛУКИ КРАУН-ЕТЕРІВ З СУМІШШЮ ФЛУОРОКОМПЛЕКСНИХ КИСЛОТ

5.1 Супрамолекулярні сполуки ціс-сін-ціс діциклогексано-18-краун-6 та флуорокомплексних кислот ніобію і танталу

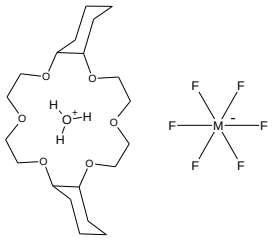
Відомо, що галогеніди металів, таких як олово, цирконій, ванадій, ніобій, тантал, що знаходяться у вищих ступенях окислення, в безводих умовах або розщеплюють поліетерні кільця краун-етерів з утворенням лінійних продуктів, або, як у разі використовування пентахлориду танталу, відбувається розширювальна рециклізація 15-краун-5 (1,4,7,10,13-пентаоксациклопентадекан) у 18-краун-6 (1,4,7,10,13,16-гексаоксациклооктадекан) з утворенням комплексу $[H_3O^+ \cdot$ (18-краун-6)]$TaCl_6^-$, з виходом ~ 10% . Відомо також, що розчини ніобію і танталу у флуороводневої кислоті є лабільною сумішшю флуорокомплексних кислот HMF_6 та H_2MF_7, де M = Nb, Ta.

З урахуванням однієї з приоритетних задач супрамолекулярной хімії по виявленню селективних взаємодій і стабілізації краун-етерами малостійких з'єднань в стабільні кристалічні сполуки включення, метою роботи було визначення можливості селективної екстракції і синтезу супрамолекулярних комплексів краун-етеру з гекса- або гептафлуорокомплексамі ніобія і танталу з їх розчинів у флуороводневої кислоті.

Встановлено, що при випаровуванні розчинників з розчинів ніобія або танталу і ціс-сін-ціс ізомеру діциклогексано-18-краун-6 (I) у флуороводневої кислоті, селективно утворюються кристалічні супрамолекулярні комплекси (IIа,б) з гексафлуороніобатом або гексафлуоротанталатом гидроксонія відповідно. З урахуванням відомих даних, а також характерної тенденції краун-етеру (I) по стабілізації "закритою" стороною порожнини макроциклічного кільця катіонів гидроксонію, для синтезованих об'єктів можна припустити вірогідним будову (II) – (рис. 5.1).



I



IIа,б

Рис. 5.1 Будова кристалічних супрамолекулярних сполук

5.2 Супрамолекулярні сполуки 1,5-дібензо-18-краун-6 та флуорокомплексних кислот ніобію І танталу

Відомо, що галогеніди металів, таких як олово, цирконій, ванадій, ніобій, тантал, що знаходяться у вищих ступенях окислення, в безводих умовах або розщеплюють поліетерні кільця краун-етерів з утворенням лінійних продуктів, або, як у разі використовування пентахлориду танталу, відбувається розширювальна рециклізация 15-краун-5 (1,4,7,10,13-пентаоксациклопентадекан) у 18-краун-6 (1,4,7,10,13,16-гексаоксациклооктадекан) з утворенням комплексу $[H_3O^+ \cdot$ (18-краун-6)]$TaCl_6^-$, з виходом ~ 10% . Відомо також, що розчини ніобію і танталу у флуороводневої кислоті є лабільною сумішшю флуорокомплексних кислот HMF_6 та H_2MF_7, де M = Nb, Ta.

З урахуванням однієї з приоритетних задач супрамолекулярной хімії по виявленню селективних взаємодій і стабілізації краун-етерами малостійких сполук в стабільні кристалічні сполуки включення, метою роботи було визначення можливості селективної екстракції і синтезу супрамолекулярних комплексів 1,5-дібензо-18краун-6 з гекса- або гептафлуорокомплексамі ніобія і танталу з їх розчинів у флуороводневой кислоти.

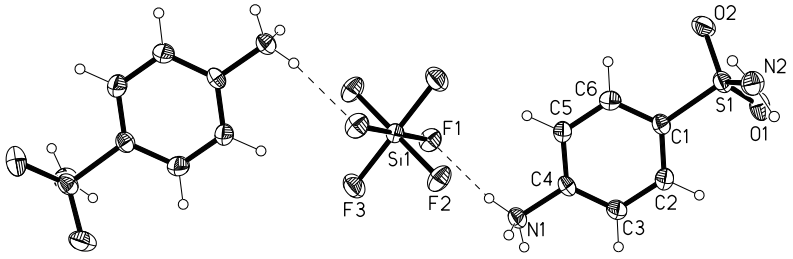
Встановлено, що при випаровуванні розчинників з розчинів ніобія або танталу і 1,5-дібензо-18краун-6 у флуороводневої кислоті, селективно утворюються кристалічні супрамолекулярні комплекси з гексафлуороніобатом або гексафлуоротанталатом гидроксонія відповідно.

Одержані кристалічні супрамолекулярні сполуки є прикладом селективної екстракції краун-етером флуорокомплексих кислот ніобію і танталу з кислотних розчинів; вони стабільні і можуть бути цікавими як контейнери цих кислот.

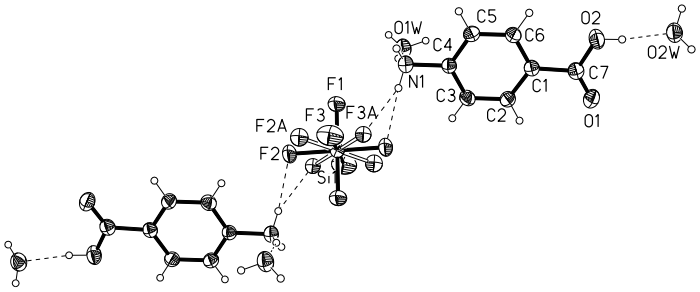
5.3 Взаємодія молекул "хазяЇнів" – 4-амінобензолсульфамиду та 4-амінобензолсульфокислоти з H_2SIF_6

Відомо що H_2SiF_6, представляє собою суміш гекса- пента- і тетра флуоридів кремнію.

Взаємодією кислоти з сумішшю флуорокомплексних кислот селективно одержані відповідні гексафлуоросилікати, будова яких представлена на рис. 5.2.



(**I**)



(**II**)

Рис. 5.2 Структури комплексів гексафлуоросилікату 4-амінобензолсульфаміду (I) та 4-амінобензолсульфокислоти (II), відповідно

5.4 Структура дігідрату гексафлуоросилікату $H_2SIF_6 \cdot 2H_2O$

Раніше при вивченні системи H_2SiF_6 – H_2O у області концентрацій 80 – 100 мол. % H_2O методом низькотемпературного диференційного термічного аналізу було встановлено існування кристалічних гідратів складу $H_2SiF_6 \cdot nH_2O$ (n = 4, 6, 9,5; т.пл. 20, –12, –54 ^oC відповідно), які за даними рентгеноструктурного аналізу (РСА) є солями оксонію $(H_5O_2)_2SiF_6$, $(H_5O_2)_2SiF_6 \cdot 2H_2O$ і $(H_5O_2)(H_7O_3)SiF_6 \cdot 4{,}5H_2O$. Повідомлялося також про отримання нестійкої дігідрата $H_2SiF_6 \cdot 2H_2O$ невстановленої будови, що легко розкладається при температурі «декілька нижче кімнатної».

Нами при взаємодії 45 %-ной кремнійфлуороводневої кислоти (КФК) з гидразідом нітрілуксусної кислоти (L) (молярне співвідношення КФК : L = 3 : 1) був виділений безбарвний кристалічний продукт, плавкий з розкладанням при 60 ^oC і ідентифікований методом РСА як гексафлуоросилікат гидроксонію (рис. 4.3). Таким чином, вперше отримані об'єктивні докази будови індивідуального найпростішого дігідрату гексафлуоросилікату.

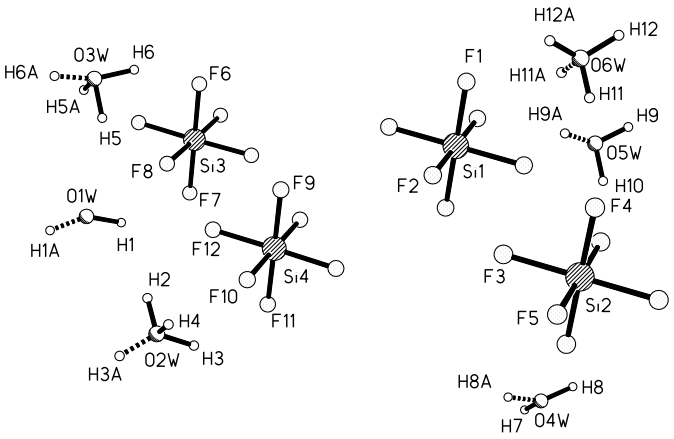


Рис. 5.3 Структура гексафлуоросилікату $H_2SiF_6 \cdot 2H_2O$

5.5 Комплекс дібензодіаза-18-краун-6 з тетрафлуороборатом

Взаємодією етерату трифлуороборату з дібензодіаза-18-краун-6 отриманий кристалічний супрамолекулярний комплекс. Краун-етер у комплексі потерпає істотну конформаційну перебудову (рис. 5.4, 5.5).

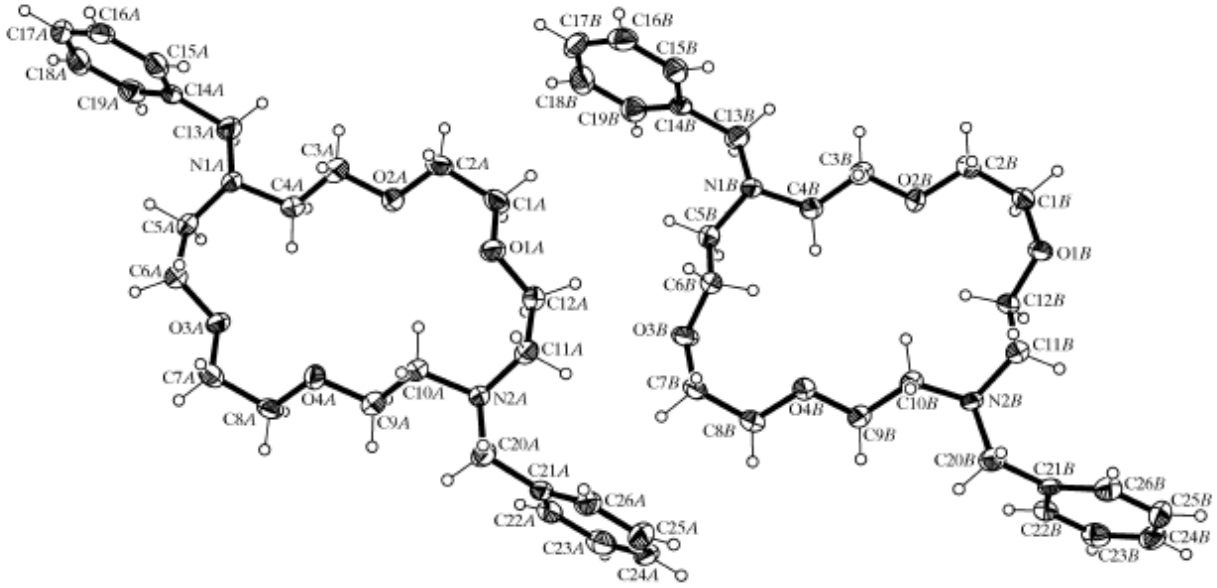


Рис. 5.4 Структура вільного дібензодіаза-18-краун-6краун-етера

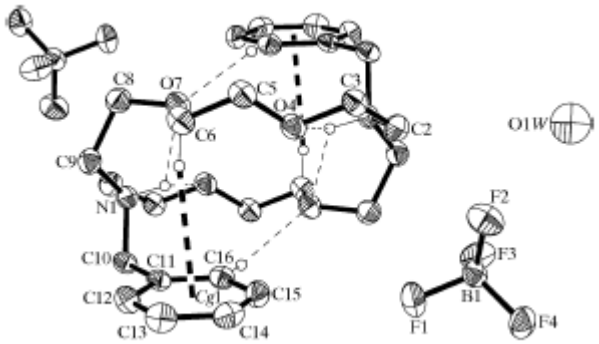


Рис. 5.5 Структура супрамолекулярного комплекса тетрафлуороборату з дібензодіаза-18-краун-6

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ВИСНОВКИ

1. Неодмінною умовою утворення кристалічних молекулярних комплексів "хазяїн-гість" краун-етерів ("хазяїнів") з нейтральними "гостьовими" молекулами є присутність у "гостьовій" компоненті Н-донорних центрів при одному С, N чи О-атомах, зокрема H_2N-, H_2NSO_2-, H_2NCS-, H_2NHNCO-, H_3N^+-, H_3C-, CH_3O-, H_2C= груп чи молекул води, що забезпечують стабілізацію компонентів комплексу водневими зв'язками. У зв'язуванні, як правило, беруть участь пари протонів Н-донорного центру "гостя".

2. Найбільш ефективними для координації Н-донорних молекул у кристалічні молекулярні комплекси "гість-хазяїн" можна вважати 18-членні краун-етери які мають у своєму складі 6 кисневих гетероатомів. Ці критерії можуть бути використані при виборі партнерів комплексоутворення при цілеспрямованому синтезі кристалічних молекулярних комплексів "хазяїн-гість" краун-етерів на базі краун-етерів.

3. Синтезом ряду комплексів із краун-етерів та похідних трифенілметану а також діфенілтіосечовини відзначені деякі неточності прийнятої класифікації партнерів комплексоутворення у хімії комплексів "гість-хазяїн". Утворення стійких кристалічних молекулярних комплексів "гість-хазяїн" нейтральних органічних молекул з краун-етерами різної будови можливо також при використуванні порівняно великих "гостьових" молекул, які було прийнято розглядати як молекули "хазяїни"..

4. Утворення стійких кристалічних молекулярних комплексів "гість-хазяїн" нейтральних органічних молекул з краун-етерами різної будови можливо при використуванні молекул, яки мають по одному протону при двох протонодонорних атомах, розділених валентним зв'язком.

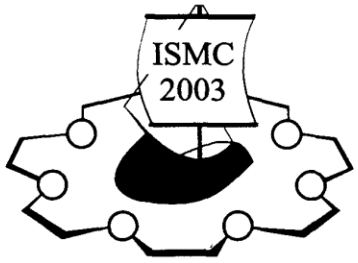
5. Встановлено, що при випаровуванні розчинників з розчинів ніобію або танталу і ціс-сін-ціс ізомеру діциклогексано-18-краун-6 у флуороводневої кислоті, селективно утворюються кристалічні супрамолекулярні комплекси з гексафлуороніобатом або гексафлуоротанталатом гидроксонія відповідно. Аналогічні дані отримані на таких елементах, як кремній, германій, бор. Отримані супрамолекулярні комплекси можуть являти інтерес як контейнери флуорокомплесних кислот.

Додаток 1

Копія доповіді

“Creation of hydrogen bonded networks in the crown ether – dithiooxamide / dithiobiurea binary compounds”

XXVIII INTERNATIONAL SYMPOSIUM ON MACROCYCLIC CHEMISTRY



13 - 18 July 2003
Gdańsk University of Technology
Gdańsk, Poland

Book of Abstracts

This book contains abstracts of the Plenary, Invited, Symposium Lectures and Short Oral Presentations, as well as the Posters accepted for presentation at the Symposium

The index pages show the names of all presenting authors together with their associated abstract reference number.

CREATION OF HYDROGEN BONDED NETWORKS IN THE CROWN ETHER – DITHIOOXAMIDE / DITHIOBIUREA BINARY COMPOUNDS

Yu.A. Simonov,[a] M.S. Fonari,[a] M.J. Zaworotko,[b] H. Abourahma,[b] J. Lipkowski,[c] Ed.V. Ganin,[d] A.A. Yavolovskii[e]

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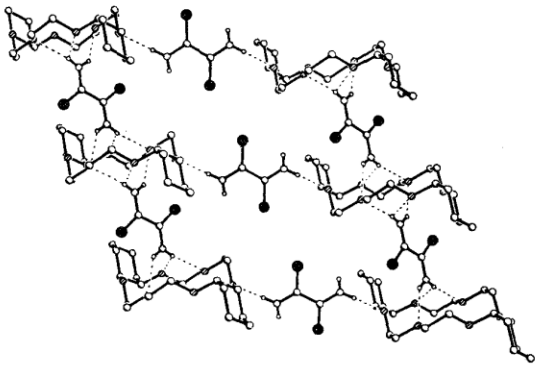
The hydrogen–bonding networks in binary compounds of dithiooxamide, $(NH_2CS)_2$ (dtox) and dithiobiurea, $(NHCSNH_2)_2$ (dtur) with crown ethers, 18–crown–6 (18C6), 15–crown–5 (15C5), 12–crown–4 (12C4), *cis–syn–cis–* (DCHA), and *cis–anti–cis–* (DCHB) isomers of dicyclohexyl–18–crown–6 are discussed. 15C5·dtox, 18C6·dtur and DCHB·dtur afford *via* N–H···O hydrogen bonds the 1D polymeric *strands* with the alternating component molecules. DCHA·2dtox and DCHB·2dtox (Fig.) display rather similar *layered* packing arrangements with the N–H···O bonded dtox and crown molecules alternating in the chains that are further interlinked *via* next dtox molecule to generate 2D sheet. 15C5·2dtur and 12C4·dtur reveal different 3D *networks*. The dtur molecules in 15C5·2dtur are consolidated in the layers where each molecule is bound with four closest neighbors *via* N–H···S hydrogen bonds, elaborating only one amine group for the interactions with the crown ether. 15–Crown–5 connectors that reside on the inversion centers link the adjacent layers. The dtur molecules in 12C4·dtur are assembled in the chains *via* the couple of N–H···S interactions with the involvement of the central NH–groups in these contacts. Both primary amine groups are engaged into the interaction with 12C4 and each of them serves as a bridge between two crown spacers.



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Додаток 2

Копія доповідей

“Структурні аспекти взаємодії кремнефторо-водородной кислоти з органічними підставами”

та

“Поліморфізм трикомпонентної системи”

РОССИЙСКАЯ АКАДЕМИЯ НАУК
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им.Н.С.Курнакова

КИЕВСКИЙ НАЦИОНАЛЬНЫЙ УНИВЕРСИТЕТ
ИМЕНИ ТАРАСА ШЕВЧЕНКО

НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК УКРАИНЫ
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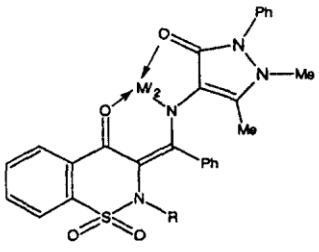
им.В.И.Вернадского

XXI
МЕЖДУНАРОДНАЯ ЧУГАЕВСКАЯ КОНФЕРЕНЦИЯ ПО КООРДИНАЦИОННОЙ ХИМИИ

10-13 июня 2003 года
г. Киев

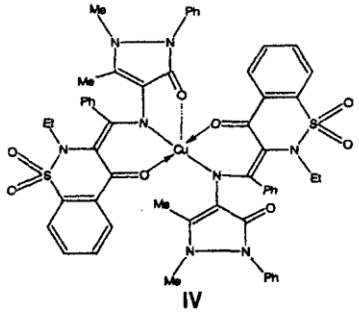
Тезисы докладов

КИЇВСЬКИЙ УНІВЕРСИТЕТ 2003



III

M=Co, Ni, Cu, Zn;



IV

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СТРУКТУРНЫЕ АСПЕКТЫ ВЗАИМОДЕЙСТВИЯ КРЕМНЕФТОРОВОДОРОДНОЙ КИСЛОТЫ С ОРГАНИЧЕСКИМИ ОСНОВАНИЯМИ

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Кремнефтороводородная кислота (КФК) является крупнотоннажным побочным продуктом предприятий, перерабатывающих фторидное сырье, а также апатиты и фосфориты (производство фосфорных удобрений, фосфорной кислоты, элементного фосфора) и рассматривается в качестве наиболее перспективного источника фтора для химической промышленности [1]. Как и многие другие комплексные фторокислоты, КФК не существует в индивидуальном состоянии (последняя по времени неудачная попытка изолировать соединение состава H_2SiF_6 принадлежит авторам [2]). В водных растворах КФК реализуется комплекс гидролитических равновесий, причем вопросы состава присутствующих в растворах КФК форм остаются предметом дискуссии [1, 3]; до недавнего времени структурно изученными солями КФК оставались лишь гекса- и пентафторосиликаты. В настоящем сообщении представлены результаты систематических исследований строения продуктов взаимодействия КФК с органическими основаниями, в составе которых удается стабилизировать сосуществующие в растворах КФК гидролитически лабильные формы.

Для осуществления взаимодействия с КФК были использованы основания следующих классов:

- краун-эфиры;
- азакраун-эфиры;
- двенадцатичленные тетраазамакроциклы;
- гидразиды карбоновых кислот;
- тиосемикарбазиды.

Установлено, что КФК реагирует с краун-эфирами и их аза-аналогами с образованием комплексов типа "гость-хозяин" (Г-Х) на основе межмолекулярных Н-связей, в составе которых в зависимости от строения макроциклического лиганда стабилизируются анион SiF_6^{2-} и все возможные продукты его гидролитических превращений: $[SiF_5 \cdot H_2O]^-$ [4], $SiF_4 \cdot 2H_2O$, SiF_5^- [5]. Методом РСА в составе комплексов Г-Х впервые были структурно охарактеризованы "гостевые" фторокомплексы *транс*-$SiF_4 \cdot 2H_2O$ (d_{Si-O} = 1.841(2) Å, d_{Si-F} = 1.655(1), 1.658(1) Å) и $[SiF_5 \cdot H_2O]^-$ (средние значения по двум структурам d_{Si-O} = 1.880 Å, d_{Si-F} = 1.663 Å). Краун-эфиры с эквивалентно стерически экранированными сторонами плоскости макроцикла селективно извлекают из растворов КФК аквакомплекс *транс*-$SiF_4 \cdot 2H_2O$; *цис-син-цис*-дициклогексано-18-краун-6 (ДЦГ-6А) с неэквивалентно стерически экранированной полостью образует ионный комплекс $[ДЦГ\text{-}6А \cdot H_3O]SiF_5$, в котором катион гидроксония триподно связан с каждым вторым О-атомом лиганда прочными Н-связями OH···O (расстояния O···O 2.615(3)-2.637(3) Å). Судя по данным ЯМР ^{19}F, ^{29}Si [6], указанное строение комплекса с тригонально-бипирамидальной геометрией аниона сохраняется и в растворе ацетона. Протонирующиеся в кислых средах азакраун-эфиры стабилизируют в составе комплексов Г-Х анионы $[SiF_5 \cdot H_2O]^-$ (моноаза-18-краун-6, 1,10-диаза-18-краун-6) и SiF_6^{2-} (1,7-диаза-15-краун-5). Тетраазамакроциклы (L = 1,4,7,-10-тетраазациклододекан, 1,4,7,10-тетрааза-2,6-пиридинофан [12], *мезо*-5,-7,7,12,12,14-гексаме-тил-1,4,8,11-тетраазациклотетрадекан) образуют гексафторосиликаты соответствующих катионов LH_4^{4+}; в состав комплексов входит от 4 до 7 внешнесферных молекул воды [7-9]. В гептагидрате $(LH_4)_2(SiF_6)_4 \cdot 7H_2O$ (L = 1,4,7,10-тетраазациклододекан) пять молекул воды посредством прочных Н-связей формируют линейный кластер, что является редким случаем такого крупного водного ассоциата в гидратных комплексах КФК. В целом для продуктов взаимодействия КФК с макроциклическими основаниями характерно образование гидратных форм, причем участвующие в системах Н-связей молекулы воды выполняют важную структурную функцию, зачастую являясь мостиками между различными фрагментами комплекса.

Взаимодействие КФК с N,O- и N,S-амбидентатными гидразидами карбоновых кислот [9, 10] и тиосемикарбазидами [11, 12] приводит к гексафторосиликатам N-протонированных форм оснований; центром протонирования является терминальный атом азота гидразинового фрагмента. Интересной особенностью реакции с тиосемикарбазидом (L^1) является вовлечение части лиганда в процесс циклизации с образованием протонированного 2,5-диамино-1,3,4-тиадиазола (L^2H^+), стабилизирующего вместе с L^1H^+ структуру двойного гексафторосиликата $(L^1H^+)_2(L^2H^+)(SiF_6)_{1.5}$ [11]. Компоненты структуры объединены межионными Н-связями типа NH···F и NH···S. Для всех структурно изученных соединений КФК с органическими основаниями наблюдается диспропорционирование длин связей Si–F фтороанионов в зависимости от того, участвует или нет соответствующий фторолиганд в Н-связывании и какова прочность Н-связи; наиболее короткие связи Si–F отмечены для атомов фтора, не вовлеченных в Н-связи. В системах Н-связей, реализующихся в соединениях N-протонированных органических оснований, превалируют взаимодействия типа NH···F. В заключение отметим, что приведенные результаты дают прямое структурное подтверждение факта сосуществования в растворах КФК фторокомплексов

$[SiF_{6-n}(H_2O)_n]^{n-2}$ (n = 0 – 2); в формировании и стабилизации кристаллических структур комплексов – продуктов взаимодействия КФК с органическими основаниями, главная роль принадлежит системам Н-связей.

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ДИАРИЛАЛКИЛАРСИНЫ И ГАЛОГЕНИДЫ ЧЕТВЕРТИЧНЫХ АРСОНИЕВ – КОМПЛЕКСООБРАЗУЮЩИЕ РЕАГЕНТЫ

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Третичные арсины типа R_2AsR', где R и R' – органические радикалы, получают, в основном, взаимодействием реактива Гриньяра с вторичными галогенарсинами. Однако все известные методы получения диалкил(арил)галогенарсинов отличаются либо многостадийностью, либо низкими выходами, или трудностью выделения целевых продуктов, получающихся в смеси с другими соединениями.

Нами впервые показано, что с целью получения вторичных галогенарсинов успешно может быть применен мышьяковистый ангидрид, если реакционную массу, полученную взаимодействием соответствующего алкил(арил)магнийбромида с оксидом мышьяка(III), обработать избытком коцентрированной соляной кислоты. Образование целевых продуктов объясняется протеканием следующих последовательных реакций:

$$As_2O_3 \xrightarrow[-2MgBr_2;\,-2MgO]{4ArMgBr} Ar_2AsOAsAr_2 \xrightarrow[-2H_2O]{2HCl} 2Ar_2AsCl,$$

где Ar=C_6H_5 или о-$CH_3C_6H_4$.

Выход ди-о-толилхлорарсина на 12-15% больше, достигая 80%, по сравнению с выходом дифенилхлорарсина.

Выяснилось, что третичные арсины со смещанными радикалами получаются взаимодействием дифенил- и ди-о-толилхлорарсинов с реактивом Вринъяра – реакция протекает в среде диэтилового эфира:

$$Ar_2AsCl + RMgBr \rightarrow Ar_2AsR + MgClBr,$$

где Ar=C_6H_5 или о-$CH_3C_6H_4$, а R=C_3H_7, C_4H_9, изо-C_4H_9, C_5H_{11} или изо-C_5H_{11}. Выход диарилалкиларсинов колебается в пределах 60-85% и отчетливо зависит от состава и строения исходных галогенарсинов. Выход дифенилалкиларсинов превышает выхода ди-о-толилалкиларсинов, что объясняется объёмним препятствием о-толилного радикала.

Обработка ацетата кобальта(III) смесью ацетон-этанол-вода позволяет выделить комплекс, которому на основании элементного анализа, ИК, и MALDI масс-спектрометрии можно приписать формулу

$[Co^{II}_4Co^{III}_4(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CCH_3)_6(O_2CCH_3)_2(H_2O)_6]$, (II).

Последнее позволяет предположить, что именно этот комплекс является основной составляющей 'ацетата кобальта(III)'.

Действие пиридина на комплексы I и II в метанольном растворе в присутствии ClO_4^- иона приводит к образованию известного трехъядерного комплекса $[Co^{III}_3(\mu_3\text{-}O)(\mu\text{-}OCH_3)(\mu\text{-}O_2CCH_3)_5(C_5H_5N)_3]ClO_4$.

ПОЛИМОРФИЗМ ТРЕХКОМПОНЕНТНОЙ СИСТЕМЫ: ТРИКЛИННАЯ И МОНОКЛИННАЯ ФОРМЫ $(LH_4)(GeF_6)_2\,4H_2O$ (L-*мезо*-5,7,7,12,12,14-ГЕКСАМЕТИЛ-1,4,8, 11-ТЕТРААЗАЦИКЛО-ТЕТРАДЕКАН)

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Методом РСА для соединения $(LH_4)(GeF_6)_2 4H_2O$ определены две полиморфные модификации, полученные при различных условиях кристаллизации. Триклинная форма, (I), пр.гр. *P-1*, *a*=9.627(3), *b*=9.358(3), *c*=8,497(4) Å, α=106.02(2), β=83.74(2), γ=106.06(2)° [1]. Моноклинная форма, (II), пр.гр. $P2_1/c$, *a*=9.565(2), *b*=16.522(3), *c*=9,021(2) Å, β=96.28(3)° [2]. В обоих случаях ближайшее окружение тетраазамакроциклического катиона формируют два GeF_6^{2-} аниона и две молекулы воды, объединенные водородными связями. Дальнейшая организация трехмерных каркасов в кристаллах двух полиморфов различна. В (I) в каркасе можно выделить слои, построенные за счет чередования макроциклических катионов и центросимметричных неорганических тетрамеров, $(GeF_6)_2 2H_2O$. Между собой слои объединены мостиковыми молекулами воды, которые формируют линейные четырехзвенные цепочки, $(H_2O)_4$. В (II) молекулы воды объединены в бесконечные цепочки, в которых каждая из них взаимодействует попеременно то с макроциклом, то с GeF_6^{2-}-анионом, а трехмерная сетка построена по принципу слоистого пирога с чередованием рядов органических катионов и неорганических цепочек $(GeF_6)_n (H_2O)_{3n}$.

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Додаток 3

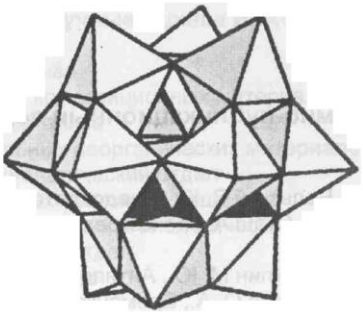
Копія доповіді

“Супрамолекулярна архітектура двухкомпонентних систем: краун-етер - дітіооксамид/ дітіосечовина”

РОССИЙСКАЯ АКАДЕМИЯ НАУК
СЕКЦИЯ КРИСТАЛЛОХИМИИ НАУЧНОГО СОВЕТА
ПО КИНЕТИКЕ И РЕАКЦИОННОЙ СПОСОБНОСТИ
ИНСТИТУТ ПРОБЛЕМ ХИМИЧЕСКОЙ ФИЗИКИ

III НАЦИОНАЛЬНАЯ КРИСТАЛЛОХИМИЧЕСКАЯ КОНФЕРЕНЦИЯ

ТЕЗИСЫ ДОКЛАДОВ



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7) Примесь фтора, типичная для продажных Ta_2O_5 и Nb_2O_5, снижает температуру разложения протонных проводников; ее можно избежать, окисляя металлы на воздухе.

8) Неполное замещение A на протонсодержащие частицы не приводит к полищелочному эффекту; ионная проводимость почти та же, что при полном замещении, а температуры разложения заметно выше.

На основе этих принципов уже получены и исследованы три новых типа среднетемпературных протонных проводников, работоспособных до 450–500 °C.

Работа поддержана РФФИ (проект № 00-03-32469a).

39. СУПРАМОЛЕКУЛЯРНАЯ АРХИТЕКТУРА ДВУХКОМПОНЕНТНЫХ СИСТЕМ: КРАУН-ЭФИР–ДИТИООКСАМИД / ДИТИОДИМОЧЕВИНА

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Кристаллохимические данные получены для семи новых двухкомпонентных систем, содержащих краун-эфир и дитиооксамид, $(H_2NCS)_2$ (дитиодимочевину, $(H_2NCSNH)_2$). Стехиометрия комплексов 1:1 или 1:2. В ряду комплексов с дитиооксамидом наблюдается последовательное усложнение супрамолекулярной архитектуры от одномерных цепочек к двумерной стенке и трехмерной сетке при замене 15-членного краун-эфира (15-краун-5, бензо-15-краун-5) изомерами дициклогексил–18-краун-6 (А и Б) и далее 18-краун-6. В ряду комплексов с дитиодимочевиной переход от 12-членного к 18-членному макроциклу сопровождается упрощением упаковочных мотивов, от трехмерного каркаса (12-краун-4) к слоистой структуре (15-краун-5) и далее к цепочкам (18-краун-6, дициклогексил-18-краун-6). Наряду с оригинальными результатами авторов к обсуждению привлечены литературные данные.

40. МОЛЕКУЛЯРНЫЕ ПРОВОДНИКИ НА ОСНОВЕ КАТИОН-РАДИКАЛЬНЫХ СОЛЕЙ BEDT-TTF С ФОТОХРОМНЫМИ МОНОНИТРОЗИЛЬНЫМИ МЕТАЛЛОКОМПЛЕКСНЫМИ АНИОНАМИ $[RuNOX_5]^{2-}$ (X = Br, Cl)

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Как часть наших исследований в области изучения новых гибридных молекулярных материалов, комбинирующих проводящие свойства с другими физическими явлениями, была синтезирована серия катион-радикальных солей на основе бис(этилендитио) тетратиафульвалена (BEDT-TTF) с фотохромными металлокомплексными анионами: κ-(BEDT-TTF)$_4$[RuNOBr$_5$]C$_6$H$_5$CN (**1**), δ-(BEDT-TTF)$_4$[RuNOCl$_5$]$_{1.33}$ (**2**), κ-(BEDT-TTF)$_4$[RuNOCl$_5$]C$_6$H$_5$CN (**3**) и δ-(BEDT-TTF)$_4$[RuNOBr$_5$] (**4**). Изучены их кристаллическая и электронная структура, а также транспортные свойства. Показано присутствие соизмеримой и несоизмеримой структурной

Додаток 4

Копія доповіді

“Supramolecular networks in binary compounds: crown-ether – dithiooxamid / dithiobiurea”



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ABSTRACT BOOK

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f4.m6.o3 **DNA intercalation of disaccharide anthracyclines: crystal structures of the complexes with the DNA hexamer d(CGATCG).**

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Keywords: *DNA intercalation, drug-DNA complexes, X-ray structure.*

DNA intercalation is a specific mode of binding in which a molecule inserts its chromophore moiety, formed by aromatic fused rings, between adjacent base pairs of the DNA double helix. Two main modes of DNA intercalation have been observed. The long fused rings can be inserted perpendicularly to the long axis of the stacked base pairs or lie parallel to it.

Anthracycline antibiotics are widely known as important antitumor drugs currently used in cancer chemoterapy. Like many other antitumor compounds anthracyclines work by DNA intercalation. Though other cellular interactions may play a role as well, the mode of DNA interaction and the geometry of drug-DNA intercalation appear to be the most critical factors for drug activity.

Anthracyclines from natural origin often contain two or more sugar rings in the glycosidic moiety. Recently, in the search for more therapeutic drugs a third generation of disaccharide derivatives which exhibit a broader spectrum of antitumor activity has been developed. We have solved the crystal structures of two disaccharide anthracyclines bound to the DNA hexamer d(CGATCG). One of these disaccharide analogues is biologically active, [1] the other is not. The structure of the two complexes reveals that the intercalation of the chromophore is the same for both drugs. The long fused rings intercalate from the minor groove at CpG steps in a perpendicular base-stacking fashion. Major differences were observed for the disaccharide moiety. In the complex with the non active analogue both sugar rings lie in the minor groove. In the other complex in one binding site the second sugar protrudes out from the double helix and is hydrogen bonded to a second DNA molecule. This is the first evidence of such cross-linking interaction. We will discuss these findings with respect to the relevance of a charged substituent on the disaccharide chain and to the potential role played by the orientation of the second sugar in the interactions with other cellular targets such as topoisomerases.

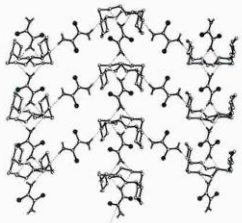
[1] Temperini C., Messori L., Orioli P., Di Bugno C., Animati F., Ughetto G., *Nucleic Acid Res.*, 2003, **31**, 1464-1469.

f4.m6.o4 **Supramolecular Networks in Binary Dithiooxamide / Dithiobiurea – Crown Ether Compounds**

Yu.A. Simonov[a], M.S. Fonari[a], M.J. Zaworotko[b], H. Abourahma[b], J. Lipkowski[c], Ed.V. Ganin[d], A.A. Yavolovskii[e], [a] *Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, Moldova;* [b] *Department of Chemistry, University of South Florida, 4202 East Fowler Avenue (SCA400), Tampa, Florida, 33620;* [c] *Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland;* [d] *Odessa State Environmental University of the Ministry of Education and Science of Ukraine, Odessa, Ukraine;* [e] *Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, Odessa, Ukraine.*

Keywords: *binary compounds, hydrogen bonding assemblies, dithiooxamide, dithiobiurea, crown spacer.*

The hydrogen–bonding networks in binary compounds of dithiooxamide, (dtox) and dithiobiurea (dtur) with crown ethers, 18–crown–6 (18C6), 15–crown–5 (15C5), 12–crown–4 (12C4), *cis–syn–cis–* (DCHA), and *cis–anti–cis–* (DCHB) isomers of dicyclohexyl–18–crown–6 are discussed. 15C5·dtox, 18C6·dtur and DCHB·dtur afford one–dimensional hydrogen–bonded polymeric *arrays* where the components alternate. DCHA·2dtox (Fig.) and DCHB·2dtox display very similar *layered* packing arrangements where the N–H···O bonded dtox – crown chains are further interlinked *via* next dtox molecule to generate two-dimensional sheet In these complexes only H_2N-primary amine binding sites are responsible for the interactions with the molecules of crown ethers. 15C5·2dtur and 12C4·dtur reveal different *three dimensional networks*: in 15C5·2dtur the dtur molecules are consolidated in the layers where each molecule is bound with four closest neighbors *via* N–H···S hydrogen bonds, elaborating only one amine group for the interactions with crown ether. 15–Crown–5 connectors that reside on the inversion centers link the adjacent layers. In 12C4·dtur the dtur molecules are assembled in the chains *via* the couple of N–H···S interactions with the involvement of the central NH–groups in these contacts. Both primary amine groups are engaged into the interaction with 12C4 and each of them serves as a bridge between two crown spacers.



Support of this research from CRDF(USA)– MRDA(Moldova) (grant MP2-3021) is gratefully acknowledged.

Додаток 5

Копія доповіді

“Some fresh examples of assembly and self- assembly of thiosemicarbazide and dihydropyromidine-2,4-(1H,3H)-dione derivatives in the co-crystals with crown-ethers”

November 21-22

Arrival of the participants to Kyiv, registration

November 23

Arrival of the participants to Kyiv, registration and other organization measures, cultural program

19-00 - ***friendly meeting of the participants***

November 24

INSTITUTE OF ORGANIC CHEMISTRY
(Murmanska, 5)

10-00 –10-30 – ***opening ceremony***

Speakers:

The Director of the IOCh of the NAS of Ukraine,
Chairman of the Organizing Committee Acad. M.O. Lozinskii (Ukraine)

Co-Chairman of the Organizing Committee Acad. J. Lipkowski (Poland)

Member of the Organizing Committee Prof. Yu. Simonov (Moldova)

Member of the Organizing Committee Acad. S.A. Andronati (Ukraine)

10-30 - 10-40 - laying wreaths to Alexander V. Kirsanov and Leonid N. Markovskii monuments.

10-40 - 10-50 - break

November 25
MORNING SESSION
(conference-hall)
Chairmen: Acad. S. Andronati, Dr. K. Suwinska

10-10 – 10-30 M.S. Fonari[1], Yu.A. Simonov[1], Yu.M. Chumakov[1], J. Lipkowski[2], G. Bocelli[3], E.V. Ganin[4], A.A. Yavolovskii[5]
SOME FRESH EXAMPLES OF ASSEMBLY AND SELF-ASSEMBLY OF THIOSEMICARBAZIDE AND DIHYDRO-PYRIMIDINE–2,4–(1H,3H)–DIONE DERIVATIVES IN THE CO-CRYSTALS WITH CROWN ETHERS

SOME FRESH EXAMPLES OF ASSEMBLY AND SELF-ASSEMBLY OF THIOSEMICARBAZIDE AND DIHYDROPYRIMIDINE–2,4–(1H,3H)– DIONE DERIVATIVES IN THE CO-CRYSTALS WITH CROWN ETHERS

Marina S. Fonari[1], Yurii A. Simonov[1], Yurii M. Chumakov[1], Janusz Lipkowski[2], Gabriele Bocelli[3], Eduard V. Ganin[4], Arkadii A.Yavolovskii[5]

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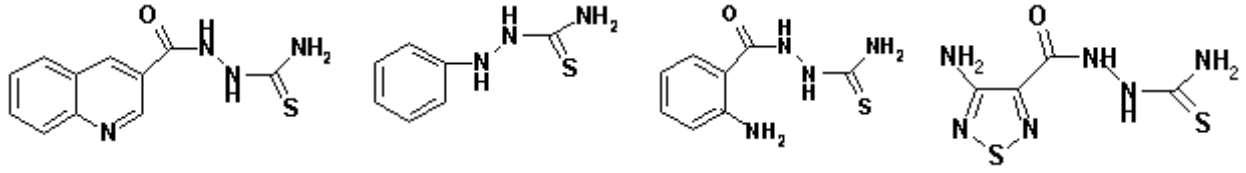
Crown ethers and their complexes have been intensively studied during the last 30 years.[1] The interest stems not only from the fact that these studies provide unlimited exploration of structural assembly but also from the chemical and biological potential of these compounds as ion exchangers and possible agents for transporting ionic species in living tissues. The relative simplicity of the appropriate model system allows for specific interactions to be isolated and studied in the absence of the many other interactions that may be present in biological macromolecules. Verification of unusual properties in synthetic receptor systems and the general extensibility of the chemistry can give inside into the biological implications for such chemical interactions.

This paper will outline further studies on hydrogen–bonded polymeric networks constructed through the interaction of 18-crown-6 with thiosemicarbazide ligands (Scheme 1), and 18-crown-6, *cis-syn-cis* isomer of dicyclohexyl-18-crown-6, diaza-18-crown-6 and tet b with dihydropyrimidine–2,4–(1H,3H)–dione derivatives (Scheme 2) possessing the multisite–connecting geometry. In the first series all the complexes possess 1:2 stoichiometry.

QH **PH** **TB** **HT**

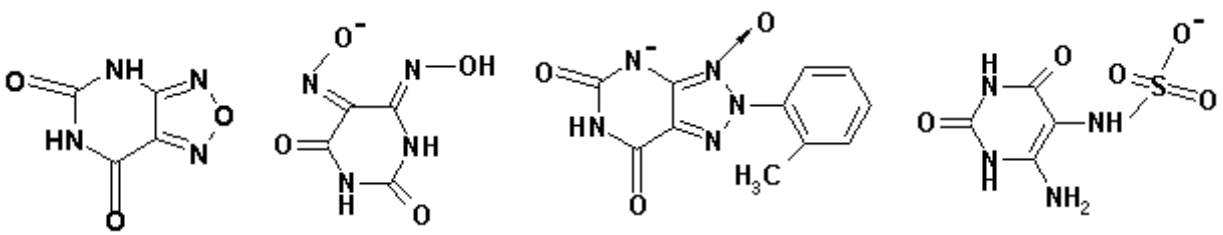


Scheme 1

QH are *self-assembled into dimers* (synthon I in Chart 1) and alternate with 18-crown-6 spacer in the *chains.* Single N-H···S hydrogen bond combines the PH molecules in the *chains* and 18-crown-6 molecules are attached to each PH molecule in chain *via* terminal NH_2-functionality, thus providing the *layer* structure. The center–of–symmetry–related TB molecules *are self–assembled into the chains via* three hydrogen bonding patterns (including I and II in Chart 1). These *chains* and the *rows* of 18–crown–6 molecules attached to them formulate the H-bonding *layers*. Being rich in H-donor and H-acceptor binding sites, HT molecules are self-assembled into ribbons and assembled with the crown spacers into the *3D network*.

The novel pyrimidine derivatives, being well endowed with hydrogen-bond donors and acceptors, have the potential to adopt and really exhibit several modes of inter-ligand hydrogen bonding.

OPD **(**H–PTD**)**$^-$ **(**PD**)**$^-$ **(**PS**)**$^-$



Scheme 2

OPD alternate with water and diaza-18-crown-6 spacers in the hydrogen-bonding *chains*. (H–PTD)$^-$ are *self-assembled into chains* and further *assembled in the ribbons* with ammonium cations and *cis-syn-cis* isomer of dicyclohexyl-18-crown-6. (H–PTD)$^-$ are *self-assembled in the dimers* and further into *3D network* with

diazonia-18-crown-6. $(PD)^-$ and water molecules are *assembled in the layers* with diazonia-18-crown-6 cations being occupied the holes in them. $(PS)^-$ are *self-assembled in the layers* (synthons III-V in Chart 1) and further *assembled into 3D network* through the intermediate water molecules and diazonia-18-crown-6 cations.

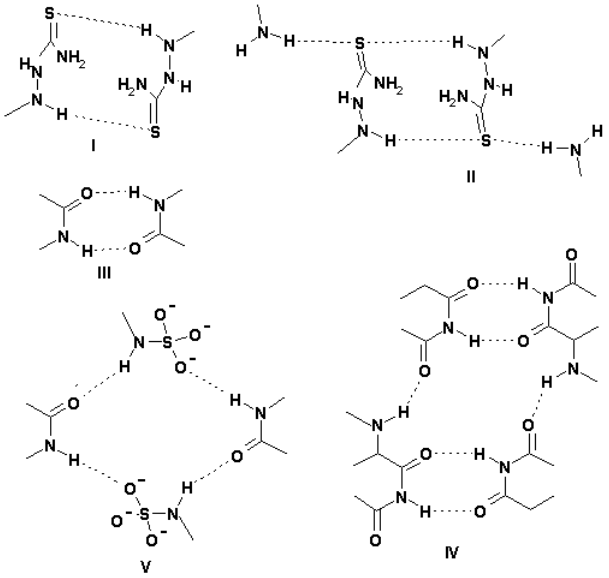


Chart 1. Supramolecular synthons that sustain the self-assembly of thiosemicarbazide and pyrimidone derivatives in the complexes with crown ethers.

Додаток **6**

Копія статті.

“The hydrogen-bonded adduct 7,16-diazonia-18-crown-6 – 4-aminobenzenesulfonate – water ”

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The hydrogen-bonded adduct 7,16-diazonia-18-crown-6–4-aminobenzenesulfonate–water (1/2/2)

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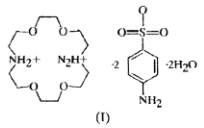
In the title hydrated adduct, 1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(4-aminobenzenesulfonate) dihydrate, $C_{12}H_{28}N_2O_4^{2+}\cdot 2C_6H_6NO_3S^-\cdot 2H_2O$, formed between 7,16-diaza-18-crown-6 and the dihydrate of 4-aminobenzenesulfonic acid, the macrocyclic cations lie across centres of inversion in the orthorhombic space group *Pbca*. The anions alone form zigzag chains, and the cations and anions together form sheets that are linked *via* water molecules and anions to form a three-dimensional grid.

Comment

N-containing crown ethers merit considerable attention for their host behaviour as receptors for anions and neutral organic molecules (Goldberg, 1984; Lehn, 1995; Vögtle & Weber, 1985). These receptors are capable of being included in the extended supramolecular networks formed by self-assembled organic molecules, rich in both hydrogen-donor and -acceptor centres, with partial preservation or rearrangement of the hydrogen bonds which sustain the supramolecular architecture.

Diaza-18-crown-6 has attracted our attention as a suitable macrocycle to provide hydrogen-bonded frameworks. A search of the Cambridge Structural Database (CSD, April 2002 release; Allen, 2002) yielded a list of 17 entries covering complexes of 7,16-diazonia-18-crown-6 with different anions and water molecules with extended hydrogen-bonded architectures. The closest crown environment that includes both water molecules and anions in an inversion symmetry-related fashion is found in the 7,16-diazonia-18-crown-6 hydrates with tetrahydroxypentaborate (Chekhlov & Martynov, 1998), a 1,10-dioate derivative (Chekhlov, 2000) and hydrogen sulfate (Chekhlov, 1995). Another route for macrocyclic cation coordination also exists when the anions (formate, tartrate, hydrogen tartrate, sulfate) are bound directly to the macrocycle *via* hydrogen bonds, while the water molecules are not involved in direct contacts with the macrocycle but bridge the anions in the chains (Chekhlov, 1999; Chekhlov & Martynov, 1999*a*,*b*; Chekhlov, 1996). 7,16-Diaza-18-crown-6 and the dihydrate of 4-aminobenzenesulfonic acid form the title hydrated salt, (I), and its structure is presented here.



(I)

The centrosymmetric formula unit of (I) is shown in Fig. 1. This salt crystallizes in space group *Pbca* with $Z = 4$. The macrocyclic cation adopts a C_i conformation and lies across a centre of inversion. The water molecule acts as a double donor, using O—H···O hydrogen bonds between the crown cation and the anion (Table 1), and as a single acceptor, in N—H···O hydrogen bonds with the crown cation. The 4-aminobenzenesulfonate anion and the macrocyclic cation are arranged in a T-shaped mode, with the dihedral angle between the mean planes of the aromatic ring and the six-membered set of N and O atoms of the crown ether being 80.63 (6)°.

It is possible to identify one-component hydrogen-bonded zigzag chains built from the anions running along the [100] direction. The amino atom N11 of the anion at the original position forms a weak hydrogen bond with atom O11 of the anion at $(\frac{1}{2}+x, y, \frac{1}{2}-z)$, with N11···O11 3.052 (5) Å and the angle subtended at the H atom being 168 (3)°.

Each anion in the self-assembled chain interacts with the macrocyclic cation *via* the same atom O11, with N1···O11 2.920 (3) Å [angle subtended at the H atom 175 (3)°]. The anionic chains and the cations attached to them generate sheets running parallel to the (101) plane (Fig. 2). These sheets are built from the centrosymmetric six-membered fused rings that combine two cations and four anions, each component being shared between two neighbouring rings.

The water molecules are located 1.702 (2) Å above and below the macrocyclic cavity and are bound to the macrocycle *via* the above-mentioned O—H···O and N—H···O hydrogen bonds (Table 1). The water molecule acts as a hydrogen-bond donor to sulfonate atom O12 of the anion related to that at the origin by a twofold screw axis, with O1*W*···O12$(\frac{3}{2}-x, y-\frac{1}{2}, z)$ 2.764 (3) Å [angle subtended at the H atom 161 (3)°], and functions as a bridge between adjacent sheets, consolidating them into a three-dimensional network. The architecture of (I) strictly resembles that of 7,16-diazonia-18-crown-6 bis(-hydrogen sulfate) dihydrate (Chekhlov, 1995).

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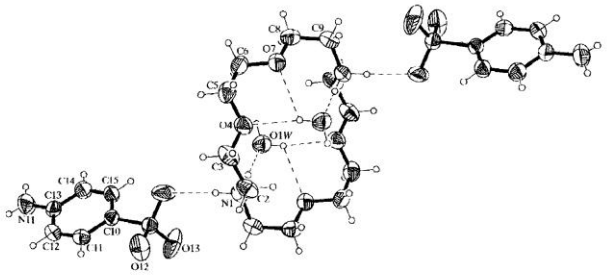

Figure 1
The structure of (I) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the asymmetric unit is numbered. The minor site of the disordered SO_3 group has been omitted for clarity.

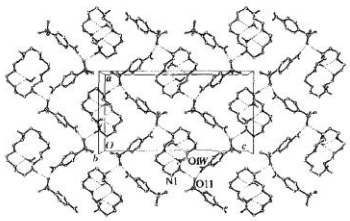

Figure 2
Part of the crystal structure of (I) showing the (101) sheets formed by the hydrogen-bonded anions and cations. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Experimental

Diaza-18-crown-6 (52.4 mg, 0.02 mmol) and 4-$H_2NC_6H_4SO_3H$ (83.6 mg, 0.04 mmol) were dissolved in a mixture of water (1.5 ml), methanol (2 ml) and *n*-butanol (4 ml). The resulting clear solution was slowly reduced in volume by evaporating the solvents at room temperature. Crystals of (I) suitable for X-ray analysis were selected directly from the analytical sample in a yield of 85% (110 mg) [m.p. 498–500 K]. Analysis, found: C 44.73, H 6.85, N 8.74%; $C_{24}H_{44}N_4O_{12}S_2$ requires: C 44.71, H 6.88, N 8.69%.

Crystal data

$C_{12}H_{28}N_2O_4^{2+}\cdot 2C_6H_6NO_3S^-\cdot 2H_2O$	Mo $K\alpha$ radiation
M_r = 644.75	Cell parameters from 5186 reflections
Orthorhombic, *Pbca*	θ = 1.0–25.0°
a = 12.319 (2) Å	μ = 0.24 mm^{-1}
b = 10.976 (2) Å	T = 293 (2) K
c = 22.826 (4) Å	Plate, white
V = 3086.4 (9) Å^3	0.25 × 0.15 × 0.10 mm
Z = 4	
D_x = 1.388 Mg m^{-3}	

Data collection

Nonius KappaCCD area-detector diffractometer	R_{int} = 0.030
φ scans	θ_{max} = 25.2°
5052 measured reflections	$h = -14 \rightarrow 14$
2730 independent reflections	$k = -13 \rightarrow 13$
1821 reflections with $I > 2\sigma(I)$	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 0.3407P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.042	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.118	$\Delta\rho_{max}$ = 0.35 e Å^{-3}
S = 1.04	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
2730 reflections	Extinction correction: *SHELXL97* (Sheldrick, 1997)
226 parameters	Extinction coefficient: 0.0081 (9)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O11	0.94 (2)	1.99 (2)	2.920 (3)	175 (3)
N1—H1N···O11A	0.94 (2)	2.02 (3)	2.84 (2)	146 (3)
N1—H2N···O1W	0.95 (2)	1.84 (2)	2.778 (3)	170 (3)
O1W—H2W···O4^{i}	0.83 (2)	2.11 (3)	2.933 (3)	170 (3)
O1W—H2W···O7^{i}	0.83 (2)	2.39 (3)	2.848 (3)	115 (3)
O1W—H1W···O12^{ii}	0.84 (2)	1.95 (2)	2.764 (3)	161 (3)
O1W—H1W···O12A^{ii}	0.84 (2)	2.21 (4)	2.88 (2)	136 (3)
N11—H11N···O12^{iii}	0.87 (3)	2.66 (3)	3.407 (5)	146 (3)
N11—H11N···O12A^{iii}	0.87 (3)	1.84 (4)	2.682 (17)	162 (3)
N11—H12N···O11^{iv}	0.82 (4)	2.25 (4)	3.052 (5)	168 (3)
N11—H12N···O11A^{iv}	0.82 (4)	2.47 (4)	3.25 (2)	161 (3)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (iii) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $\frac{1}{2}+x, y, \frac{1}{2}-z$.

Anisotropic displacement parameters were used for all non-H atoms except the O atoms of the SO_3-group minor site. This group was found to be disordered over two sites rotated about the C—S axis, with occupancy factors of 0.932 and 0.068. The major site was refined with anisotropic displacement parameters and the minor site was treated with *SADI* (*SHELXL97*; Sheldrick, 1997) restraints for

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three S—O distances and a group-value isotropic displacement parameter. The coordinates of the H atoms on atoms N1, N11 and O1*W* were determined from a difference map and were then allowed to refine isotropically subject to a *DFIX* (*SHELXL97*) restraint. All other H atoms were riding, with C—H distances in the range 0.93–0.97 Å. **Is this added text OK?** The final difference Fourier map did not show positions for disordered H atoms on the water molecule. The hydrogen-bonding system is the same for the two positions of the SO_3 group, as shown in Table 1.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *ORTEPIII* (Farrugia, 1997); software used to prepare material for publication: *SHELXS97*.

Financial support from the MRDA–CDRF (research grant MP2-3021) is kindly acknowledged. The diffraction data were collected at the Department of Chemistry, Technion, Haifa, through the cooperation of Professor Menahem Kaftory, whom the authors would like to acknowledge.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1151). Services for accessing these data are described at the back of the journal.

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Додаток 7

Копія статті.

“Hydrogen bonding assemblies in host-guest complexes with 18-crown-6”

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Journal of Molecular Structure 647 (2003) 129–140

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Hydrogen bonding assemblies in host–guest complexes with 18-crown-6

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Abstract

Recent X-ray crystal structural data for two novel 1:2 host-guest complexes of 18-crown-6 with neutral organic molecules, thiaamide hydrazide of 2-aminobenzoic acid and thiaamide hydrazide of 4-amino-1,2,5-thiadiazole-3-carbonic acid are reported. The supramolecular structures of these two and five relative complexes are discussed from the point of view of participation of donor groups in coordination with the crown ether, and donor and acceptor groups in the self-assembly of the guest molecules. Guest molecules have incorporated amine and hydrazine moieties as proton donors and carbonyl oxygen and sulfur (in thiadiazole and in thiaamine moieties) as proton acceptors. The guest–guest interactions appeared to be crucial in the final architecture.
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Keywords: Crown ether; Host–guest complex; H-bonding; X-ray crystallography

1. Introduction

The macrocycles that Pedersen named crown ethers [1] have now been known for more than three decades and their structures, free and bound with metallic and organic cations as well as with neutral species, have been reported [2,3]. Despite extensive study and application of crowns, novel properties continue to emerge. The relative simplicity of an appropriate model system based on the crown ether allows specific interactions to be isolated and studied in the absence of many other interactions that are present in natural biological systems.

We are interested in the 18-crown-6 chemistry using this suitable module in complexes with neutral organic molecules to obtain extended supramolecular networks. Some previous examples [4,5] seemed interesting and encouraged us to study novel supramolecular complexes.

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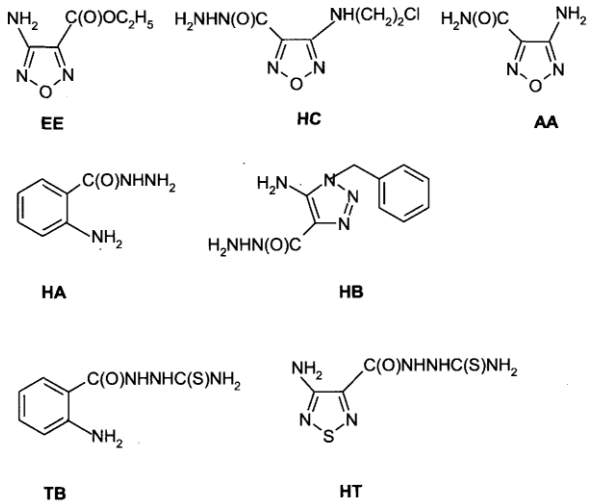

Scheme 1. Guest molecules incorporated into molecular complexes **I–VII**.

Crystal structures of the 18-crown-6 complexes with the ethyl ester of 4-amine-1,2,5-oxadiazole-3-carbonic acid (EE), (complex **I**, composition 1:1), hydrazide of 4-(2-chloroethylamino)-1,2,5-oxadiazole-3-carbonic acid (HC), (**II**, 1:2), amide of 4-amine-1,2,5-oxadiazole-3-carbonic acid monohydrate (AA), (**III**, 1:1:1) [6], hydrazide of 2-aminobenzoic acid monohydrate (HA), (**IV**, 1:2:2), hydrazide of 5-amine-1-benzyl-1,2,3-triazole-4-carbonic acid (HB), (**V**, 1:2) [7], thiaamide hydrazide of 2-aminobenzoic acid (TB), (**VI**, 1:2), and thiaamide hydrazide of 4-amino-1,2,5-thiadiazole-3-carbonic acid (HT), (**VII**, 1:2) are discussed. The neutral organic molecules have an amine or hydrazine group as a suitable H-donor for complex formation and different acceptor centers in the neighboring position of five-membered (diazole, triazole, thiadiazole) or aromatic rings to provide an opportunity for self-assembly (Scheme 1).

For the formulation of a linear (1D), sheet (2D) or carcass (3D) structure in complexes with 18-crown-6, not only the mutual complementarity of the guest donor and crown acceptor binding sites is important, but also the capability of guest molecule for the self-assembly.

2. Discussion

2.1. Chain structures

In the structure of **I** the components are assembled into alternating chains running along the *b* direction in the unit cell (Fig. 1). The crown ether exhibits unusual 'different-faced' geometry due to asymmetric binding with amine and ethyl groups of EE coordinated to macrocyclic rings in a face-to-tail manner. The amine group forms two NH···O hydrogen bonds, N(3)···O(4) 3.087(2) and N(3)···O(16) 3.202(2) Å, while the ethyl group donates two hydrogens, one from the methyl and one from the methylene group for CH···O interactions, both being approximately linear, C(4)···O(1) 3.311(3), C(4)–H···O(1) 2.43 Å, angle C(4)–H···O(1) 150°, and C(5)···O(7) 3.537(3), C(5)–H···O(7) 2.58 Å, angle C(5)–H···O(7) 175°. Apart from geometric details, the range of C–H···O interactions is very similar to that observed in the binary complexes of 18-crown-6, with, for example, dimethylsulfoxide (C···O 3.287(3)–3.598(3) Å) [8] or with methyl 10-camphor sulfonate (C···O distances from 3.264(7) to 3.801(7) Å) [9]. The weak

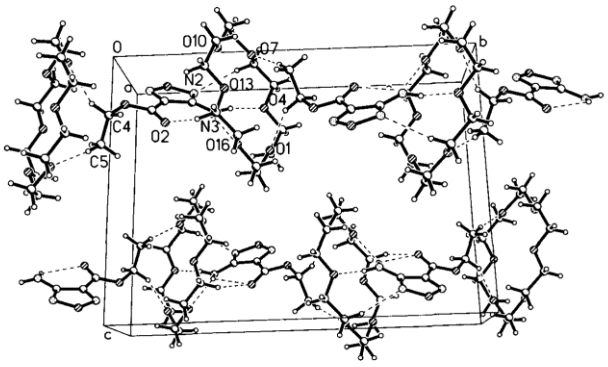

Fig. 1. Chains in **I**.

CH···O=C and CH···N hydrogen bonds, C···O 3.311(3) and C···N 3.417(3) Å between the hydrogen atoms of the crown-ether methylene groups and carbonyl oxygen and diazole nitrogen atoms as acceptor binding sites of the EE molecule also contribute to the overall system of interaction. The mutual arrangement of the components is characterized by a dihedral angle of 57.4(1)° between the mean plane of the oxadiazole moiety and the mean plane of six oxygen atoms of the crown ring.

The distinctive feature of **I** is the participation of ethyl moiety in coordination to the crown ether. The numerous previously described examples for 18-crown-6 complexes [10] show the involvement of guest methyl [11–26] or methylene group [27–30] in the center-of-symmetry related C–H···O hydrogen bonds. The different-faced coordination for the 18-crown-6 molecule often provides the host-guest alternate chain structure and was found previously in its 1:1 complex with 6-chloro-7-sulphamido-3, 4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide [31], and in the ternary 18-crown-6 complexes with the hydrates of acetic [32], maleic [33], succinic [34] acids, and isonitrosocyanoacetamide [35].

The chain motif for complex **II** is depicted in Fig. 2 It is developed along the [110] direction in the unit cell. Two HC molecules approach in a similar face-to-face manner to the crown ring, and each affords three NH···O(crown) hydrogen bonds with the participation of all hydrazine hydrogen atoms and all crown ether oxygen atoms in coordination, N···O distances N(1)···O(4) 2.905(4), N(2)···O(1) 3.110(4), N(2)··· O(7) 3.092(4) Å. The hydrogen atoms of the hydrazine group are in a *cis*-position to the N(1)–N(2) covalent bond in HC, that ensures their complete involvement in the coordination to the same crown molecule, unlike the *trans*-orientation of these hydrogen atoms in phenylhydrazide monohydrate [36], that provides hydrogen bonds with the different molecules. Two center-of-symmetry-related HC molecules in **II** via NH···O=C hydrogen bonding mode form a planar centrosymmetric dimer, N(3)···O(2)$(-x+1, -y, -z)$ 2.873(4) Å, graph set $R_2^2(12)$ [37]. Crown molecules and HC dimers alternate in the chain. The mutual arrangement of the components is characterized by a dihedral angle of 47.0(1)° between the mean plane of oxadiazole moiety and the mean plane of six oxygen atoms of the crown ring. Chlorine atoms do not contribute to the overall system of H-bonded interactions.

Both in **I** and **II** the interactions shorter than the sum of van der Waals radii are absent between the neighboring chains.

2.2. Ribbon structure

In **III** co-crystallisation leads to a ternary complex with stoichiometry 1:1:1. The polar water solvent is inserted as an ambifunctional complementary mediator between AA and the macrocyclic

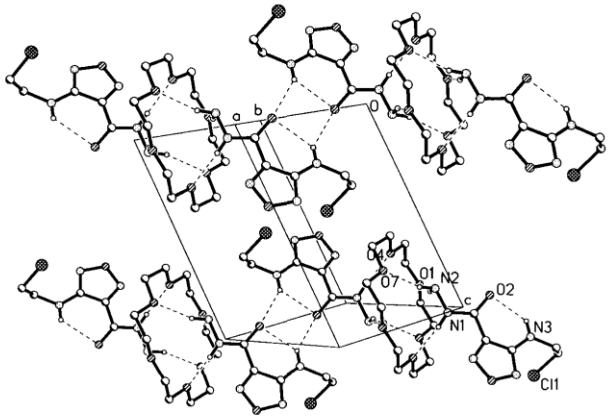

Fig. 2. Chains in **II**. All H-atoms except those of hydrazine groups are omitted for the sake of clarity.

heterocycle (Fig. 3). It provides two OH···O hydrogen bonds, O(1w)···O(10) 2.842(4) and O(1w)···O(16) 2.959(5) Å with two crown oxygen atoms. As H-acceptor, water molecule is involved in NH···O hydrogen bond with the amine group of the AA molecule, N(4)···O(1w) 2.783(4) Å. The dihedral angle between the mean plane of the oxadiazole moiety and the mean plane of the six oxygen atoms of the crown ring is 70.0(1)°. The organization of the 18-crown-6-water-AA associate in **III** resembles the arrangement of the ternary complex of 18-crown-6 with water and 3,4-diamino-1,2,5-oxadiazole [38], where the water molecule provides two OH···O hydrogen bonds with the macrocycle, and donates a lone pair for the interaction with the 3,4-diamino-1,2,5-oxadiazole molecule. In **III** the AA molecules related by the glide plane are organised into a planar herringbone chain through the NH···N, N(3)···N(2)(x, $-y+2$, $z+1/2$) 3.077(5) Å and NH···O=C, N(3)···O(2)(x, $-y+2$, $z-1/2$) 2.854(5) Å hydrogen bonds, $R_2^2(10)$. The chain is imprisoned between two successive rows of crown molecules, thus constituting the ribbon propagated in the bc plane. The ribbons are mutually oriented by the crown-ethers' hydrophobic parts in the direction of each other and the contacts shorter than the sum of van der Waals radii were not found between

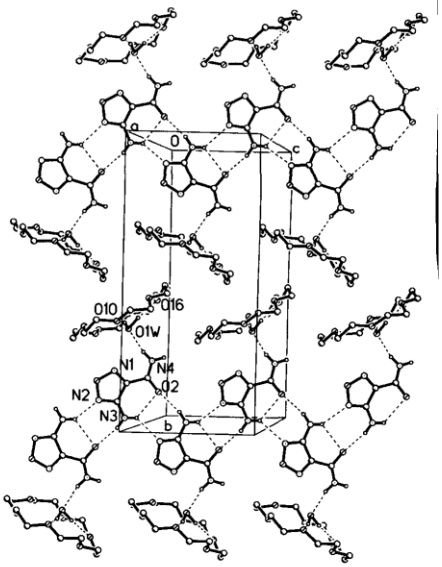

Fig. 3. Ribbons in **III**. H-atoms of crown molecules are omitted for the sake of clarity.

the neighboring ribbons (Fig. 3). In **III** the 18-crown-6 molecule exhibits a rare, single-faced coordination mode. A search of CSD [10] gave only a few examples of single-faced coordination of neutral molecules such as amminetrihydroboron [39], monoaqua-trifluoroborone [40], benzenesulfonamide [41], and nitrosoaniline [42] in their 1:1 complexes with 18-crown-6. Commonly, water molecules as mediators between crown ring and neutral molecules interact in the same way on the both sides of the centrosymmetric cavity and donate two hydrogen atoms for H-bonds with 18-crown-6 and a lone pair for an H-bond with the guest molecule. As examples one should mention of the hydrates of 18-crown-6 complexes with the derivatives of phenol [43–47], acids [48–51], sulfonyl derivatives [52–54], and hydrates of 18-crown-6 itself [55,56].

2.3. Layer structures

We succeeded in setting up 2D structures when the water molecule served as a pyramidal connector between HA and 18-crown-6 in the ternary complex **IV**, when the methylene group was introduced as an angular fragment into the HB molecule between phenyl and triazole rings in **V**, and when sulfur atoms of the thiadiasole ring and terminal S=C group of the TB molecule contributed to the overall system of interactions in **VI**. These neutral molecules afford an opportunity for the structures to develop in two directions, and facilitate the formation of 2D networks.

In **IV** the centrosymmetric complex HA-18-crown-6-HA is stabilized by six center-of-symmetry-related NH···O hydrogen bonds between three hydrogen atoms of the hydrazine fragment of the HA molecule and all oxygen atoms of the macrocycle; N···O N(1)···O(4)($-x+2$, $-y$, $-z+1$) 2.961(1), N(2)···O(1) 2.995(1), N(2)···O(7) 3.141(1) Å (Fig. 4). As in HC, the hydrogen atoms of the hydrazine group are located in *cis*-positions with respect to the N(1)–N(2) bond. The HA and 18-crown-6 molecules in **IV** are arranged in such a way that the dihedral angle between the mean plane of the phenyl ring of HA and the mean plane of six oxygen atoms of the crown ether is 23.5(4)°. The water molecule behaves as a bridge between two, glide-plane-related, HA molecules. It affords two hydrogen bonds: with a lone pair of the nitrogen atom of the amine-group, and the carbonyl oxygen atom of the HA molecule, O(1w)···N(2) 2.925(1), and O(1w)···O(2) 2.913(1) Å. The lone pair of the water molecule accepts the H-atom of the amine-group of the HA molecule, N(3)···O(1w) 3.102(1) Å. Thus, via NH···O hydrogen bonds, HA and the water molecules alternate in the chains. Due to the pyramidal geometry of water, these chains are developed in a staircase mode, and the centrosymmetric crown molecules attached to them form closed centrosymmetric cages that combine four crown molecules, six HA, and four water molecules. Each associate is stabilized by 32 NH···O hydrogen bonds, which are NH···O(crown) and NH···O(water) interactions. The assembly of these cages forms the layer. The layers are propagated parallel to the *bc* plane in the unit cell.

The host–guest interaction mode between HB and the crown ether in **V** closely resembles **IV** (Fig. 5). The hydrazine group donates all hydrogens for NH···O hydrogen bonds: N(1)···O(4)($-x$, $-y+1$, $-z$) 2.897(3), N(2)···O(1) 3.223(4), and N(2)···O(7) 3.082(4) Å. The HB molecules related by a twofold screw axis form corrugated chains via NH···O and NH···N hydrogen bonds, N(3)···O(2)($-x$, $y-1/2$, $-z+1/2$) 3.075(3), and N(3)···N(2)($-x$, $y-1/2$, $-z+1/2$) 3.116(4) Å. In the complex the dihedral angle between the mean plane of six oxygen atoms of the macrocycle and the triazole ring of HB is equal to 76.8(1)°. This T-shaped arrangement is rather typical for the complexes of eighteen-membered crown ethers (for example, 18-crown-6 and the A and B isomers of dicyclohexyl-18-crown-6) with amino derivatives of benzene and five-membered heterocycles [57, 58]. The HB chains associated with the crown molecules provide a pleated layer structure. In the layer six HB and two 18-crown-6 molecules are joined to form a centrosymmetric cage which is stabilized by 16 intermolecular hydrogen bonds of the NH···O(crown) and NH···O=C types.

The centrosymmetric formula unit of the 1:2 molecular complex **VI** is shown in Fig. 6. The amine group of each TB molecule defined by N(3) atom, provides two N–H···O hydrogen bonds with crown oxygen atoms, N(3)···O(14) 2.960(2) Å,

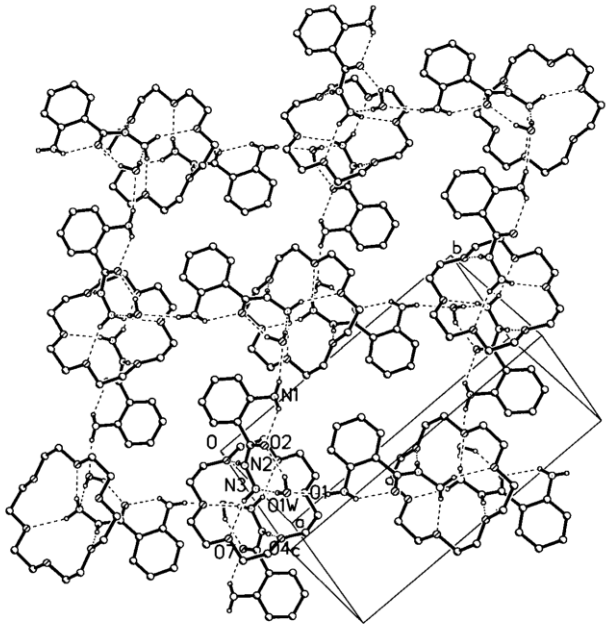

Fig. 4. Layer in **IV**. Non-functional H-atoms are omitted for the sake of clarity.

N(3)···O(17)($-x+1$, $-y+2$, $-z$) 3.175(2) Å (details of hydrogen bonding for **VI** and **VII** are given in Table 1). Besides, in host–guest interactions the closest to the thiaamide fragment amine group of hydrazine moiety defined by the N(2) atom, takes part, N(2)···O(11)(x, $y-2$, z) 3.173(2) Å. Its hydrogen atom is directed in the opposite side with respect to the hydrogen atoms of N(3) amine group and provides the assembly of the TB-18-crown-6-TB complexes into the chains, running along b direction in the unit cell. The dihedral angle between the mean plane of phenyl ring in TB and the mean plane of the six oxygen atoms of the macrocycle is equal 39.62(3)°. The intramolecular NH···O hydrogen bond closes the 6-membered ring, N(4) ···O(1) 2.762(2) Å, and affords a system of two conjugated rings with a dihedral angle between the mean planes of phenyl ring and H-cycle equal 9.6(2)°. The center-of-symmetry-related TB molecules are self-assembled into the chains via three different hydrogen bonding patterns (Fig. 7). In two of them the amine group attached to the phenyl ring takes part, N(4)···O(1)($-x+2$, $-y+1$, $-z$) 2.951(2) Å, $R_2^2(12)$; N(4)···S(1)($-x+2$, $-y+1$, $-z$) 3.636(2) Å, $R_2^2(18)$. The third supramolecular synthon combines nitrogen and sulfur atoms of two center-of-symmetry-related thiosemicarbazide moieties, N(1)···S(1)($-x+1$, $-y+1$, $-z$) 3.316(2) Å, $R_2^2(10)$. In **VI** the chains of TB molecules running along a direction in the unit cell and the rows of 18-crown-6 molecules attached to them alternate in the layers developed in the ab plane (Fig. 8).

2.4. 3D network

The centrosymmetric formula unit of the 1:2 molecular complex **VII** is shown in Fig. 9.

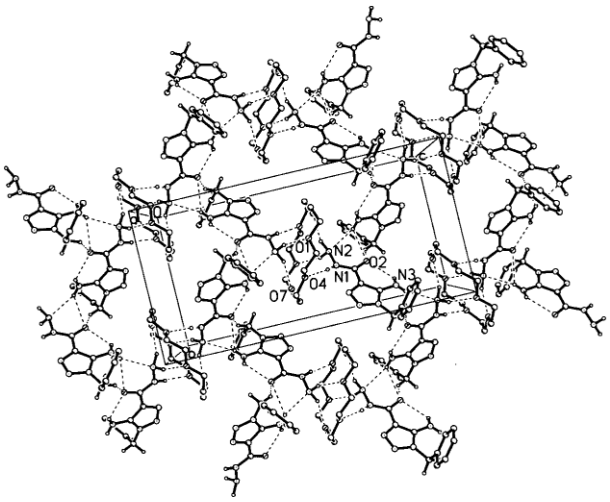

Fig. 5. Layer in **V**. H-atoms of crown molecules are omitted for the sake of clarity.

The amine group of each HT molecule is bonded to the crown ether through a set of N–H···O interactions, N···O 2.970(2) −3.170(2) Å (details in Table 1); each hydrogen atom of the amine group is involved in bifurcated NH···O hydrogen bonds. The C(8)–N(3) bond deviates at an angle of 6° from the normal to the mean plane of the six oxygen atoms of the macrocycle. The thiadiazole

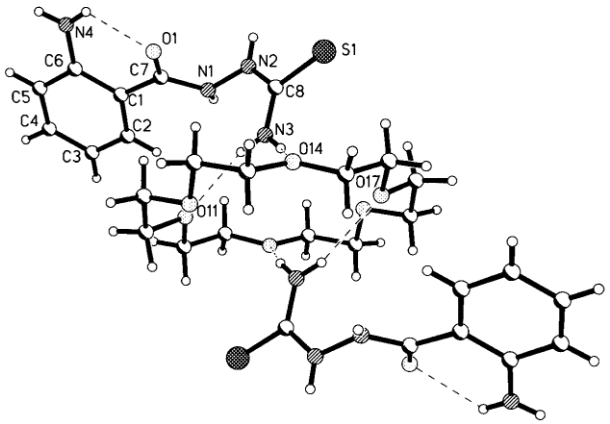

Fig. 6. Side view of **VI**. Intra- and intermolecular hydrogen bonds are shown as dashed lines.

Table 1
Hydrogen bonds in complexes **VI** and **VII**

D–H···A	d(D–H), Å	d(H···A), Å	d(D···A), Å	∠(DHA),°	Symmetry operation for the H-acceptor
Complex **VI**					
N(1)–H(1N1)···S(1)	0.81(2)	2.60(2)	3.316(2)	147(2)	$-x+1, -y+1, -z$
N(2)–H(1N2)···O(11)	0.82(2)	2.41(2)	3.173(2)	154(2)	$x, y-y+1, z$
N(3)–H(1N3)···O(17)	0.88(2)	2.34(2)	3.175(2)	158(2)	$-x+1, -y+2, -z$
N(3)–H(2N3)···O(14)	0.83(2)	2.20(2)	2.960(2)	152(2)	X, y, z
N(4)–H(1N4)···S(1)	0.81(2)	2.87(2)	3.636(2)	158(2)	$-x+2, -y+1, -z$
N(4)–H(2N4)···O(1)	0.87(2)	2.15(2)	2.951(2)	153(2)	$-x+2, -y+1, -z$
N(4)–H(2N4)···O(1)	0.87(2)	2.18(2)	2.762(2)	124(2)	x, y, z
Complex **VII**					
N(2)–H(2N)···S(1)	0.86(2)	2.53(2)	3.344(1)	158(2)	$-x+1, -y+1, -z+1$
N(3)–H(1N3)···O(14)	0.84(2)	2.38(2)	3.038(2)	136(2)	x, y, z
N(3)–H(1N3)···O(17)	0.84(2)	2.49(2)	3.170(2)	139(2)	x, y, z
N(3)–H(2N3)···O(17)	0.86(2)	2.21(2)	3.033(2)	160(2)	$-x+1, -y, -z;$
N(3)–H(2N3)···O(11)	0.86(2)	2.42(2)	2.970(2)	122(2)	$x, y, z;$
N(4)–H(1N4)···S(1)	0.86(2)	2.53(2)	3.374(1)	167(2)	$x-1, y-1, z$
N(4)–H(2N4)···O(1)	0.89(2)	2.17(2)	2.819(2)	129(2)	$x, y, z;$

ring forms a dihedral angle of 21.2° with the same plane. In HT, as in all the guest molecules described above, the intramolecular NH···O hydrogen bond closes the 6-membered ring, N(4)···O(1) 2.819(2) Å, and provides an almost planar system of two conjugated rings, with a dihedral angle of 2.82(2)°.

The **HT**-18-crown-6-**HT** complexes are combined into chains via a centrosymmetric module of two NH···S hydrogen bonds, N(2)···S(1)($-x+1$, $-y+1$, $-z+1$) 3.344(1) Å, $R_2^2(8)$. The chains run along c direction in the unit cell (Fig. 10).

The **HT** molecule is rich in donor and acceptor binding sites, namely two primary and two secondary amine groups as H-donors, and two sulfur atoms, one carbonyl oxygen and two nitrogen atoms of thiadiazole ring as acceptors. It facilitates the self-assembly of HT molecules via a plethora

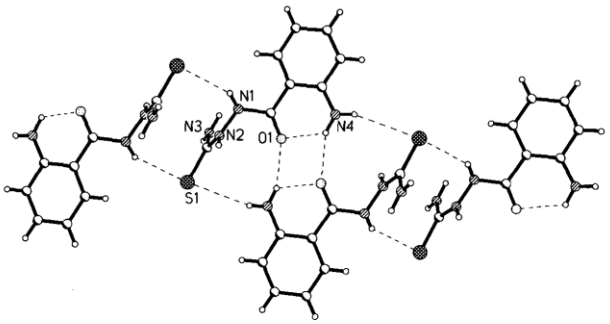

Fig. 7. Chain constituted of **TB** molecules in **VI**. H-bonds are shown as dashed lines.

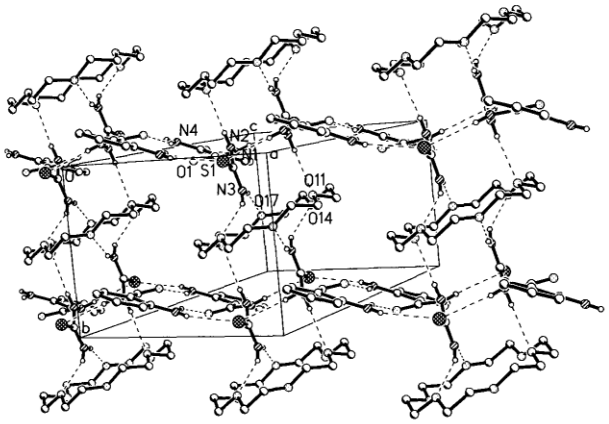

Fig. 8. Layer in **VI**. Non-functional H-atoms are omitted for the sake of clarity.

of diverse hydrogen bonds and non-hydrogen interactions. Two center-of-symmetry-related **HT** molecules are linked in the dimer through four short interactions arranged in zipper-like mode, two NH···N hydrogen bonds, N(1)···N(5)($-x+1$, $-y$, $-z+1$) 3.013(2) Å, $R_2^2(10)$ and two N(2)···S(2)($-x+1$, $-y$, $-z+1$) contacts of 3.259(2) Å which close the 12-membered ring. The pair of N···S centrosymmetric interactions, N(6) ···(2)($-x$, $-1-y$, $1-z$) 3.236(2) Å combines these dimers in the ribbon (Fig. 11). The ribbons are also sustained by two NH···S hydrogen bonds between the hydrogen atom of the primary amine group defined by N(4) and the terminal sulfur atom S(1), N(4)···S(1)($x-1$, $y-1$, z) 3.374(1) Å. The guest ribbons run in the [110] direction, and along c axis direction they are linked into the 3D network via a centrosymmetric module of two above mentioned NH···S hydrogen bonds, N(2)···S(1)($-x+1$, $-y+1$, $-z+1$) (Fig. 10).

Thus, self-assembly of HT molecules in **VII** provides a 3D network unlike **IV**, **V**, and **VI**, where the 2D structures are built of the combination of the guest chains and 18-crown-6 molecules.

In all the complexes **I**–**VII** the conformation of 18-crown-6 molecule corresponds to the ideal D_{3d} geometry.

2.5. X-ray crystallography

Crystals of compounds **VI** and **VII** were obtained in nearly quantitative yield from slow evaporation of the reactants at room temperature. Intensity data for both complexes were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo Kα radiation using ω rotation with sample-to-detector distance of 40 mm. Preliminary orientation matrix and unit cell parameters were obtained from the peaks of the first 10 frames, respectively, and refined using the whole data set. Frames were integrated and corrected for Lorentz and

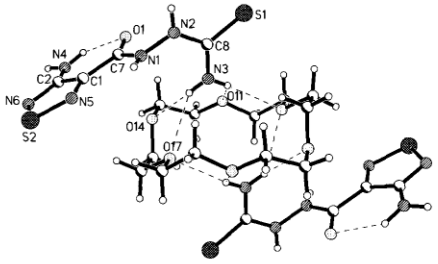

Fig. 9. Side view of **VII**. Intra- and intermolecular hydrogen bonds are shown as dashed lines.

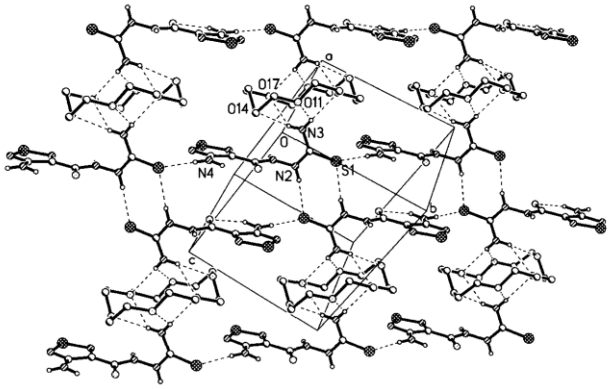

Fig. 10. Layer in **VII**. Non-functional H-atoms are omitted for the sake of clarity.

polarization effects using DENZO [59]. The scaling and global refinement of crystal parameters were performed by SCALEPACK [59]. Reflections, which were partly measured on previous and following frames, are used to scale these frames. The structures were solved by direct methods using SHELXS [60] and refined by full-matrix least-squares based on F^2 using SHELXL-97 [61]. Hydrogen atoms of methylene groups were included in calculated positions and refined with isotropic displacement parameters according to the riding model, while the N-bound H-atoms were found from Fourier maps and refined without any constraints.

2.6. Crystal data

The structures of **I–V** were taken from published reports [6,7].

Crystal data for **VI**: $M = 684.83$, pale yellow, prismatic, $0.25 \times 0.25 \times 15$ mm, monoclinic, sp.gr. $P2_1/c$, $a = 10.437(1)$ Å, $b = 7.942(1)$ Å, $c = 19.958(1)$ Å, $\beta = 90.89(2)°$, $Z = 2$, $V = 1654.13(9)$ Å^3 $D_c = 1.375$ g/mm^3; final $GoF = 1.180$, $R1 = 0.0537$, $wR2 = 0.0957$ based on 3740 reflections with $I > 2\sigma(I)$. Crystallographic data for **VI** have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-182691.

Crystal data for **VII**: $M = 700.85$, pale yellow, prismatic, $0.15 \times 0.15 \times 25$ mm, triclinic, sp.gr. $P-1$, $a = 9.112(3)$ Å, $b = 9.637(2)$ Å, $c = 10.479(3)$ Å, $\alpha = 111.89(1)°$, $\beta = 90.69(1)°$, $\gamma = 113.62(1)°$, $Z = 1$, $V = 768.06(4)$ Å^3 $D_c = 1.515$ g/mm^3; final $GoF = 1.077$, $R1 = 0.0466$, $wR2 = 0.0868$ based on 5296 reflections with $I > 2\sigma(I)$. Crystallographic data for **VII** have been deposited with the Cambridge

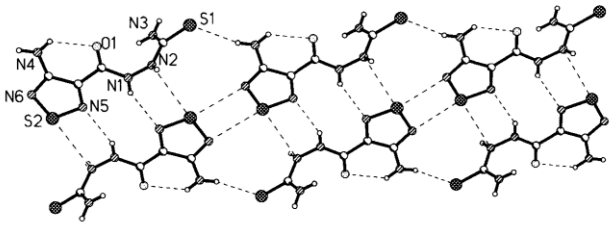

Fig. 11. Ribbon constituted of **HT** molecules in **VII**. H-bonds are shown by dashed lines.

Crystallographic Data Center as Supplementary Publication No. CCDC-175853.

3. Conclusions

The crucial factor that determines the structural type and architecture (one-, two- or three dimensionality) of 18-crown-6 complexes with neutral organic molecules is the mutual complementarity of donor and acceptor groups in the guest and complex stoichiometry.

4. Supplementary data

(cif files) for the complexes discussed in this article, have been deposited at the Cambridge Crystallographic Data Center under the deposition numbers 143357 (**I**), 143358 (**II**), 143359 (**III**), 160249 (**IV**), 160250 (**V**), 182691 (**VI**), 175853 (**VII**). The lists of F_o^2 and F_{calc}^2 for all the structures are available from the authors upon request.

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Додаток 8

Копія статті.

“Monoclinic polymorph of rac-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazoniacyclo-tetradecane bis(hexafluorogermanate) tetrahydrate”

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The monoclinic polymorph of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazoniacyclotetradecane bis(hexafluorogermanate) tetrahydrate

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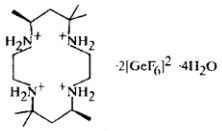
X-ray data were obtained for the monoclinic polymorph of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazoniacyclotetradecane bis(hexafluorogermanate) tetrahydrate, $(C_{16}H_{40}N_4)[GeF_6]_2{\cdot}4H_2O$. The tetraaza-macrocyclic cations lie across inversion centers in space group $P2_1/c$. Water molecules and $[GeF_6]^{2-}$ anions form zigzag chains, which alternate in a three-dimensional network with the macrocyclic cations. The structure is sustained by multiple hydrogen bonds.

Comment

The ability of crown ethers to stabilize in the form of the proper host–guest complexes normally unstable or volatile species is well known (Bott *et al.*, 1991; Chuit *et al.*, 1993; Feinberg *et al.*, 1993). Previously, we have shown that crown ethers (18-crown-6, isomers of dicyclohexyl-18-crown-6, mono- and diaza-18-crown-6, and diaza-15-crown-5) provide the opportunity to hold harmful gaseous (SiF_4; Simonov *et al.*, 1994), intermediate $[(SiF_5{\cdot}H_2O)^-$ and SiF_5^-; Simonov *et al.*, 1996; Gelmboldt *et al.*, 1999] or low-melting substances ($BF_3{\cdot}H_2O$; Fonari *et al.*, 1997) in the form of hydrogen-bonded molecular or ionic complexes. The Ge-containing species $GeF_4{\cdot}2H_2O$ and $(GeF_5{\cdot}H_2O)^-$, which are similar to the Si-containing complexes, were obtained by direct reaction between GeO_2–HF solution and 18-crown-6 and diaza-18-crown-6 (Gelmboldt *et al.*, 1996). The general tendency is that partial replacement of O atoms by N atoms in the macrocyclic ring or the application of aza-macrocycles (Simonov, Fonari *et al.*, 1998; Simonov, Lipkowski *et al.*, 1998; Fonari *et al.*, 1998, 1999) provokes the extraction of charged species, *viz.* $(SiF_5{\cdot}H_2O)^-$, SiF_6^{2-}, $(GeF_5{\cdot}H_2O)^-$ and GeF_6^{2-}, from aqueous solutions of fluorosilicic acid, H_2SiF_6, or its germanium analog, H_2GeF_6.

We recently reported the single-crystal X-ray structure of triclinic *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazoniacyclotetradecane bis(hexafluorogermanate) tetrahydrate (space group $P\overline{1}$; Fonari *et al.*, 1999), which shows extended intermolecular hydrogen bonding. As part of this study, we redetermined the structure of the title compound, (I), in order to improve on earlier structure determinations. Unexpectedly, the X-ray analysis revealed a new monoclinic (space group $P2_1/c$) polymorph of (I), which is the subject of the present communication.



(I)

The centrosymmetric formula unit of (I) is shown in Fig. 1. The slightly distorted $[GeF_6]^{2-}$ octahedron is characterized by Ge—F distances in the range 1.746 (1)–1.825 (1) Å and F—Ge—F angles that deviate slightly (3°) from 90 or 180° (Table 1); the geometry of the anion coincides with previously reported data (Fonari *et al.*, 1999; Simonov, Fonari *et al.*, 1998). The tetraprotonated macrocyclic tetraamine cation, $[H_4(C_{16}H_{36}N_4)]^{4+}$, resides on the inversion center, and the first coordination sphere of this cation is comprised of two $[GeF_6]^{2-}$ anions and two water molecules. Atom F4 bridges atoms N1 and N4 of the basic macrocycle *via* two N—H···F hydrogen bonds (N1···F4 and N4···F4; Table 2); the same N atoms are also bound *via* N1···F6 and N4···F2 interactions.

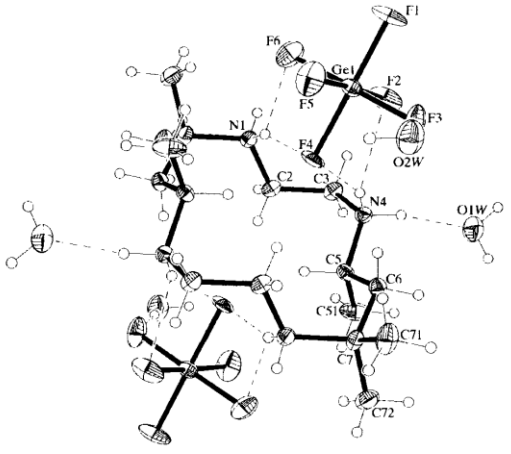


Figure 1
A view of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level, and only the asymmetric unit is labelled.

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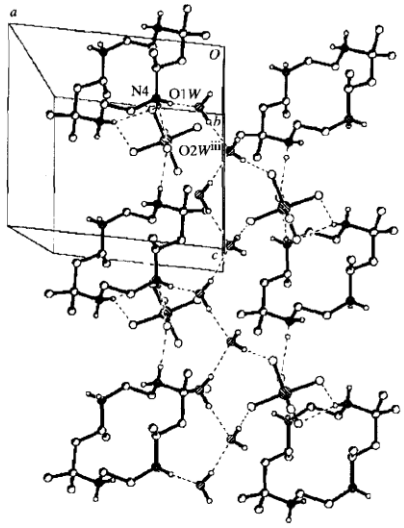

Figure 2
Part of the crystal structure of (I), showing the inorganic anionic chains, formed by hydrogen-bonded anions and water molecules, that alternate with macrocyclic cations. For the sake of clarity, H atoms bonded to C atoms have been omitted. [Symmetry code: (iii) $-x, 1-y, -z$.]

Atom F2 links two macrocycles translated along the *c* axis (*via* N—H···F interactions; see Table 2 for symmetry code).

Water molecule O2*W* has no direct contacts with the macrocycle but is involved in a negatively charged zigzag chain, which develops along the *c* direction in the unit cell and combines inorganic species, $[GeF_6]^{2-}$ anions and water molecules (Fig. 2). In this chain, O2*W* acts as a double hydrogen-bond donor and bridges two $[GeF_6]^{2-}$ anions that are related by the glide plane [O2*W*···F3 = 2.795 (2) Å and O2*W*···F1^{v} = 2.739 (2) Å; see Table 2 for symmetry code]. In the function of double acceptor, each O2*W* water molecule bridges two O1*W* molecule [O1*W*···O2*W*^{iii} = 2.911 (2) Å and O1*W*···O2*W*^{iv} = 2.820 (3) Å; see Table 2 for symmetry codes], and thus the alternating water molecules themselves form chains. These chains are further complicated by $[GeF_6]^{2-}$ anions, attached to O2*W* molecules in such a way that each anion and three water molecules form a ten-membered cage closed by four hydrogen bonds [$R_4^4(10)$ in graph-set notation; Etter, 1990]. The above-mentioned N—H···F and N—H···O hydrogen bonds between the negatively charged chains and positively charged macrocycles combine the components into a three-dimensional network, in which the inorganic chains alternate with the rows of macrocyclic cations (Fig. 2).

In the previously reported triclinic polymorph of the title compound (Fonari *et al.*, 1999), the immediate environment of the macrocyclic cation is the same as in (I), while the hydrogen-bonding motifs that consolidate the components into a three-dimensional network differ from those in (I) (Fig. 3). Two $[GeF_6]^{2-}$ anions and two O2*W* water molecules related by the inversion center are combined into hetero-tetramers [graph set $R_4^4(12)$]. These alternate with the macrocyclic cations in chains propagated along the *c* direction in the unit cell. These chains are further combined in layers arranged parallel to the *ac* plane *via* two O1*W* water molecules related by a center of symmetry. Water molecules are themselves organized into a four-membered chains that differ from the infinite water chains in (I). Along the *b* direction, the above-mentioned layers are joined into a three-dimensional network through N—H···O and N—H···F hydrogen bonds.

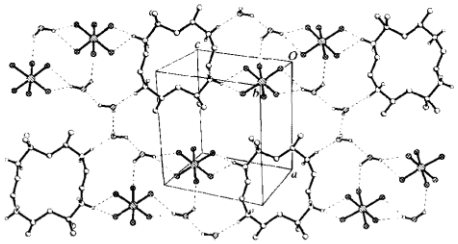

Figure 3
Part of the crystal packing for the triclinic polymorph. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Experimental

To a solution of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (1 mmol) in methanol (10 ml), a solution of H_2GeF_6 (3 *M* in 1.5 ml) was added, and the mixture boiled on a water bath. The resulting clear solution was reduced slowly in volume by evaporating the solvent at room temperature [m.p. of (I) is 343 K]. Analysis found: C 24.39, H 6.28, F 36.01, N 7.26%; $C_{16}H_{48}F_{12}Ge_2N_4O_4$ requires: C 24.53, H 6.17, F 35.48, N 7.15%.

Crystal data

$(C_{16}H_{40}N_4)[GeF_6]_2{\cdot}4H_2O$
M_r = 733.76
Monoclinic, $P2_1/c$
a = 9.5650 (19) Å
b = 16.522 (3) Å
c = 9.0210 (18) Å
β = 96.28 (3)°
V = 1417.1 (5) Å^3
Z = 2
D_x = 1.720 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 5.6–16.2°
μ = 2.23 mm^{-1}
T = 293 (2) K
Plate, white
0.25 × 0.20 × 0.20 mm

Data collection

Phillips PW1100 four-circle diffractometer
ω–2θ scans
Absorption correction: empirical (North *et al.*, 1968)
T_{min} = 0.606, T_{max} = 0.664
4350 measured reflections
4137 independent reflections
3251 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 30.0°
$h = 0 \rightarrow 13$
$k = -23 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections
every 100 reflections
intensity decay: 0.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{max} = 0.002$
$S = 0.95$	$\Delta\rho_{max} = 0.65$ e Å^{-3}
4137 reflections	$\Delta\rho_{min} = -0.62$ e Å^{-3}
208 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0035 (6)

The coordinates of the H atoms attached to atoms N1 and N4 and of the water H atoms were determined from a difference map and were refined isotropically, subject to a DFIX restraint. All other H atoms were treated as riding.

Data collection: Lehmann & Larsen (1974); cell refinement: *FEBO* (Belletti, 1996); data reduction: Lehmann & Larsen (1974); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Table 1
Selected geometric parameters (Å, °).

Ge1—F5	1.7459 (12)	Ge1—F6	1.7805 (15)
Ge1—F1	1.7703 (13)	Ge1—F2	1.8081 (12)
Ge1—F3	1.7708 (14)	Ge1—F4	1.8246 (11)
F5—Ge1—F1	94.30 (7)	F3—Ge1—F2	90.02 (7)
F5—Ge1—F3	90.76 (7)	F6—Ge1—F2	88.10 (7)
F1—Ge1—F3	92.34 (8)	F5—Ge1—F4	92.44 (6)
F5—Ge1—F6	90.98 (7)	F1—Ge1—F4	173.00 (6)
F1—Ge1—F6	91.75 (8)	F3—Ge1—F4	89.45 (7)
F3—Ge1—F6	175.42 (7)	F6—Ge1—F4	86.24 (7)
F5—Ge1—F2	177.94 (6)	F2—Ge1—F4	85.66 (6)
F1—Ge1—F2	87.58 (7)		
N1—C2—C3—N4	83.49 (18)	C5—C6—C7—N1^{i}	−48.63 (19)
C2—C3—N4—C5	54.5 (2)	C6—C7—N1^{i}—C2^{i}	−64.22 (18)
C3—N4—C5—C6	−172.17 (13)	C7—N1^{i}—C2^{i}—C3^{i}	176.76 (13)
N4—C5—C6—C7	163.92 (14)		

Symmetry code: (i) $1-x, 1-y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2N···F4	0.85 (2)	2.26 (2)	3.061 (2)	157.2 (18)
N1—H2N···F6	0.85 (2)	2.31 (2)	2.988 (2)	137.0 (17)
N1—H1N···F2^{ii}	0.81 (2)	2.09 (2)	2.894 (2)	172 (2)
N4—H3N···O1*W*	0.92 (2)	1.86 (2)	2.764 (2)	169 (2)
N4—H4N···F4	0.80 (2)	2.03 (2)	2.771 (2)	154 (2)
N4—H4N···F2	0.80 (2)	2.33 (2)	2.948 (2)	135 (2)
O1*W*—H1*W*···O2*W*^{iii}	0.854 (16)	2.086 (18)	2.911 (2)	162 (2)
O1*W*—H2*W*···O2*W*^{iv}	0.814 (16)	2.017 (17)	2.820 (3)	169 (3)
O2*W*—H3*W*···F3	0.811 (17)	1.988 (17)	2.795 (2)	173 (3)
O2*W*—H4*W*···F1^{v}	0.835 (18)	1.921 (19)	2.739 (2)	166 (3)

Symmetry codes: (ii) $1-x, 1-y, 1-z$; (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $-x, 1-y, -z$; (v) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1019). Services for accessing these data are described at the back of the journal.

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Додаток 9

Копія статті.

“Кристалічна структура тригідрату гексафторосилікаті гідразонія 5-аміно-1-бензіл-1,2,3-триазол-4-карбонової кислоти”

КРИСТАЛЛОГРАФИЯ, 2003, том 48, № 3, с. 482–489

СТРУКТУРА ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

УДК 548.736.547.89.541.49:546.273'16

КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА ТРИГИДРАТА ГЕКСАФТОРОСИЛИКАТА ГИДРАЗОНИЯ 5-АМИНО-1-БЕНЗИЛ-1,2,3-ТРИАЗОЛ-4-КАРБОНОВОЙ КИСЛОТЫ

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Синтезирован тригидрат гексафторосиликат гидразония 5-амино-1-бензил-1,2,3-триазол-4-карбоновой кислоты (I) и определена его кристаллическая структура. Кристаллы моноклинные, a = 13.353(1), b = 21.094(2), c = 20.23392) Å, β = 94.05(3)°, пр. гр. $P2_1/c$, R = 0.0584 по 16 601 отражению с $I > 2\sigma(I)$. В независимой части элементарной ячейки четыре органических катиона, протонированных по концевому гидразиновому атому азота, два гексафторосиликат-аниона и шесть молекул воды объединены водородными связями типа N–H···F, N–H···O и O–H···F в трехмерный каркас.

Гидразиды карбоновых кислот как N,O-амбидентатные лиганды широко используются в синтезе комплексов *p*- и *d*-металлов, отличающихся разнообразием реализующихся способов координации [1, 2]. Проявляя основные свойства ($pK_a \approx 3$) [3], гидразиды легко протонируются в кислых средах и представляют интерес в качестве моделей для изучения направленности взаимодействий с протоном как простейшей "жесткой" кислотой Льюиса. Однако литературные сведения о строении соединений гидразидов с минеральными кислотами немногочисленны. В [4–6] приведены данные о синтезе, строении и свойствах продуктов взаимодействия кремнефтороводородной кислоты (КФК) с N,O- и N,S-амбидентатными органическими основаниями. Данные о кристаллической структуре соединения КФК с гидразидом изоникотиновой кислоты опубликованы в [5, 6]. Заключение о вероятном строении соединений КФК с рядом гидразидов было сделано на основании анализа их ИК-спектров [6]. Настоящая работа продолжает исследования [5, 6] и посвящена изучению продукта взаимодействия КФК с гидразидом 5-амино-1-бензил-1,2,3-триазол-4-карбоновой кислоты.

ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

Гидразид 5-амино-1-бензил-1,2,3-триазол-4-карбоновой кислоты (*L*) получали по методике [7]. 232 мг (1 ммоль) *L* растворяли в 50 мл метанола при 64°C, добавляли 7.5 мл (30 ммоль) 45%-ной КФК и оставляли реакционную смесь для самопроизвольного испарения метанола и воды до начала кристаллизации. Монокристаллы комплекса были получены путем перекристаллизации выделенного продукта из смеси 30 мл метанола и 0.5 мл КФК.

Найдено, %:	Si 4.12;	F 18.31.
Для $[HL]_2 \cdot [SiF_6] \cdot 3H_2O$ (I)		
вычислено, %:	Si 4.24;	F 17.20.

В масс-спектре I (спектрометр МХ-1321, прямой ввод образца в источник, энергия ионизирующих электронов 70 эВ) регистрируются пики ионов M^+L (m/z = 232, I = 32%), $[C_7H_7]^+$ (m/z = 91, I = 100%), $[C_2H_5]^+$ (m/z = 65, I = 11%) и $[SiF_3]^+$ (m/z = 85, I = 36%). Рентгеноструктурный эксперимент для соединения I выполнен на дифрактометре Nonius CCD (MoK_α-излучение, графитовый монохроматор). Обработка экспериментальных данных выполнена по программе DENZO [8]. Приведение измеренных отражений к общей шкале проведено по программе SCALEPACK [8]. Структура решена прямыми методами по программе SHELXS [9] и уточнена по комплексу программ SHELX97 [10]. В одном из гексафторосиликат-анионов экваториальные атомы фтора F(3), F(4), F(5), F(6) разупорядочены по двум позициям с кратностью их заполнения 62.3(1) и 37.7(1)% соответственно.

Таблица 1. Кристаллографические данные, характеристики эксперимента и параметры уточнения структуры комплекса I

Комплекс	I
Брутто-формула	$C_{40}H_{64}F_{12}N_{24}O_{10}Si_2$
Молярная масса	1324.83
T, K	150
Сингония	Моноклинная
Пространственная группа	$P2_1/c$
Параметры ячейки	
a, Å	13.353(1)
b, Å	21.094(2)
c, Å	20.233(2)
β, град	94.05(3)
V, Å^3	5684.8(1)
Z	4
$d_{выч}$, г/см^3	1.548
μ, мм$^{-1}$	0.178
F(000)	2750
Размер кристалла, мм	0.20 × 0.25 × 0.30
Диапазон θ для собранных данных, град	2.12–30.04
Диапазон индексов собранных данных	$0 < h < 18$, $0 < k < 29$, $-28 < l < 28$
Дифрактометр	Nonius CCD
Метод съемки	ω/2θ
Измерено отражений	17034
Независимых отражений	16601
Метод уточнения	Полноматричный, на основе F^2
Параметр качества уточнения S на основе F^2	1.129
Заключительные R-факторы по отражениям с $I > 2\sigma(I)$	$R_1 = 0.0584$, $wR_2 = 0.1048$
Заключительные R-факторы по всем отражениям	$R_1 = 0.0838$, $wR_2 = 0.1124$
	$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$
	$P = \max(F_o^2) + 2F_c^2/3$
	$a = 0.0366$, $b = 3.16$
Остаточные пики $\Delta\rho_{max}$, $\Delta\rho_{min}$, э Å^{-3}	0.425 и −0.416

Обсуждение геометрии дано только для позиции с большей заселенностью. Молекула воды O(1W) также разупорядочена с равной вероятностью по двум системам точек пр. гр. $P2_1/c$. При уточнении структуры атомы водорода при атомах углерода были помещены в вычисленные идеальные позиции и уточнялись как жесткосвязанные с соответствующим атомом углерода. Функциональные атомы водорода (при атомах азота и в молекулах воды) найдены из разностного синтеза Фурье и уточнялись изотропно. Уточнение проведено методом наименьших квадратов в полноматричном варианте по F^2. Кристаллографические данные, условия измерений, а также параметры уточнения для исследованного соединения приведены в табл. 1. Заключительные координаты базисных неводородных атомов приведены в табл. 2, параметры водородных связей – в табл. 3.

ОБСУЖДЕНИЕ РЕЗУЛЬТАТОВ

В независимой части элементарной ячейки четыре катиона гидразония 5-амино-1-бензил-1,2,3-

Таблица 2. Координаты базисных неводородных атомов ($\times 10^4$) и эквивалентные изотропные температурные параметры $U_{экв}(Å^3 \times 10^3)$ для комплекса I

Атом	x	y	z	$U_{экв}$	Атом	x	y	z	$U_{экв}$
Si(1)	1028(1)	3869(1)	4492(1)	19(1)	C(6*B*)	6526(2)	1722(1)	5395(1)	29(1)
F(1)	1065(1)	3188(1)	4921(1)	31(1)	C(7*B*)	7668(1)	2075(1)	6379(1)	22(1)
F(2)	1006(1)	4546(1)	4035(1)	34(1)	C(8*B*)	6367(1)	1739(1)	7169(1)	16(1)
F(3)	126(10)	3550(6)	3965(5)	34(2)	C(9*B*)	6418(1)	1286(1)	7690(1)	17(1)
F(4)	1801(8)	3561(7)	3942(5)	36(2)	C(10*B*)	5607(1)	1122(1)	8075(1)	15(1)
F(5)	2086(8)	4117(3)	4935(5)	50(2)	O(1*C*)	3645(1)	2618(1)	6751(1)	23(1)
F(6)	332(12)	4212(5)	5007(4)	48(2)	N(1*C*)	989(1)	1605(1)	7045(1)	17(1)
F(3*A*)	21(16)	3604(10)	4033(9)	37(3)	N(2*C*)	424(1)	1937(1)	6567(1)	19(1)
F(4*A*)	1918(12)	3604(11)	4057(11)	41(4)	N(3*C*)	1016(1)	2340(1)	6305(1)	19(1)
F(5*A*)	1761(14)	4205(7)	5047(5)	55(2)	N(4*C*)	2683(1)	1595(1)	7517(1)	28(1)
F(6*A*)	−25(9)	4118(4)	4911(5)	27(2)	N(5*C*)	2691(1)	3011(1)	5884(1)	23(1)
Si(1*B*)	3850(1)	6069(1)	4246(1)	13(1)	N(6*C*)	3503(1)	3411(1)	5746(1)	21(1)
F(1*B*)	3485(1)	5374(1)	4564(1)	24(1)	C(1*C*)	510(1)	471(1)	7058(1)	18(1)
F(2*B*)	4276(1)	6739(1)	3916(1)	23(1)	C(2*C*)	1347(1)	79(1)	7082(1)	28(1)
F(3*B*)	4199(1)	6332(1)	5015(1)	24(1)	C(3*C*)	1327(2)	−494(1)	6742(1)	34(1)
F(4*B*)	2712(1)	6383(1)	4309(1)	27(1)	C(4*C*)	467(2)	−676(1)	6372(1)	33(1)
F(5*B*)	3487(1)	5794(1)	3481(1)	30(1)	C(5*C*)	−374(2)	−295(1)	6345(1)	34(1)
F(6*B*)	5003(1)	5741(1)	4193(1)	28(1)	C(6*C*)	−353(1)	274(1)	6691(1)	26(1)
O(1*A*)	975(1)	6704(1)	3008(1)	28(1)	C(7*C*)	526(1)	1099(1)	7416(1)	19(1)
N(1*A*)	−1728(1)	6860(1)	1773(1)	24(1)	C(8*C*)	1950(1)	1808(1)	7087(1)	17(1)
N(2*A*)	−2213(1)	6412(1)	2125(1)	20(1)	C(9*C*)	1961(1)	2280(1)	6604(1)	16(1)
N(3*A*)	−1580(1)	6211(1)	2595(1)	21(1)	C(10*C*)	2825(1)	2642(1)	6433(1)	17(1)
N(4*A*)	−116(1)	7343(1)	1786(1)	30(1)	O(1*D*)	1963(1)	7584(1)	1568(1)	24(1)
N(5*A*)	66(1)	5923(1)	3443(1)	25(1)	N(1*D*)	4734(1)	6697(1)	1966(1)	18(1)
N(6*A*)	868(1)	5802(1)	3921(1)	23(1)	N(2*D*)	5213()	7025(1)	1490(1)	20(1)
C(1*A*)	−2166(1)	6665(1)	590(1)	25(1)	N(3*D*)	4560(1)	7404(1)	1194(1)	19(1)
C(2*A*)	−2978(2)	6283(1)	398(1)	40(1)	N(4*D*)	3096(1)	6646(1)	2372(1)	22(1)
C(3*A*)	−2914(2)	5843(1)	−108(1)	57(1)	N(5*D*)	2734(1)	8048(1)	741(1)	25(1)
C(4*A*)	−2041(2)	5790(1)	−427(1)	53(1)	N(6*D*)	1815(1)	8358(1)	559(1)	22(1)
C(5*A*)	−1235(2)	6166(1)	−244(1)	43(1)	C(1*D*)	5186(1)	5563(1)	2012(1)	18(1)
C(6*A*)	−1291(2)	6608(1)	261(1)	33(1)	C(2*D*)	5955(1)	5348(1)	1644(1)	30(1)
C(7*A*)	−2230(1)	7115(1)	1163(1)	24(1)	C(3*D*)	5868(2)	4779(1)	1303(1)	36(1)
C(8*A*)	−774(1)	6940(1)	2029(1)	18(1)	C(4*D*)	5015(2)	4415(1)	1332(1)	32(1)
C(9*A*)	−684(1)	6515(1)	2556(1)	18(1)	C(5*D*)	4250(2)	4618(1)	1708(1)	32(1)
C(10*A*)	189(1)	6397(1)	3003(1)	18(1)	C(6*D*)	4335(1)	5187(1)	2047(1)	26(1)
O(1*B*)	4785(1)	1381(1)	8016(1)	20(1)	C(7*D*)	5270(2)	6200(1)	2355(1)	20(1)
N(1*B*)	7301(1)	1739(1)	6950(1)	19(1)	C(8*D*)	3765(1)	6878(1)	1968(1)	16(1)
N(2*B*)	7902(1)	1305(1)	7290(1)	23(1)	C(9*D*)	3657(1)	7330(1)	1467(1)	17(1)
N(3*B*)	7368(1)	1036(1)	7725(1)	21(1)	C(10*D*)	2733(1)	7655(1)	1271(1)	18(1)
N(4*B*)	5611(1)	2102(1)	6918(1)	21(1)	O(1W)	1939(3)	5349(2)	5337(2)	35(1)
N(5*B*)	5811(1)	656(1)	8541(1)	19(1)	O(1WA)	2407(2)	5438(1)	5597(2)	27(1)
N(6*B*)	5027(1)	535(1)	8966(1)	19(1)	O(2W)	−2898(1)	5547(1)	3498(1)	52(1)
C(1*B*)	7458(1)	1698(1)	5751(1)	24(1)	O(3W)	−700(1)	2909(1)	5506(1)	37(1)
C(2*B*)	8185(2)	1289(1)	5542(1)	36(1)	O(4W)	3874(1)	3279(1)	4433(1)	30(1)
C(3*B*)	7987(2)	901(1)	5001(1)	50(1)	O(5W)	−996(1)	4770(1)	3406(1)	28(1)
C(4*B*)	7054(2)	915(1)	4657(1)	47(1)	O(6W)	3021(1)	4508(1)	3428(1)	25(1)
C(5*B*)	6326(2)	1326(1)	4853(1)	38(1)					

Таблица 3. Геометрические параметры водородных связей в I

D–H···*A*	*d*(*D*–H), Å	*d*(H···*A*), Å	*d*(*D*···*A*), Å	∠(*D*H*A*), град
Внутримолекулярные водородные связи				
N(4*A*)–H(1N*A*)···O(1*A*)	0.86(3)	2.54(3)	3.090(2)	123(2)
N(6*A*)–H(5N*A*)···O(1*A*)	0.85(3)	2.21(2)	2.644(2)	113(2)
N(4*B*)–H(1N*B*)···O(1*B*)	0.88(2)	2.41(2)	2.9685(2)	122(2)
N(6*B*)–H(5N*B*)···O(1*B*)	0.89(2)	2.25(2)	2.6259(2)	105(2)
N(4*C*)–H(1N*C*)···O(1*C*)	0.87(3)	2.42(3)	2.998(2)	125(2)
N(6*C*)–H(5N*C*)···O(1*C*)	0.91(2)	2.14(2)	2.6290(2)	113(2)
N(4*D*)–H(2N*D*)···O(1*D*)	0.85(2)	2.34(2)	2.916(2)	125(2)
N(6*D*)–H(4N*D*)···O(1*D*)	0.91(2)	2.09(2)	2.6092(2)	115(2)
Межмолекулярные водородные связи				
N(4*A*)–H(1N*A*)···O(1*D*)	0.86(3)	2.27(2)	2.886(2)	129(2)
N(4*A*)–H(2N*A*)···F(3)^{i}	0.85(3)	2.19(3)	2.964(1)	151(2)
N(5*A*)–H(3N*A*)···O(5*W*)	0.80(2)	2.04(2)	2.183(2)	162(2)
N(6*A*)–H(4N*A*)···F(2)	0.95(2)	1.73(2)	2.663(2)	166(2)
N(6*A*)–H(5N*A*)···F(4*B*)	0.85(3)	2.13(3)	2.8118(2)	136(2)
N(6*A*)–H(6N*A*)···F(6)^{ii}	0.94(3)	1.93(3)	2.786(8)	151(3)
N(4*B*)–H(1N*B*)···O(1*C*)	0.88(2)	2.24(2)	2.840(2)	125(2)
N(4*B*)–H(2N*B*)···F(2*B*)^{iii}	0.86(2)	2.14(2)	2.981(2)	167(2)
N(5*B*)–H(3N*B*)···O(2*W*)^{v}	0.77(3)	2.43(3)	3.072(2)	141(3)
N(6*B*)–H(4N*B*)···F(3*B*)^{iv}	0.93(3)	1.92(3)	2.802(2)	157(2)
N(6*B*)–H(5N*B*)···O(6*W*)^{vi}	0.89(2)	1.98(2)	2.821(2)	157(2)
N(6*B*)–H(6N*B*)···F(6*B*)^{vi}	0.91(2)	1.82(3)	2.731(2)	171(2)
N(4*C*)–H(1N*C*)···O(1*B*)	0.87(3)	2.35(3)	2.949(2)	126(2)
N(4*C*)–H(2N*C*)···O(6*W*)^{vi}	0.84(2)	2.18(2)	2.983(2)	159(2)
N(5*C*)–H(3N*C*)···F(1)	0.86(2)	1.99(2)	2.837(2)	166(2)
N(6*C*)–H(4N*C*)···O(4*W*)	0.95(2)	1.80(2)	2.749(2)	173(2)
N(6*C*)–H(5N*C*)···F(2*B*)^{iii}	0.91(2)	2.24(2)	3.012(2)	143(2)
N(6*C*)–H(6N*C*)···O(2*W*)^{ii}	0.90(3)	1.98(3)	2.830(2)	156(2)
N(4*D*)–H(2N*D*)···O(1*A*)	0.85(2)	2.54(2)	3.195(2)	134(2)
N(4*D*)–H(1N*D*)···F(5*B*)	0.87(2)	2.03(2)	2.895(2)	171(2)
N(5*D*)–H(3N*D*)···F(3*W*)^{viii}	0.82(2)	2.06(2)	2.847(2)	158(2)
N(6*D*)–H(4N*D*)···F(3)^{i}	0.91(2)	2.18(3)	2.857(1)	130(2)
N(6*D*)–H(5N*D*)···O(1*W*)^{viii}	0.96(3)	1.82(3)	2.771(4)	169(2)
N(6*D*)–H(6N*D*)···O(3*W*)^{i}	0.95(3)	1.77(3)	2.703(2)	168(2)
O(1*W*)–H(1*W*1)···F(1*B*)	0.86(1)	1.88(3)	2.677(3)	152(5)
O(1*W*)–H(2*W*1)···F(5)	0.85(1)	2.30(5)	2.735(9)	111(4)
O(2*W*)–H(1*W*2)···N(3*A*)	0.86(1)	2.15(1)	2.975(2)	162(3)
O(2*W*)–H(2*W*2)···F(5)^{ii}	0.84(1)	2.53(2)	3.354(9)	165(3)
O(3*W*)–H(1*W*3)···F(1)	0.85(1)	2.01(2)	2.773(2)	150(3)
O(3*W*)–H(1*W*3)···N(3*C*)	0.85(1)	2.50(3)	2.964(2)	115(2)
O(4*W*)–H(1*W*4)···N(3*D*)^{viii}	0.85(1)	2.27(1)	3.125(2)	177(2)
O(4*W*)–H(2*W*4)···F(4)	0.85(1)	2.16(2)	2.935(12)	152(2)
O(5*W*)–H(1*W*5)···N(3*B*)^{ix}	0.86(1)	2.18(1)	3.023(2)	171(2)
O(5*W*)–H(2*W*5)···F(3)	0.85(1)	2.34(2)	3.148(1)	159(2)
O(5*W*)–H(2*W*5)···F(2)	0.85(1)	2.25(2)	2.916(2)	136(2)
O(6*W*)–H(1*W*6)···F(5*B*)	0.86(1)	1.95(1)	2.783(2)	163(2)
O(6*W*)–H(2*W*6)···F(4)	0.87(1)	2.10(2)	2.824(1)	140(2)
O(6*W*)–H(2*W*6)···F(2)	0.87(1)	2.32(2)	3.037(2)	139(2)

Примечание. Отмечены атомы, связанные с базисными преобразованиями симметрии: *i*: $-x, y + 1/2, -z + 1/2$; *ii*: $-x, -y + 1, -z + 1$; *iii*: $-x + 1, -y + 1, -z + 1$; *iv*: $-x + 1, -y - 1/2, -z + 3/2$; *v*: $x + 1; -y + 1/2; z + 1/2$; *vi*: $x, -y + 1/2, z + 1/2$; *vii*: $x, -y + 3/2, z - 1/2$; *viii*: $-x + 1, y - 1/2, -z + 1/2$; *ix*: $x - 1, -y + 1/2, z - 1/2$.

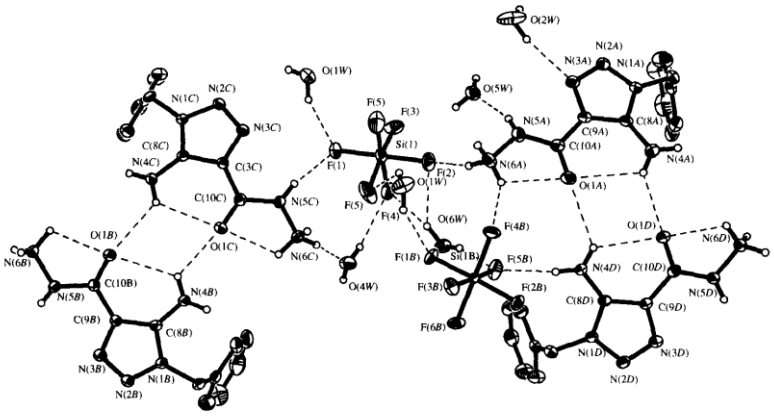

Рис. 1. Состав независимой части элементарной ячейки для соединения I с частичной нумерацией атомов. Для гексафторосиликат-аниона, определяемого атомом Si(1) и молекулы воды O(1*W*), показано одно из двух разупорядоченных положений. Пунктиром отмечены внутримолекулярные и межмолекулярные водородные связи.

триазол-4-карбоновой кислоты, протонированные по терминальной амино-группе гидразинового фрагмента (обозначенные буквами *A*, *B*, *C*, *D* соответственно), два гексафторосиликат-аниона и шесть молекул воды занимают общие позиции, такая стехиометрия соответствует составу $[HL]_2 \cdot [SiF_6] \cdot 3H_2O$ (рис. 1). Органические катионы характеризуются примерно одинаковыми межатомными расстояниями и валентными углами. Геометрия остова катионов близка к описанной для родственных соединений, включающих бензотриазольный фрагмент [11–12], а также для молекулы гидразида 5-амино-1-бензил-1,2,3-триазол-4-карбоновой кислоты в комплексе с 18-краун-6 [13]. Все органические катионы имеют уголковое строение. Угол на мостиковом метиленовом атоме углерода C(7*n*) (*n* = *A*, *B*, *C*, *D*) несколько увеличен в сравнении с идеальным тетраэдрическим и принимает значения в интервале 110.8(1)°–112.6(1)°. Двугранный угол между плоскостями триазольного и фенильного колец принимает значения в интервале 70.86(5)°–79.26(6)°. Конформация катионов стабилизирована внутримолекулярными N–H···O водородными связями с участием карбонильного атома кислорода O(1*n*) в качестве H-акцептора и терминальной аммонийной группы $N(6n)H_3^+$ и аминогруппы триазольного цикла N(4*n*) в качестве H-доноров. При этом формируются два цикла, замыкаемые H-связями: шестичленный цикл ···H–N(4*n*)–C(8*n*)–C(9*n*)–C(10*n*)–C(1*n*)···, где расстояния N(4*n*)···O(1*n*) находятся в интервале 2.916(2) Å (катион *D*) – 3.090(2) Å (катион *A*), и пятичленный цикл ···H–N(6*n*)–N(5*n*)–C(10*n*)–O(1*n*)···, расстояния N(6*n*)···O(1*n*) в интервале 2.609(2) Å (катион *D*) – 2.664(2) Å (катион *A*) (табл. 3). Двугранный угол между шестичленным H-циклом и триазольным циклом, сопряженными по связи C(8*n*)–C(9*n*), находится в интервале 1.60(5)° (катион *A*) – 2.19(4)° (катион *D*), а для двух H-циклов, сопряженных по связи O(1*n*)–C(10*n*), значение соответствующего двугранного угла находится в интервале 3.66(7)° (катион *A*) – 5.64(6)° (катион *C*). Таким образом, триазольный цикл и два соседних H-связанных цикла формируют практически плоскую трициклическую систему. Пары органических катионов *A*, *D* и *B*, *C* объединены в димеры двумя межмолекулярными водородными связями типа N(4*n*)···O(1*n*). Расстояния N···O в первом димере равны 2.886(2) и 3.195(2) Å, а во втором – 2.840(2) и 2.949(2) Å. В результате димеризации образуются два 12-членных псевдомакроцикла, относительно средней плоскости которых фенильные заместители ориентированы в одну сторону.

Неорганическая составляющая кристалла включает два гексафторосиликат-аниона и шесть молекул воды. Оба аниона характеризуются геометрией искаженного октаэдра с Si–F расстояниями в интервале 1.64(2)–1.704(2) Å. В анионе с индексом *B* межатомные расстояния более выровнены и находятся в интервале 1.671(1)–1.697(1) Å. Максимальное отклонение валентного угла F–Si–F от прямого не превышает 4°, а от развернутого

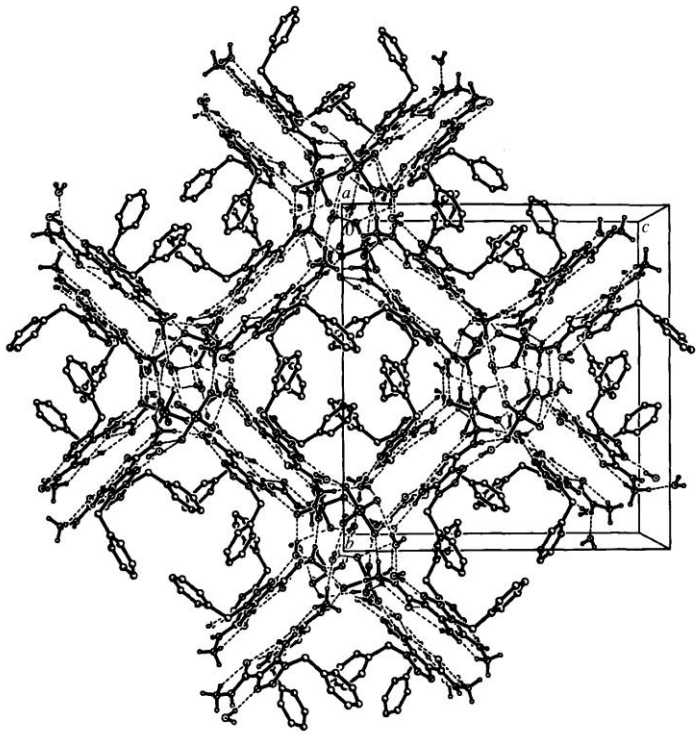

Рис. 2. Фрагмент упаковки для соединения I.

– 3.2°. Геометрия обоих анионов соответствует данным [14].

Молекулы воды O(1*W*) и O(6*W*) служат мостиками между двумя гексафторосиликат-анионами, участвуя в O–H···F водородных связях обоими атомами водорода, O(1*W*)···F(1*B*) 2.677(3), O(1*W*)–F(5) 2.735(9) Å; O(2*W*)···F(5*B*) 2.783(2), O(6*W*)···F(4) 2.824(1), O(6*W*)···F(2) 3.037(2) Å. Молекула воды O(4*W*) выполняет роль мостика между гексафторосиликат-анионом и катионом с индексом *C*, соответствующие водородные связи O(4*W*)···F(4) 2.94(1), N(6*C*)···O(4*W*) 2.749(2) Å. При участии молекулы воды O(4*W*) и этого катиона вокруг центров инверсии формируются ассоциаты, объединяющие четыре гексафторосиликат-аниона и шесть молекул воды (рис. 2).

У димеров *A*–*D* и *B*–*C* одни и те же функциональные группы, а именно терминальная аммонийная группа $N(6n)H_3^+$ и аминогруппа триазольного цикла $N(4n)H_2$ сходным образом участвуют в системе водородных связей. Атом фтора F(3) в качестве мостика между катионами *A* и *D* вовлечен в систему N–H···F водородных связей: N(4*A*)···F(3) ($-x, y + 1/2, -z + 1/2$) 2.964(1), N(6*D*)···F(3) ($-x, y + 1/2, -z + 1/2$) 2.857(1) Å. Другая пара таких же функциональных групп, $N(6A)H_3^+$ и $N(4D)H_2$, вовлечена в N–H···F водородные связи с трехатомным мостиком, F(4*B*)–Si(1*B*)–F(5*B*), расстояния N(4*D*)···F(5*B*) 2.895(2) и N(6*A*)···F(4*B*) 2.812(2) Å. В паре катионов *B*–*C* структурная роль атома F(2*B*) подобна функции атома F(3), параметры H-связей с его участием: N(4*B*)···F(2*B*) ($-x + 1, -y + 1, -z + 1$) 2.981(2) и N(6*C*)···F(2*B*) ($-x + 1, -y + 1, -z + 1$) 3.012(2) Å. Моле-

вуют прямые контакты типы вода–вода. Только две из шести молекул воды, O(2*W*) и O(6*W*), реализуют все свои донорно-акцепторные возможности в четырех водородных связях каждая (табл. 3). В кембриджском банке структурных данных [15] найдено около десяти примеров гидратных комплексов КФК с различными N-содержащими органическими молекулами. Общим для них является точечный характер вхождения молекул воды во взаимодействие с КФК и N-лигандом: молекула воды, выполняя мостиковую функцию, предоставляет свои атомы водорода для участия в O(*W*)–H···F водородных связях, а НЭП – для участия в N–H···O взаимодействиях с лигандом [14, 16–19]. Авторами отмечены различные способы включения молекул воды в трехмерный каркас в комплексах КФК с N-содержащими макроциклами. Так, в дигидрате КФК с 1,4,7,10-тетрааза-пиридинофаном [20] без молекулы воды выполняют мостиковую функцию между двумя гексафторосиликат-анионами, в дигидрате КФК с мезо-5,7,7,12,12,14-гексаметил-1,4,8,11-тетраазациклотетрадеканом [21] две молекулы воды связаны в димер на расстоянии O(1*W*)···O(2*W*) 2.743(9) Å, а в гептагидрате КФК с 1,4,7,10-тетраазациклодеканом [22] пять молекул воды формируют линейный кластер. На наш взгляд, это редкий случай такого большого водного ассоциата в гидратных комплексах КФК. Помимо этого примера, можно упомянуть комплекс $\{[Pt_2(NH_3)_4(\mu\text{-}CH_3CO_2)_2][(SiF_6)(H_2O)_4]\}_n$, где четыре молекулы воды создают гидратный мостик между двумя гексафторосиликат-анионами [23].

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Додаток 10

Копія статті.

“Комплекси краун-етерів з діаміномалеодінітрилом”

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КОМПЛЕКСЫ КРАУН-ЭФИРОВ С ДИАМИНОМАЛЕОДИНИТРИЛОМ

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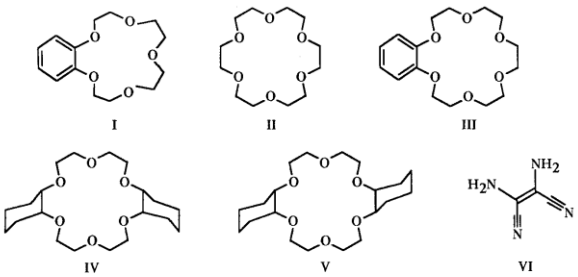
1,2-Диаминомалеодинитрил (тетрамер HCN) принято рассматривать как одну из ключевых структур химической эволюции [1—4] на пути превращения цианистого водорода в аминокислоты и гетероциклы [4—6]. Согласно источникам [7,8], при моделировании биохимических процессов важным является обнаружение межмолекулярных нековалентных взаимодействий сравнительно небольших молекул с полостными структурами, в частности с краун-эфирами.

Целью работы являлось определение возможности синтеза кристаллических молекулярных комплексов краун-эфиров с 1,2-диаминомалеодинитрилом и выявление селективности во взаимодействиях этих партнеров комплексообразования.

Установлено, что при самопроизвольном испарении растворителей из растворов краун-эфиров — бензо-15-краун-5 (I), 18-краун-6 (II), бензо-18-краун-6 (III), смеси *цис,син,цис*-(IV) и *цис,анти,цис*-изомеров (V) дициклогексано-18-краун-6 с 1,2-диаминомалеодинитрилом (VI) — образуются кристаллические молекулярные комплексы (VII—X).



I – 2,3,5,6,8,9,11,12-октагидробензо-1,4,7,10,13-пентаоксациклопентадецин, II – 18c6 - 1,4,7,10,13,16-гексаоксациклооктадекан, III – 1,2,3,5,6,8,9,11,12,14,15-декагидробензо-1,4,7,10,13,16-гексаоксациклооктадецин, IV – *цис,син,цис*-пергидродибензо[*b,k*][1,4,7,10,13,16]гексаоксациклооктадецин, V – *цис,анти,цис*-пергидродибензо[*b,k*][1,4,7,10,13,16]гексаоксациклооктадецин, VI – 1,2-диаминомалеодинитрил.

Отметим, что при взаимодействии 1,2-диаминомалеодинитрила со смесью *цис,син,цис*- и *цис, анти,цис*-изомеров (IV, V) дициклогексано-18-краун-6 комплекс (X) образуется селективно лишь с *цис,анти,цис*-изомером (V), имеющим эквивалентно пространственно-экранированные стороны полости макроциклического кольца (ср. [9]). Описанные взаимодействия могут быть учтены как составная часть при моделировании молекулярных взаимодействий природных молекул [7]. Полученные комплексы (VII—X) могут представлять интерес в качестве контейнеров [10] высокореакционноспособного 1,2-диаминомалеодинитрила.

Кристаллические молекулярные комплексы (VII—X). Растворы 1.5 ммоля диаминомалеодинитрила (VI) и 1 ммоля краун-эфиров (I—III, V) или 2 ммолей эквимольной коммерческой смеси изомеров (IV, V) в 3 мл метанола и 3 мл бензола фильтровали, затем испаряли при 20°C. Выделившиеся бесцветные монокристаллы отделяли, промывали эфиром и сушили на воздухе.

Комплекс 2,3,5,6,8,9,11,12-октагидробензо-1,4,7,10,13-пентаоксациклопентадецина с 1,2-диаминомалеодинитрилом, 1:1 (VII). Выход 52%, т. пл. 109—110°C. Спектр ЯМР ^{1}H (ДМСО-d_6),

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δ, м. д.: 3.60 м, 3.77 м, 4.02 м (16H, $8CH_2$), 5.28 с (4H, NH), 6.90 м (4H, CH). Найдено, %: C 57.39; H 6.48; N 14.93. $C_{18}H_{24}N_4O_5$. Вычислено, %: C 57.44; H 6.43; N 14.88.

Комплекс 1,4,7,10,13,16-гексаоксациклооктадекана с 1,2-диаминомалеодинитрилом, 1:1 (VIII). Выход 65%, т. пл. 76—78°C. Спектр ЯМР ^1H (ДМСО-d_6), δ, м. д.: 3.50 с (24H, $12CH_2$), 5.28 с (4H, NH). Найдено, %: C 51.56; H 7.63; N 15.10. $C_{16}H_{28}N_4O_6$. Вычислено, %: C 51.60; H 7.58; N 15.04.

Комплекс 1,2,3,5,6,8,9,11,12,14,15-декагидробензо-1,4,7,10,13,16-гексаоксациклооктадецина с 1,2-диаминомалеодинитрилом, 1:1 (IX). Выход 67%, т. пл. 108—110°C. Спектр ЯМР ^1H (ДМСО-d_6), δ, м. д.: 3.60 м, 3.74 м, 4.05 м (20H, $10CH_2$), 5.29 с (4H, NH), 6.90 м (4H, CH). Найдено, %: C 57.08; H 6.67; N 13.39. $C_{20}H_{28}N_4O_6$. Вычислено, %: C 57.13; H 6.71; N 13.33.

Комплекс *цис,анти,цис*-пергидродибензо-[*b,k*][1,4,7,10,13,16]гексаоксациклооктадецина с 1,2-диаминомалеодинитрилом, 1:1 (X). Выход 78%; при использовании эквимольной смеси изомеров (IV, V) выход комплекса (IV) составлял 62%, т. пл. 150—152°C. Спектр ЯМР ^1H (ДМСО-d_6), δ, м. д.: 1.19—1.71 м и 3.53 м (36H), 5.28 с (4H, NH). Найдено, %: C 59.95; H 8.43; N 11.77. $C_{24}H_{40}N_4O_6$. Вычислено, %: C 59.98; H 8.39; N 11.66.

Спектры ЯМР ^1H регистрировали на приборе Varian VXR-300 (300 МГц), внутренний стандарт — ТМС.

Работа финансировалась в рамках проекта NCS 90-2811-M-032.

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Додаток 11

Копія статті.

“From 1D strands to extended molecular assemblies in the binary compounds of dithiooxamide and dithiobiurea with crown ethers”

From 1D strands to extended molecular assemblies in the binary compounds of dithiooxamide and dithiobiurea with crown ethers

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The hydrogen-bonding networks for seven new binary compounds of dithiooxamide, $(NH_2CS)_2$ (**dtox**) and dithiobiurea $(NH_2CSNH)_2$ (**dtur**) with crown ethers, 18-crown-6 (18C6), 15-crown-5 (15C5), 12-crown-4 (12C4), *cis–syn–cis*– (DCHA), and *cis–anti–cis*– (DCHB) isomers of dicyclohexyl-18-crown-6 are discussed. (15C5·**dtox**), (18C6·**dtur**) and (DCHB·**dtur**) afford one-dimensional hydrogen-bonded polymeric arrays where the components alternate. In (DCHA ·**2dtox**) and (DCHB ·**2dtox**) the similar hydrogen-bonded chains are further interlinked *via* **dtox** molecules to generate layered motifs. In (15C5·**2dtur**) the **dtur** molecules are self-assembled into layers *via* N–H ··· S hydrogen bonds. 15C5 spacers link adjacent layers into a three-dimensional network. In (12C4·**dtur**) the **dtur** molecules are arranged in chains. These chains alternate with the crown molecules attached to them through N–H ··· O hydrogen bonds in such a way that each 12C4 appears to be linked with four **dtur** molecules and *vice versa* thus providing a three-dimensional grid.

The last decade has witnessed tremendous advances in the understanding of, and the ability to manipulate, molecular and supramolecular assemblies.[1] There are new paradigms concerning the design and synthesis of a new generation of functional materials and molecules. Such advances are a consequence of the fundamental importance of intermolecular interactions, structure and cooperativity in many aspects of molecular science, from environmental science to molecular biology, pharmacology, and materials science. Thus, the prospects for control and manipulation of materials at the molecular level, particularly in areas related to non-covalent bonding and nanotechnology, are now truly exceptional.

Crystal engineering[2] is predicated on the assumption that crystals are *de facto* examples of self-assembly, *i.e.* crystals are comprised from a series of molecular recognition events or *supramolecular synthons*.[3] It also offers a more realizable goal than crystal structure prediction since it relies on design and allows for careful selection of substrates, *i.e.* substances that are predisposed to form predictable self-assembled superstructures can be targeted for study. Furthermore, the prototypal molecules used in crystal engineering contain *exofunctional molecular recognition sites* and they can be complementary with themselves (self-assembly)[4] or with other molecules (modular self-assembly).[5] Coincidentally, most pharmaceutical or biologically important molecules also contain exterior molecular recognition sites and, although this makes them susceptible to polymorphism and solvate formation, it also makes them attractive candidates for crystal engineering studies. The ability of crystalline self-assemblies to be built from a bottom-up approach[6] could provide an exceptional control of the design of new phases at a molecular level.

Supramolecular chemistry through hydrogen bonding is a driving force for the formation of binary compounds involving crown ethers. Our longstanding interest in multiply H–bonded complexes has aimed at utilizing the small biologically important organic molecules, rich in both H–donor and acceptor groups, in the construction of supramolecular networks with classic crown molecules. We have used hydrogen bonds successfully in purely organic crystals to build one-dimensional motifs (chains), and two-dimensional motifs (sheets).[7] Although the host–guest chemistry of 18-crown-6 (host) and its substituted analogues[8] has been widely studied, less success has been achieved in the design of diverse supramolecular architectures in the complexes based on 12-crown-4[9] and 15-crown-5.[10] Molecular complexes of 18-crown-6 with urea, thiourea and their derivatives have previously been reported.[11] The availability of two amine groups in the urea and thiourea molecules provides an opportunity for interactions with the crown molecule in addition to the self-assembly interactions of these small molecules *via* N–H ··· O or N–H ··· S hydrogen bonding. The dithiooxamide (**dtox**) $(NH_2CS)_2$ and dithiobiurea (**dtur**) $(NH_2CSNH)_2$ represent suitable candidates for building of supramolecular architectures as they contain H-bond donor groups (NH_n, $n = 1, 2$) and H-bond acceptor groups (S atoms). The crystal structures of pure **dtox**[12] and pure **dtur**[13] reveal three-dimensional networks being sustained by intermolecular N–H ··· S interactions.

We report herein the hydrogen-bonding organization and the specific features of supramolecular architectures for seven new binary compounds (Scheme 1), **dtox** with 15-crown-5 (15C5), (complex **1**, ratio 1 : 1), **dtox** with *cis–syn–cis* isomer of dicyclohexyl-18-crown-6 (DCHA), (**2**, ratio 1 : 2), **dtox** with *cis–anti–cis* isomer of dicyclohexyl-18-crown-6 (DCHB), (**3**, ratio 1 : 2); **dtur** with 18-crown-6 (18C6), (**4**, ratio 1 : 1), **dtur** with DCHB (**5**, ratio 1 : 1), **dtur** with 15C5 (**6**, ratio 1 : 2), and **dtur** with 12-crown-4 (12C4), (**7**, ratio 1 : 1) elucidated by conventional chemical methods (^1H, ^{13}C NMR and TGA) and X-ray crystal structure analysis, see Experimental.

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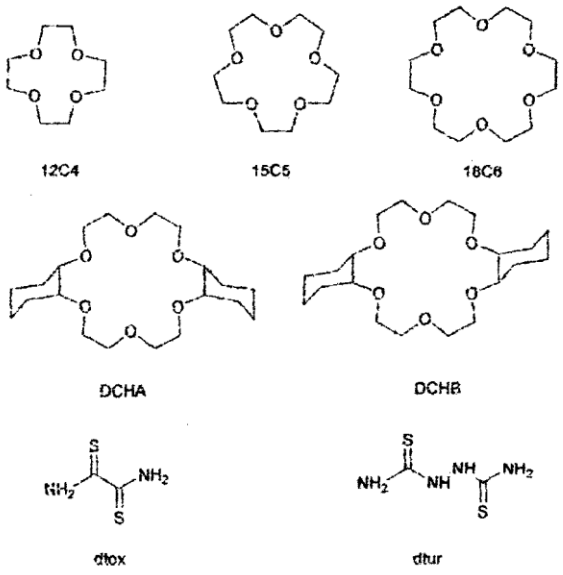

Scheme 1

Two crystalline complexes of **dtox** with benzo-5-crown-5 (B15C5), (ratio 1 : 1)[10a] and 18C6 (ratio 1 : 2)[14] were reported. In the former structure B15C5 and **dtox** molecules alternate in the chains due to N–H ··· O interactions. In the latter one, four **dtox** molecules are attached to each 18C6 and bridge four additional crown ligands *via* N–H ··· O hydrogen bonds. The alternating 18C6–**dtox** hydrogen-bonding chains are combined into a two-dimensional grid through N–H ··· S interactions. The different structural types exhibited by the system **dtox**–crown molecule provoked us to continue the study of possible supramolecular patterns in the assemblies of **dtox** with a symmetrically mismatched 15C5 molecule and with two dicyclohexyl derivatives of 18C6, DCHA and DCHB, having a restricted flexibility of the 18-membered macrocycle in comparison with the 18C6 counterpart.

Complexes of dithiooxamide with crown ethers

The ORTEP drawing for (**1**) is shown in Fig. 1. 15C5·**dtox** (**1**) crystallises in the triclinic *P*-1 space group and contains one crown and one **dtox** molecule per asymmetric unit (Fig. 1). The **dtox** molecule is disordered in two positions, **A** and **B**, with probabilities of 59.22(7) and 40.78(6)%, respectively. We will only discuss the **A** position of the **dtox** molecule, while Table 1 contains the hydrogen-bonding parameters for both positions.

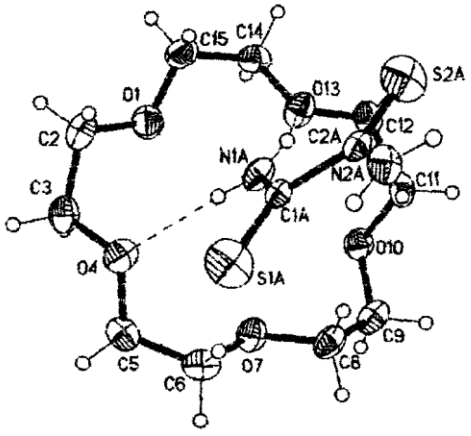

Fig. 1 ORTEP drawing for (**1**). The thermal ellipsoids are given with 30% probability level. Only one of two disordered positions are given for the **dtox** molecule.

The molecules in (**1**) are arranged in a T-shape mode with the dihedral angle between the mean plane of crown oxygen pentagon and the planar skeleton of **dtox** molecule equal to 78.7(5)°. Each **dtox** molecule bridges two adjacent 18C6 molecules translated along the *a* axis *via* two hydrogen bonds with the participation of both of the terminal amine groups, N(1A) ··· O(13) 2.98(3), N(1A) ··· O(4) 2.97(3) Å, and N(2A) ··· O(7) (*x* + 1, *y*, *z*) 3.07(2), N(2A) ··· O(10) (*x* + 1, *y*, *z*) 2.85(2) Å. The neighbouring non-centrosymmetric chains are related by an inversion centre in the crystal (Fig. 2).

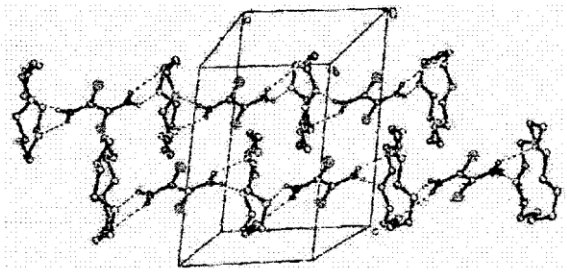

Fig. 2 Arrangement of chains in (**1**). Red: oxygens, blue: nitrogens, orange: sulfurs.

The organisation of (**1**) is similar to the complex B15C5·**dtox**.[10b] It means that the phenyl substituent influences the final architecture to a minor extent. To the best of our knowledge, it is the second example after the system of 15-membered crown ether, 15C5, B15C5–3,4-diamino-1,2,5-oxadiazole[10c] which also shows the closeness of supramolecular organization (the molecules are also arranged into the alternate chains *via* N–H ··· O hydrogen bonds).

(**2**) crystallises in the monoclinic space group *C*2/*c*. The asymmetric unit contains half of crown molecule and two halves of two crystallographically non-equivalent **dtox** molecules. The ORTEP diagram for (**2**) is shown in Fig. 3.

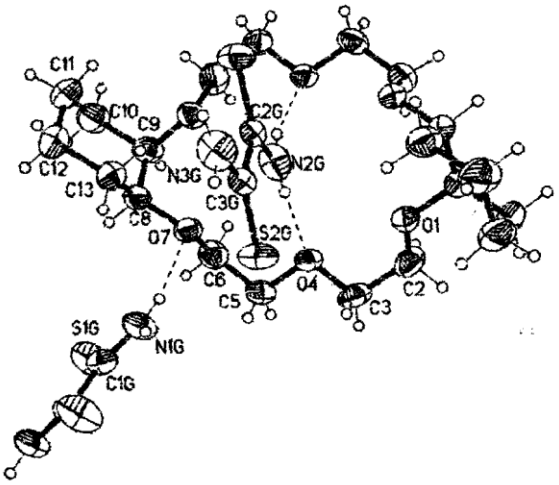

Fig. 3 ORTEP drawing for (**2**). The thermal ellipsoids are given with 50% probability level. Only one position is given for the **dtox** molecule.

DCHA and one of two **dtox** molecules (defined by the S(2G) atom and named here as **dtox2**) reside on a two-fold axis, while the second **dtox** molecule (defined by S(1G) atom and named here as **dtox1**) occupies the position around an inversion centre. The **dtox2** molecule is disordered and only one position is shown in the figures and further discussed. Two **dtox** molecules feature different structural functions in the supramolecular

Table 1 Intermolecular hydrogen bonds in (1)–(7)

D–H ··· A	d(H ··· A)/Å	d(D ··· A)/Å	∠(DHA)/°	Symmetry code for acceptor
(1)				
N(1a)–H(1Na) ··· O(13)	2.30	2.98(3)	136	x, y, z
N(1a)–H(1Nb) ··· O(4)	2.12	2.97(3)	174	x, y, z
N(2a)–H(2Na) ··· O(7)	2.58	3.07(2)	117	$x + 1, y, z$
N(2a)–H(2Nb) ··· O(10)	2.12	2.85(2)	143	$x + 1, y, z$
N(1b)–H(1Nc) ··· O(10)	2.48	2.93(3)	113	$x + 1, y, z$
N(1b)–H(1Nd) ··· O(7)	2.15	2.96(4)	157	$x + 1, y, z$
N(2b)–H(2Nc) ··· O(4)	2.50	3.14(3)	132	x, y, z
N(2b)–H(2Nd) ··· O(13)	2.05	2.89(4)	165	x, y, z
(2)				
N(1G)–H(1Nb) ··· O(7)	2.13(2)	2.994(2)	169(2)	x, y, z
N(2G)–H(2N) ··· O(4)	2.36(2)	3.107(2)	160(3)	x, y, z
N(3G)–H(3N) ··· O(4)	2.12(3)	2.938(2)	166(3)	$x, y - 1, z$
(3)				
N(1G)–H(2G1) ··· O(1)	2.20(2)	3.039(2)	164(2)	$-x + 1, -y + 1, -z$
N(2G)–H(1G2) ··· O(4)	2.18(2)	2.985(2)	163(2)	x, y, z
N(2G)–H(1G2) ··· O(7)	2.56(2)	3.100(2)	124(2)	x, y, z
N(2G)–H(2G2) ··· O(4)	2.28(2)	2.984(2)	144(2)	$-x + 1, -y + 1, -z$
(4)				
N(1G)–H(2N1) ··· O(1)	2.23(2)	3.056(2)	164(2)	x, y, z
N(1G)–H(1N1) ··· O(7)	2.15(2)	3.007(2)	165(2)	x, y, z
N(2G)–H(1N2) ··· O(13)	2.28(2)	2.982(2)	147(2)	$x, y - 1, z$
N(3G)–H(1N3) ··· O(16)	2.22(2)	2.932(2)	151(2)	x, y, z
N(4G)–H(1N4) ··· O(4)	2.38(2)	3.163(2)	160(2)	$x, y - 1, z$
N(4G)–H(2N4) ··· O(10)	2.20(2)	3.058(2)	166(2)	$x, y - 1, z$
(5)				
N(1G)–H(1N1) ··· O(4)	2.26(4)	3.091(2)	150(4)	x, y, z
N(1G)–H(2N1) ··· O(13)	2.43(4)	3.213(3)	149(3)	x, y, z
N(2G)–H(1N2) ··· O(7)	2.03(3)	2.855(2)	166(2)	$x, y - 1, z$
N(3G)–H(1N3) ··· O(13)	2.19(4)	2.946(3)	151(3)	x, y, z
N(4G)–H(1N4) ··· O(16)	2.11(3)	2.961(2)	163(2)	$x, y - 1, z$
N(4G)–H(2N4) ··· O(4)	2.11(3)	2.941(2)	157(3)	$x, y - 1, z$
(6)				
N(3G)–H(3GA) ··· S(1G)	2.47(2)	3.334(2)	170(2)	$-x + 1/2, y - 1/2, z$
N(2G)–H(2GA) ··· S(2G)	2.47(2)	3.297(2)	161(2)	$-x + 1/2, y + 1/2, z$
N(4G)–H(4GA) ··· S(1G)	2.53(2)	3.396(2)	172(2)	$-x, y - 1/2, -z + 1/2$
N(4G)–H(4GB) ··· S(2G)	2.72(2)	3.464(1)	142(2)	$-x, y + 1/2, -z + 1/2$
N(1G)–H(1GA) ··· O(4)	2.25(3)	2.940(3)	141(3)	x, y, z
N(1G)–H(1GA) ··· O(1)	2.58(3)	3.093(3)	121(2)	$-x, -y, -z$
N(1G)–H(1GB) ··· O(7)	2.08(2)	2.859(3)	151(2)	$-x, -y, -z$
N(1G)–H(1GB) ··· O(13)	2.18(2)	2.891(3)	141(2)	x, y, z
(7)				
N(1G)–H(7N) ··· O(7a)	1.95(2)	2.833(2)	171(2)	$-x, -y + 1, -z + 2$
N(1G)–H(8N) ··· O(10)	1.99(2)	2.842(2)	153(2)	$-x, -y + 1, -z + 1$
N(2G)–H(9N) ··· S(2G)	2.37(2)	3.275(2)	169(2)	$x, -y + 3/2, z + 1/2$
N(3G)–H(10N) ··· S(1G)	2.36(2)	3.252(2)	170(2)	$x, -y + 3/2, z - 1/2$
N(4G)–H(11N) ··· O(1)	2.19(2)	2.976(2)	161(2)	x, y, z
N(4G)–H(12N) ··· O(10a)	2.20(2)	2.991(2)	172(2)	$x, y, z - 1$
N(11G)–H(1N) ··· O(4)	1.99(2)	2.860(2)	170(2)	x, y, z
N(11G)–H(2N) ··· O(1a)	2.02(2)	2.864(2)	158(2)	x, y, z
N(12G)–H(3N) ··· S(12G)	2.44(2)	3.326(2)	169(2)	$x, -y + 3/2, z - 1/2$
N(13G)–H(4N) ··· S(11G)	2.37(2)	3.235(2)	170(2)	$x, -y + 3/2, z + 1/2$
N(14G)–H(5N) ··· O(7)	2.08(2)	2.953(2)	170(2)	$-x + 1, -y + 1, -z + 2$
N(14G)–H(6N) ··· O(4a)	2.08(2)	2.955(2)	161(2)	$-x + 1, -y + 1, -z + 2$

organisation. DCHA and **dtox2** alternate in the chains running along the *b* direction in the unit cell. The dihedral angle between the mean planes of planar framework of the **dtox2** molecule and the six oxygens of DCHA is 65.13(2)°. The **dtox2** molecule situated on the proximal face of DCHA affords two equal hydrogen bonds with the central oxygen atoms of the crown molecule, N(2G) ··· O(4) 3.107(2) Å. From the rear face of the same crown molecule the next **dtox2** molecule participates by N(3G) functionality in the H-bonding with the same oxygen atoms N(3G) ··· O(4) ($x, y - 1, z$) 2.938(2) Å. The **dtox1** molecule bridges the neighbouring center-of-symmetry related chains *via* one single N–H ··· O hydrogen bond, N(1G) ··· O(7) 2.994(2) Å providing the layer that is developed in the *ab* plane (Fig. 4).

The layer is built of the centrosymmetric cages that unite four crown and four **dtox** molecules in an alternative mode, each cage being closed by 12 N–H ··· O hydrogen bonds. Two crystallographically different **dtox** molecules are arranged in such a way that the dihedral angle between the mean planes of their non-hydrogen skeletons is 56.87(5)°. The arrangement of the components in the two-dimensional grid makes it impossible for sulfur atoms to participate in any self-assembled

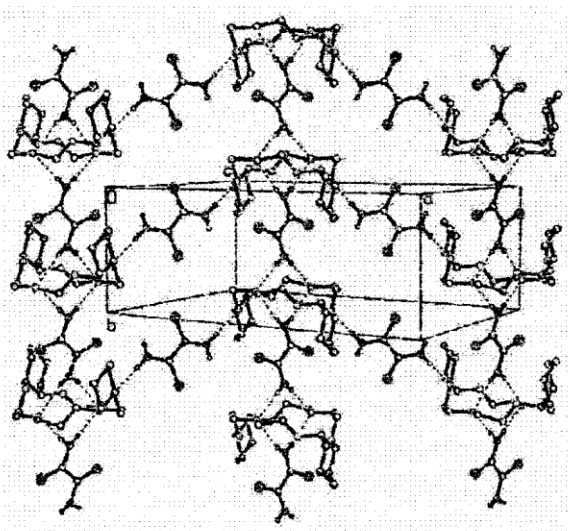

Fig. 4 View of the layer in (**2**). Red: oxygens, blue: nitrogens, orange: sulfurs.

N–H · · · S contacts found both in the structure of **dtox**[12] itself and in its complex with 18C6.[14]

(**3**) crystallises in monoclinic space group $P2_1/n$ with the asymmetric unit cell containing half of the crown molecule and two halves of two crystallographically independent **dtox** molecules, all residing on inversion centres. The ORTEP diagram for (**3**) is shown in Fig. 5.

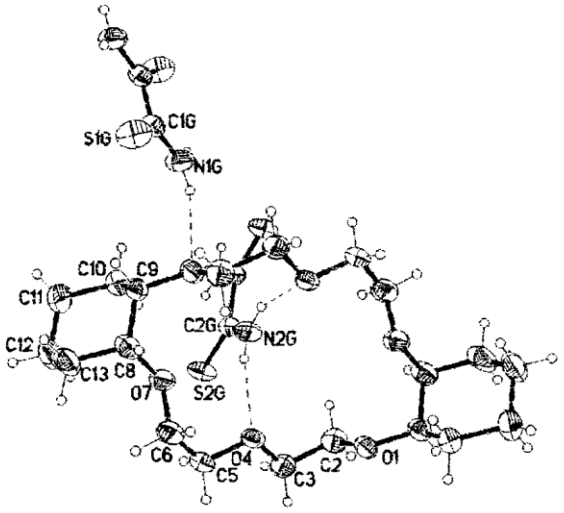

Fig. 5 ORTEP drawing for (**3**). The thermal ellipsoids are given with 50% probability level.

The two types of **dtox** molecules are arranged in perfectly the same way as in (**2**), with the dihedral angle between the mean planes of their skeletons equal to 56.68(6)°. The packing motif in (**3**) is similar to that of (**2**). DCHB and **dtox2** molecules alternate in a chain running along the *b* direction. Due to the inversion centre, each **dtox2**–DCHB–**dtox2** associate in the chain is stabilised by four center-of-symmetry-related N–H · · · O hydrogen bonds with the central oxygen atoms of the crown molecule, N(2G) · · · O(4) 2.985(2) and N(2G) · · · O(4) ($-x + 1, -y + 1, -z$) 2.984(2) Å. The same donor centre is involved in a subsidiary N–H · · · O interaction, N(2G) · · · O(7) 3.100(2) Å. The dihedral angle between the mean planes of the framework of the **dtox2** molecule and six oxygen atoms of the crown cavity is 72.42(6)°. **Dtox1** molecules bridge neighbouring chains *via* two equal N–H · · · O bonds, N(1G) · · · O(1) ($-x + 1, -y + 1, -z$) 3.039(2) Å, to generate layers that propagate parallel to the *ab* plane (Fig. 6).

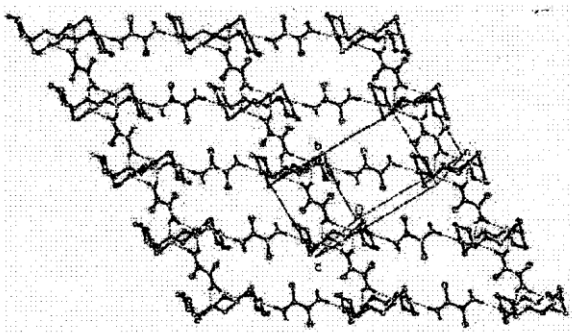

Fig. 6 View of the layer in (**3**). Red: oxygens, blue: nitrogens, orange: sulfurs.

To the best of our knowledge, this is the first example where two isomers of DCH18C6 yielded two supramolecular architectures of such pronounced similarity. It is evident that the dimensionality of **dtox** species is the crucial factor that dictates the similar arrangement of the components in the complexes with a minor influence arisen from the orientation of the cyclohexyl substituents. In the other known pairs, the clathrates of two isomers of DCH18C6 with malononitrile,[15a] zwitter-ion of amidosulfuric acid, $NH_3^+SO_3^-$,[15b] 3,5-dichlorobenzenesulfamide,[15c,d] 4-aminobenzenesulfamidine,[15e] 4-methylbenzenesulfamide,[15f] different supramolecular motifs have always been found for clathrates with the same guest.

Complexes of dithiobiurea with crown ethers

(**4**) is depicted in Fig. 7, it crystallizes with a 1 : 1 ratio of components in monoclinic space group $P2_1/c$ containing one 18C6 and one **dtur** molecule per asymmetric unit.

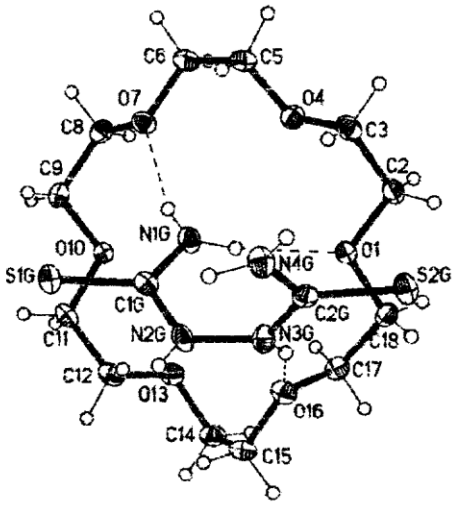

Fig. 7 ORTEP drawing for (**4**). The thermal ellipsoids are given with 50% probability level.

The molecules are held together by N–H · · · O hydrogen bonds with the participation of terminal and central amine groups of **dtur** in a twisted mode. The amine group defined by the N(1G) atom provides two hydrogen bonds with the crown oxygens, N(1G) · · · O(1) 3.056(2), N(1G) · · · O(7) 3.007(2) Å. The secondary amine group, defined by the N(3G) atom, provides a single hydrogen bond on the same face of the crown

molecule, N(3G) ··· O(16) 2.932(2) Å. The terminal amine group, defined by the N(4G) atom and secondary amine group, defined by the N(2G) atom, afford in a similar fashion N–H ··· O hydrogen bonds to the next crown molecule, N(4G) ··· O(4) (x, $y - 1$, z) 3.163(2), N(4G) ··· O(10) (x, $y - 1$, z) 3.058(2), N(2G) ··· O(13) (x, $y - 1$, z) 2.982(2) Å, generating a chain running along the b direction in the unit cell (Fig. 8). Thus, all H-acceptors (crown oxygen atoms) and all H-donors (amine groups) are involved in N–H ··· O interactions. Sulfur atoms do not contribute to any hydrogen-bonding interactions. The chains are packed in a centrosymmetric mode in the crystal with only van der Waals interactions between them, Fig. 8.

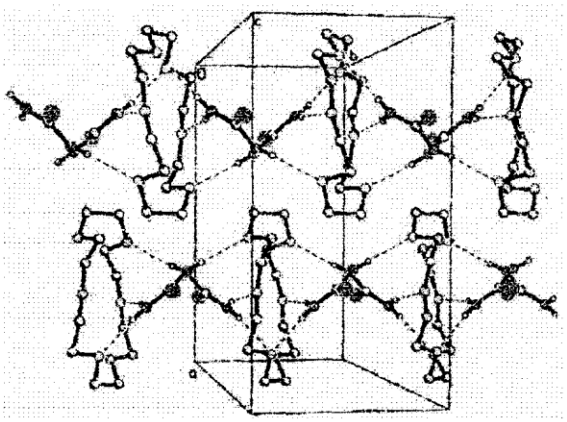

Fig. 8 Arrangement of chains in (**4**). Red: oxygens, blue: nitrogens, orange: sulfurs.

The organisation of (**5**) closely resembles (**4**) (Fig. 9). Each terminal amine group acts as H-donor in two H-bonds with the crown oxygens, N ··· O distances are N(1G) ··· O(4) 3.091(2), N(1G) ··· O(13) 3.213(3), and N(4G) ··· O4 (x, $y - 1$, z) 2.941(2), N(4G) ··· O16 (x, $y - 1$, z) 2.961(2) Å.

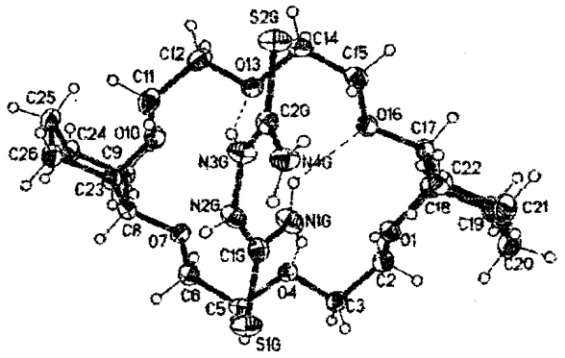

Fig. 9 ORTEP drawing for (**5**). The thermal ellipsoids are given with 50% probability level.

As in (**4**), two central amine groups of **dtur** molecule in a twisted mode are involved in short contacts with the crown spacer, N(3G) ··· O(13) 2.946(3), N(2G) ··· O(7) (x, $y - 1$, z) 2.855(2) Å. Sustained by these N–H ··· O contacts, 1 : 1 polymeric chains, where DCHB and **dtur** molecules alternate, propagate in (**5**) along the b direction in the unit cell, Fig. 10.

To our knowledge, this is the first example of the close crystal structures for 18C6 and DCHB with the same organic molecule (complexes of 18C6 and DCHB with 4-amino-benzenesulfamide[16a,b] and with 6-chloro-7-sulfamido-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide[17a,b] afford different supramolecular architectures).

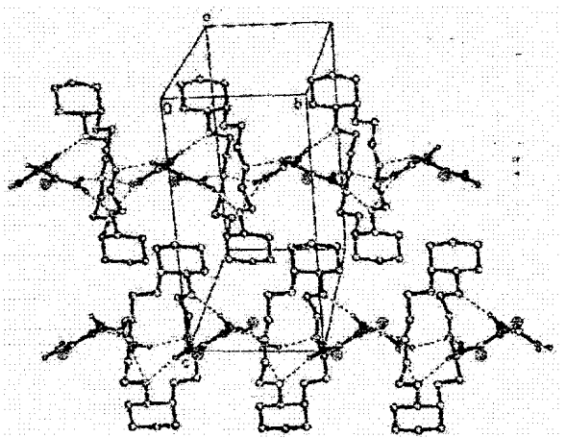

Fig. 10 Arrangement of chains in (**5**). Red: oxygens, blue: nitrogens, orange: sulfurs.

(**6**) crystallizes in the orthorhombic space group *Pbca* in a 1 : 2 ratio as shown in Fig. 11. The asymmetric unit contains a crown molecule, which sits on an inversion centre (with a probability of 50%) and a **dtur** molecule. Two **dtur** molecules approach each 15C5 molecule and the amine group defined by the N(1G) atom, participates in four N–H ··· O hydrogen bonds with the crown oxygens, the N ··· O separations are in the range 2.859(3)–3.093(3) Å (Table 1).

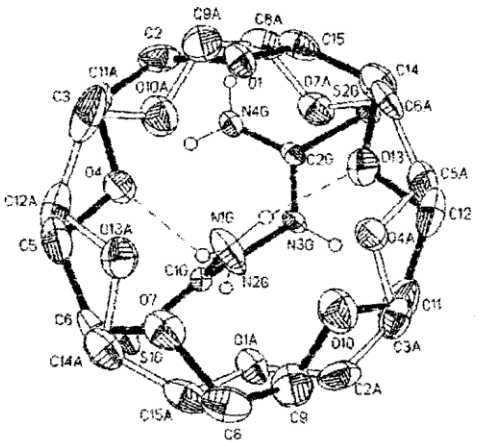

Fig. 11 ORTEP drawing for (**6**). The thermal ellipsoids are given with 30% probability level. Two positions (open and dark lines) for the 15C5 molecule are given. The centre-of-symmetry related **dtur** molecule is omitted.

The **dtur** molecules are self-assembled into pleated sheets that propagate parallel to the *ab* plane, Fig. 12. In the sheet each molecule is bound with four closest neighbours *via* N–H ··· S hydrogen bonds with three of four amine groups as H-donors and two sulfur atoms being involved in these interactions. The sheet is sustained by three different supramolecular synthons. Two secondary amine groups defined by the N(2G) and N(3G) atoms, form two similar planar supramolecular synthons, $R_2^2(8)$[18] between the molecules related by the glide plane, N(3G) ··· S(1G) ($-x + 1/2$, $y - 1/2$, z) 3.334(2), N(2G) ··· S(2G) ($-x + 1/2$, $y + 1/2$, z) 3.297(2) Å. Each synthon includes two different sulfur atoms and two secondary amine groups.[19] The same sulfur atoms are also involved in N–H ··· S hydrogen bonds with the primary amine group defined by the N(4G) atom, N(4G) ··· S(1G) ($-x$, $y - 1/2$, $-z + 1/2$) 3.396(2) Å and N(4G) ··· S(2G) ($-x$, $y + 1/2$, $-z + 1/2$) 3.464(1) Å, thus, the $R_4^2(9)$ synthon combines four **dtur**

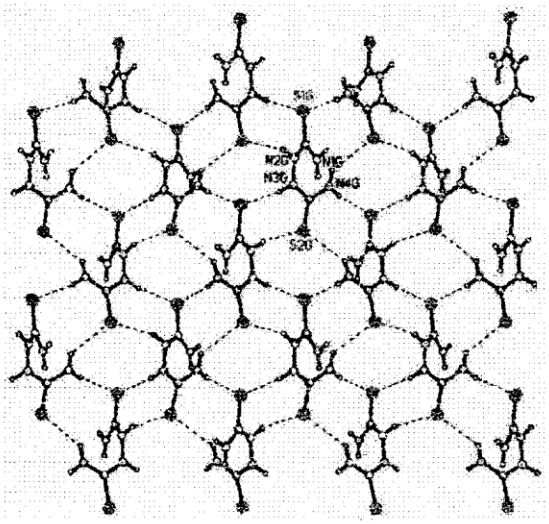

Fig. 12 View of the layer built of the **dtur** molecules in (6). Blue: nitrogens, orange: sulfurs.

molecules. In turn, each **dtur** molecule is engaged in four N–H ··· S hydrogen bonds within the sheet.

Sheets of **dtur** alternate with the sheets of 15C5 molecules along the *c* direction. The sheets are sustained by H-bonding to generate the three-dimensional grid illustrated in Fig. 13. To our knowledge, this is the first example of three-dimensional network that incorporates 15C5 molecules as the spacers between the layers of organic molecules.

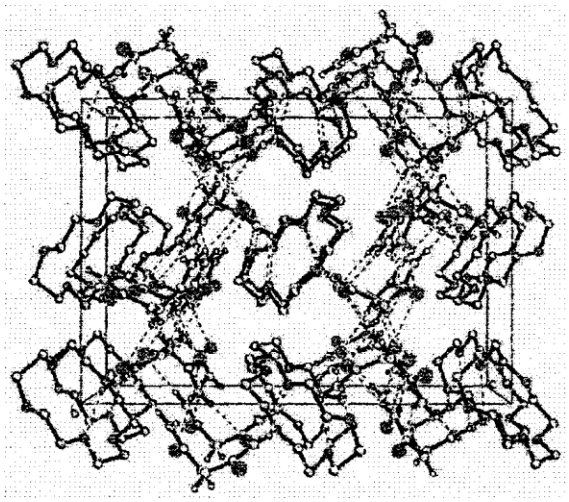

Fig. 13 Packing diagram for (6). Red: oxygens, blue: nitrogens, orange: sulfurs.

For the twinned crystal of (7) the asymmetric part of the monoclinic unit cell (space group $P2_1/c$) contains two 12C4 and two **dtur** molecules in general positions, and is depicted in Fig. 14.

Two 12C4 molecules are arranged in such a way that the dihedral angle between the mean planes through their oxygen atoms is equal to 30.80(4)°. Each primary amine group of **dtur** molecule acts as H-donor and forms two H-bonds with two crystallographically non-equivalent crown molecules, Fig. 14. Thus, each of two **dtur** molecules is joined *via* four single N–H ··· O hydrogen bonds with four crown molecules, related with the basic ones by inversion centres or translations. N ··· O distances fall in the range of 2.833(2)–2.991(2) Å for the **dtur** molecule containing the N(1G) atom and 2.860(2)–

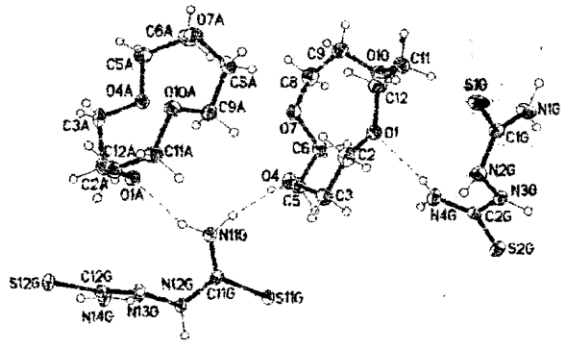

Fig. 14 ORTEP drawing for (7). The thermal ellipsoids are given with 30% probability level.

2.955(2) Å for the **dtur** molecule containing the N(11G) atom. Four molecules of 12C4 and 8 **dtur** molecules that belong to the adjacent chains are combined into centrosymmetric cages closed by 16 N–H ··· O hydrogen bonds, Fig. 15.

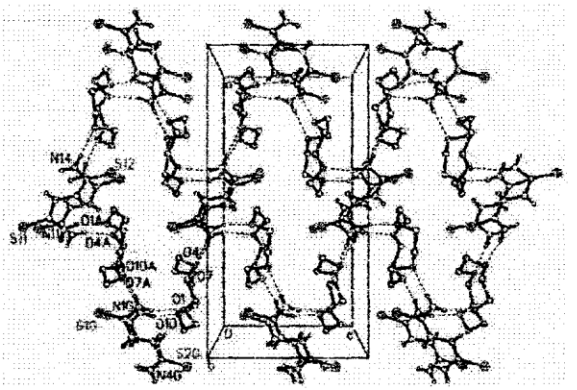

Fig. 15 Centrosymmetric cages closed by N–H ··· O hydrogen bonds in (7). The stacking **dtur** molecules belong to the neighbouring chains. Red: oxygens, blue: nitrogens, orange: sulfurs.

The crystallographically independent **dtur** molecules (defined by the S1G and S11G atoms), related by the glide plane, are consolidated into identical chains that alternate along the *a* direction in the unit cell. Two N–H ··· S hydrogen bonds N(2G) ··· S(2G) (x, $-y$ + 3/2, z + 1/2) 3.275(2) and N(3G) ··· S(1G) (x, $-y$ + 3/2, z − 1/2) 3.252(2) Å in one chain and N(12G) ··· S(12G) (x, $-y$ + 3/2, z − 1/2) 3.326(2) and N(13G) ··· S(11G) (x, $-y$ + 3/2, z + 1/2) 3.235(2) Å in another chain with participation of both central nitrogen atoms are responsible for the chain formation due to the $R_2^2(8)$ synthon,. The chains propagate along the *c* direction, Fig. 16.

In the *ab* plane the chains of **dtur** molecules of each type alternate with the rows of crown molecules attached to them. The closed cages are built of four crown molecules and two **dtur** molecules related by the inversion centre. In this layer (the second **dtur** molecule is removed to clarify the picture) the **dtur** molecules use all their proton-donor functionalities. A similar layer is formed with the participation of another **dtur** molecule and the same crown molecules. Due to the same crown connectors are involved in the both of these layers, the components in the crystal are consolidated into a three-dimensional grid where the identical **dtur** chains propagate along the *b* direction, while along the *a* direction these chains alternate, Fig. 17.

Conclusions

1. The dimensionality of the **dtox** molecule is a crucial factor that determines the close crystal packings in the complexes

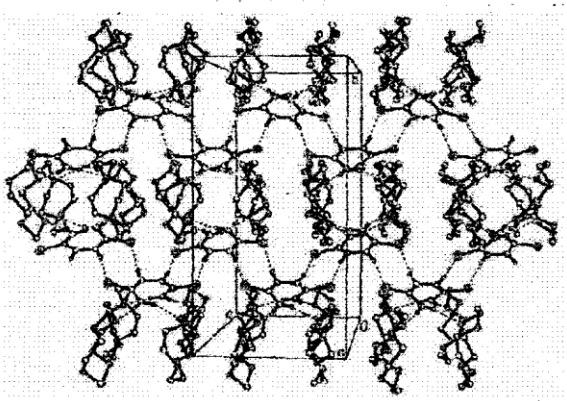

Fig. 16 Layer in (7) that combines one type of **dtur** molecules and crown ethers (the second type of **dtur** molecules is omitted). Red: oxygens, blue: nitrogens, orange: sulfurs.

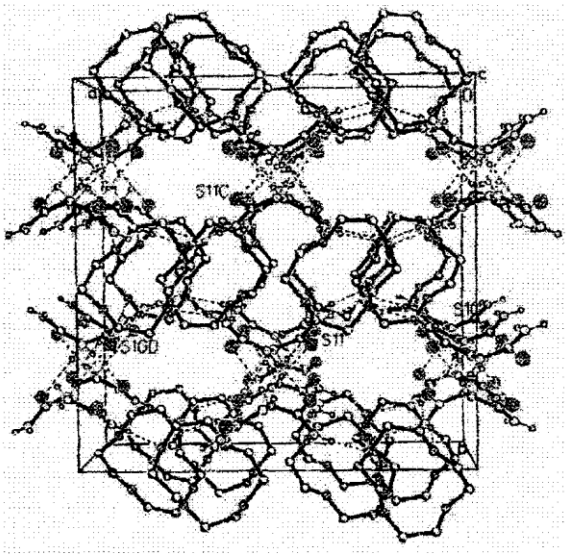

Fig. 17 Crystal packing for (7). Red: oxygens, blue: nitrogens, orange: sulfurs.

of 15-membered crown-ethers and diastereoisomers of dicyclohexyl-18-crown-6 in (**2**) and (**3**).

2. The size of 18-membered crown-rings of 18C6 and DCHB permits the accommodation of six NH ··· O hydrogen bonds and is a decisive factor for the similar crystal packings for (**4**) and (**5**).

3. The reduction of the crown ring in 15C5 and 12C4 explains the participation of only two (**6**) or one (**7**) proton of the amine group in NH ··· O crown interactions and the elaboration of another donor center in the **dtur** molecule for self-assembling and formulation of extended hydrogen-bonding networks in (**6**) and (**7**).

4. The melting points for two families of the compounds described being in the range of 160–180° for (**1**)–(**3**) and 230–240° for (**4**)–(**7**) reveal the direct relationship between the number of hydrogen bonds sustaining the two-component supramolecular architectures and the crystal stability.

5. The relative simplicity of these two model systems allow for specific interactions to be isolated and studied in the absence of the many other interactions available in natural biological systems.

Experimental

All the chemicals used (crown ethers, dithiooxamide and dithiobiurea) were purchased from Aldrich Chemical Co and were not purified prior to use. In all the experiments a 1 : 1 mixture of **dtox** or **dtur** (75 mg, 0.5 mmol) and 0.5 mmol of the corresponding crown ether was dissolved in a minimal amount (3 mL) of dimethylformamide at 100 °C and allowed to slowly evaporate. Crystals suitable for the X-ray diffraction experiments were isolated from the mass of crystals obtained. Suitable microanalyses were obtained for all compounds.

^{1}H and ^{13}C NMR spectra were obtained in DMSO-d_6 on a 250 MHz Bruker instrument. TGA data were obtained at a dynamic rate on a Hi-Res TGA 2950 thermogravimetric analyzer. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo-Kα radiation using ϖ rotations with sample-to-detector distance of 25 mm.

Red crystals of (**1**), mp 159–160 °C. Found, % C, 42.38; H, 7.14, N, 8.20 required for $C_{12}H_{24}N_2O_5S_2$: C, 42.33; H, 7.11; N, 8.23. TGA analysis shows that the complex decomposes in a single step at 169 °C (96.7%). ^{1}H NMR: δ = 10.18 (s, 2H, NH_2), 9.86 (s, 2H, NH_2), 3.52 (s, 20H, OCH_2). ^{13}C NMR: δ = 194.20 (C=S), 70.26 (OCH_2)

Crystal data for (**1**), triclinic, *P*-1, a = 8.266(5), b = 8.644(6), c = 12.532(1) Å, α = 80.05(3), β = 81.74(3), γ = 75.39(3)°, V = 848.7(1) Å^3, Z = 2, D_x = 1.332 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, μ = 3.34 cm^{-1}, F(000) = 364, GoF = 1.122, R indices (all data) $R1$ = 0.1092, $wR2$ = 0.2389 for 2943 reflections and 245 parameters and R indices $R1$ = 0.0938, $wR2$ = 0.2308 for 2471 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Red crystals of (**2**), mp 155–157 °C. Found, %: C, 47.08; H, 7.24; N, 9.19 required for $C_{24}H_{44}N_4O_6S_4$: C, 47.03; H, 7.27; N, 9.14. TGA analysis shows that the complex is stable to *ca.* 160–170 °C after which it decomposes in two steps at 177 °C (58.64%) and at 215 °C (40.95%). ^{1}H NMR: δ = 10.18 (s, 2H, NH_2), 9.59 (s, 2H, NH_2), 3.61–3.46 (m, 10H, OCH_2), 1.70 (d, 2H, CH_2), 1.46–1.21 (m, 6H, CH_2). ^{13}C NMR: δ = 194.46 (C=S), 76.84, 70.48, 67.89, 27.63, 22.01.

Crystal data for (**2**), monoclinic, *C*2/*c*, a = 23.720(1), b = 7.655(2), c = 18.364(3) Å, β = 106.98(6)°, V = 3189.1(1) Å^3, Z = 4, D_x = 1.276 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, μ = 3.39 cm^{-1}, F(000) = 1312, GoF = 1.067, R indices (all data) $R1$ = 0.0582, $wR2$ = 0.1033 for 3649 reflections and 198 parameters and R indices $R1$ = 0.0424, $wR2$ = 0.0966 for 3033 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Red crystals of (**3**), mp 179–180 °C, Found, %: C, 47.10; H, 7.28; N, 9.10; required for $C_{24}H_{44}N_4O_6S_4$: C, 47.03; H, 7.27; N, 9.14. TGA analysis shows that the complex decomposes in two steps at 173 °C (50.50%) and 207 °C (49.64%). ^{1}H NMR: δ = 10.18 (s, 2H, NH_2), 9.59 (s, 2H, NH_2), 3.61–3.46 (m, 10H, OCH_2), 1.70 (d, 2H, CH_2), 1.44–1.19 (m, 6H, CH_2). ^{13}C NMR: δ = 194.46 (C=S), 76.84, 70.48, 67.89, 27.63, 22.01.

Crystal data for (**3**), monoclinic, $P2_1/n$, a = 12.654(3), b = 7.570(2), c = 17.129(3) Å, β = 106.14(3)°, V = 1576.1(5) Å^3, Z = 2, D_x = 1.291 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, μ = 3.43 cm^{-1}, F(000) = 656, GoF = 1.097, R indices (all data) $R1$ = 0.0494, $wR2$ = 0.1144 for 3592 reflections and 184 parameters and R indices $R1$ = 0.0421, $wR2$ = 0.1103 for 3212 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Colorless needles of (**4**), mp 228–230 °C. Found, %: C, 40.61, H, 7.26, N, 13.59; required for $C_{14}H_{30}N_4O_6S_2$: C, 40.56, H, 7.29, N, 13.52. TGA analysis shows a complex multiple weight losses at 152.44 °C (29.05%), 199.37 °C (61.36%) and 613.23 °C (9.303%).

Crystal data for (**4**), monoclinic, $P2_1/c$, a = 14.196(3), b = 7.187(2), c = 19.552(3) Å, β = 92.18(2)°, V = 1993.4(8) Å^3, Z = 4, D_x = 1.381 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, μ = 3.04 cm^{-1}, F(000) = 888, GoF = 1.023, R indices (all data) $R1$ = 0.0452, $wR2$ = 0.0782 for 4532 reflections and 259 parameters and R indices $R1$ = 0.0334, $wR2$ = 0.0748 for 3860 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Colorless needles of (**5**), mp 226–228 °C. Found, %: C, 50.53, H, 8.17, N, 10.75; required for $C_{22}H_{42}N_4O_6S_2$: C, 50.55, H, 8.10, N, 10.72%. ^{1}H NMR: δ = 9.50 (s, 2H, NH–NH), 8.45 (s, 4H, $-NH_2$), 3.60 (s, 16H, $-CH_2O$); ^{13}C NMR: δ = 183.20 (C=S), 70.25 (CH_2O).

Crystal data for (**5**), monoclinic, *Pn*, a = 12.489(2), b = 7.509(2), c = 14.639(3) Å, β = 93.61(3)°, V = 1370.1(5) Å^3, Z = 2, D_x = 1.267 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, μ = 2.36 cm^{-1}, F(000) = 564, GoF = 1.067, R indices (all data) $R1$ = 0.0315, $wR2$ = 0.0796 for 3097 reflections and 331 parameters and R indices $R1$ = 0.0303, $wR2$ = 0.0789 for 3019 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Colorless needles of (**6**), mp 235–237 °C, Found, %: C, 32.25, H, 6.23, N, 21.61, required for $C_{14}H_{32}N_8O_5S_4$: C, 32.29, H, 6.19, N, 21.52.

TGA analysis indicates that the host decomposes at 187 °C (44.72 %) followed by multiple weight losses for the guest at 204.24 °C (25.06%), 280.83 °C (15.40%), and 585.60 °C (14.82%); ^{1}H NMR: δ = 9.34 (s, 2H, N*H*–N*H*), 8.01 (broad s, 2H, NH_2), 7.20 (broad s, 2H, NH_2), 3.52 (s, 10H, OCH_2); ^{13}C NMR: δ = 180.24 (C=S), 70.13 (OCH_2)

Crystal data for (**6**), orthorhombic, *Pbca*, a = 13.632(3), b = 9.475(2), c = 19.185(4) Å, V = 2478.0(9) Å^3, Z = 4, D_x = 1.396 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, μ = 4.24 cm^{-1}, F(000) = 1104, GoF = 1.079, R indices (all data) $R1$ = 0.0519, $wR2$ = 0.0971 for 3579 reflections and 232 parameters and R indices $R1$ = 0.0411, $wR2$ = 0.0917 for 3158 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Colorless needles of (**7**), mp 235–237 °C, Found, %: C, 36.76, H, 6.84, N, 17.21, required for $C_{16}H_{32}N_4O_4S_2$: C, 36.79, H, 6.79, N, 17.16. TGA analysis indicates that the host decomposes at 132.60 °C (53.25%), followed by multiple weight losses for the guest at 218.70 °C (26.88%), 314.16 °C (7.437%), 594.52 °C (12.14%); ^{1}H NMR: δ = 9.30 (s, 2H, NH–NH), 7.92 (s, 2H, NH_2), 7.26 (s, 2H, NH_2); ^{13}C NMR: δ = 182.77 (C=S), 70.312 (CH_2O).

Crystal data for (**7**), monoclinic, $P2_1/c$, a = 18.475(4), b = 18.445(4), c = 9.443(2) Å, β = 90.00(3)°, V = 3217.9(12) Å^3, Z = 8, D_x = 1.348 g cm^{-3}, λ(Mo-Kα) 0.71073 Å, μ = 3.48 cm^{-1}, F(000) = 1392, GoF = 0.926, R indices (all data) $R1$ = 0.0448, $wR2$ = 0.0828 for 9354 reflections and 404 parameters and R indices $R1$ = 0.0343, $wR2$ = 0.07 for 8171 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Tables of crystal data, atomic coordinates and thermal parameters, full bond distances and angles, and structure factors may be obtained on request from the authors. CCDC reference numbers 202644–202650 for compounds (**1**)–(**7**), respectively.

See http://www.rsc.org/suppdata/ob/b3/b301379k/ for crystallographic data in CIF or other electronic format.

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Додаток 12

Копія статті.

“Комплекси "гість-хазяїн". Селективна взаємодія молекул "хазяїнів" - краун-етерів з похідними трифенілметану”

Журнал общей химии. 2003. Т. 73. Вып. 8

КОМПЛЕКСЫ «ГОСТЬ–ХОЗЯИН». СЕЛЕКТИВНОЕ ВЗАИМОДЕЙСТВИЕ МОЛЕКУЛ «ХОЗЯЕВ» – КРАУН-ЭФИРОВ С ПРОИЗВОДНЫМИ ТРИФЕНИЛМЕТАНА

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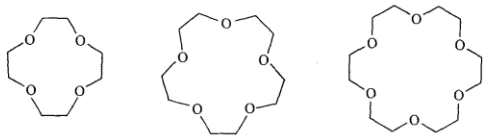
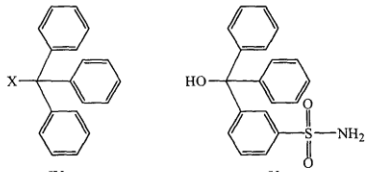
Одна из приоритетных задач химии «гость–хозяин» – это поиск селективных взаимодействий нейтральных молекул, приводящих к образованию молекулярных комплексов, которые моделируют широко распространенные процессы в биологических системах [1]. Исчерпывающим руководством [2] краун-эфиры и производные трифенилметана отнесены к молекулам – «хозяевам», способным связывать меньшие по размеру «гостевые» молекулы [3–5] в комплексы.

Цель данной работы – определение возможности синтеза кристаллических молекулярных комплексов краун-эфиров (I–III) с производными трифенилметана и выявление селективности во взаимодействиях этих партнеров комплексообразования.

Установлено, что при самопроизвольном испарении растворителей из растворов малого «короната» – 1,4,7,10-тетраоксациклододекана (I) – с трифенилметанолом (IVа), 1,1,1-трифенилметиламином (IVб) и трифенилметантиолом (IVв) образуются кристаллические молекулярные комплексы – [(I)·2 (C_6H_5)$_3$COH] – (VI), [(I)·2 (C_6H_5)$_3$CNH$_2$] – (VII), [(I)·2 (C_6H_5)$_3$CSH] – (VIII) соответственно.



I II III



IVа–в V

IV, X = OH (а), NH_2 (б), SH (в).

Обнаружено также, что в этих же условиях при использовании смеси краун-эфиров (I–III) производные трифенилметана (IVа, б) селективно образуют кристаллические комплексы лишь с краун-эфиром (I). Введение в ароматическую часть молекулы трифенилметанола H-донорной сульфамидной группы существенно изменяет результат комплексообразования. Так, при взаимодействии 3-(гидроксидифенилметил)бензолсульфамида (V) с указанной смесью краун-эфиров селективно выделяется кристаллический комплекс состава [(III)·2 *м*-H_2NSO_2·C_6H_4(C_6H_5)$_2$COH] (IX). Ранее во взаимодействии

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нейтральных молекул с перечисленными краун-эфирами селективности отмечено не было [6]. Напротив, N-(фенилсульфонил)бензолсульфамид $HN(SO_2C_6H_5)_2$ дает кристаллические молекулярные комплексы как с краун-эфиром (I) [7], так и с краун-эфиром (III) [8–10].

Таким образом, впервые описаны селективные взаимодействия краун-эфиров с объемными производными трифенилметана, приводящие к образованию кристаллических молекулярных комплексов (VI, VII, IX), что может быть учтено как составная часть при моделировании молекулярных взаимодействий сравнительно крупных природных молекул [11], а также явиться химической основой разделения смесей краун-эфиров [12] аналогично работам [13–15]. Отметим также, что полученное соединение (VIII) является первым примером фиксации краун-эфиром тиола в кристаллический молекулярный комплекс «гость–хозяин».

3-(Гидроксидифенилметил)бензолсульфамид (V). Смесь 10 ммолей трифенилхлорметана и 10 мл хлорсульфоновой кислоты 8 ч выдерживали при 150°C, затем охлаждали, выливали на 50 г льда, кристаллическую массу отделяли, помещали в 40 мл 25%-ного водного раствора аммиака и нагревали при перемешивании 12 ч. Выделившийся при 20°C кристаллический осадок отмывали водой, сушили на воздухе и перекристаллизовывали из смеси ацетон–гексан, выход 53%, т. пл. 188–190°C. Найдено, %: C 67.24; H 5.05; N 4.13; S 9.45. $C_{19}H_{17}NO_3S$. Вычислено, %: C 67.21; H 5.09; N 4.19; S 9.55.

Кристаллические молекулярные комплексы (VI–VIII). К смеси 1 ммоля краун-эфира (I), 1 ммоля краун-эфира (II), 1 ммоля краун-эфира (III) добавляли раствор 1 ммоля соединений (IVa–в) в 10 мл метанола или 1 ммоля соединения (V) в смеси 5 мл ацетона и 5 мл гексана; при 20°C растворитель постепенно испарялся. Выделившиеся монокристаллы промывали этилацетатом и сушили на воздухе. При синтезе комплекса (VIII) использовали индивидуальный краун-эфир (I) и раствор соединения (Iв) в смеси 1.5 мл бензола и 3 мл диэтилового эфира.

Комплекс 1,4,7,10-тетраоксациклододекана с трифенилметанолом, 1:2 (VI), выход 85%, т. пл. 147–148°C. Спектр ЯМР ^1H ($CDCl_3$), δ, м. д.: 1.62 с (2H, OH), 3.70 с, (16H, CH_2), 7.24–7.35 м (30H, ArH). Найдено, %: C 79.28; H 6.94. $C_{46}H_{48}O_6$. Вычислено, %: C 79.33; H 6.90.

Комплекс 1,4,7,10-тетраоксациклододекана с 1,1,1-трифенилметиламином, 1:2 (VII), выход 81%, т. пл. 94–95°C. Спектр ЯМР ^1H ($CDCl_3$), δ, м. д.: 1.86 с (4H, NH), 3.70 с (16H, CH_2), 7.20–7.32 м (30H, ArH). Найдено, %: C 79.51; H 7.25; N 4.03. $C_{46}H_{50}N_2O_4$. Вычислено, %: C 79.53; H 7.24; N 4.05.

Комплекс 1,4,7,10-тетраоксациклододекана с трифенилметантиолом, 1:2 (VIII), выход 83%, т. пл. 68–70°C. Спектр ЯМР ^1H, $CDCl_3$, δ, м. д.: 1.61 с (2H, SH), 3.71 с (16H, CH_2), 7.22–7.30 м (30H, ArH). Найдено, %: C 75.79; H 6.64; S 8.80. $C_{46}H_{48}O_4S_2$. Вычислено, %: C 75.81; H 6.69; S 8.77.

Комплекс 1,4,7,10,13,16-гексаоксациклооктадекана с 3-(гидроксидифенилметил)бензолсульфамидом, 1:2 (IX), выход 98%, т. пл. 174–176°C. Спектр ЯМР ^1H (CD_3OD), δ, м. д.: 3.62 с (24H, CH_2), 7.27–7.44 м (28H, ArH). Найдено, %: C 63.66; H 6.20; N 2.97; S 6.80. $C_{50}H_{58}N_2O_{12}S_2$. Вычислено, %: C 63.71; H 6.24; N 2.99; S 6.85.

Спектры ЯМР ^1H регистрировали на приборе Varian VXR-300 (300 МГц), внутренний стандарт – ТМС.

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Додаток 13

Копія статті.

“Preparation and X-Ray Study of Inclusion Complexes of (4 Z,5 E)-Pyrimidine-2,4,5,6(1 H,3 H)-Tetraone 4,5-Dioxime and the Product of Its Cyclization, (1,2,5)-Oxadiazolo(3,4- d)-Pyrimidine-5,7(4 H,6 H)-Dione with Two 18-Membered Macrocycles”

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Preparation and X-Ray Study of Inclusion Complexes of (4*Z*,5*E*)-Pyrimidine-2,4,5,6(1*H*,3*H*)-Tetraone 4,5-Dioxime and the Product of Its Cyclization, (1,2,5)-Oxadiazolo(3,4-*d*)-Pyrimidine-5,7(4*H*,6*H*)-Dione with Two 18-Membered Macrocycles *

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Key words: crown ether, isomers of pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime, H-bonding patterns, X-ray crystallography, host–guest complex

Abstract

The novel dioxime, (4*Z*,5*E*)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime (H_2-PTD) was obtained by the interaction of 6-amino-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dione with hydroxylamine hydrochloride. X-ray structural analysis determined the 4*Z*,5*E*-configuration of the corresponding monoanion, pyrimidine-2,6(1H,3H)-dione-4-iminole-5-iminolate in the inclusion complexes with diazonia-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane) $(H_2\text{-DA18C6})^{2+}$ (complex (**1**), stoichiometry 2 : 1), and its ammonium salt in the complex with the *cis-syn-cis* isomer of dicyclohexano-18-crown-6(DCHA) (*cis-syn-cis*-2,5,8,15,18,21-hexaoxatricyclo(20.4.0.0^{9,14})hexacosane) (complex (**2**), stoichiometry 1 : 1). X-ray data were also obtained for the complex of the product of (H_2-PTD) cyclization, (1,2,5)-oxadiazolo(3,4-d)pyrimidine-5,7(4*H*,6*H*)-dione (OPD) with diaqua diaza-18-crown-6 (complex (**3**), stoichiometry 2 : 2 : 1).

In (**1**) the $(\text{H-PTD})^-$ anions are joined into dimers through the bifurcated OH···N and OH···O hydrogen bonds and alternate with diazonia-18-crown-6 cations in the chains sustained by the NH(crown)···O and NH(crown)···N interactions. The chains are further combined into the 3D network *via* NH···O(crown) hydrogen bonds. In (**2**) the self-complementarity of the $(\text{H-PTD})^-$ anions facilitates their assembly into the chain *via* OH···N, NH···O and OH···O interactions. The ammonium cations bridge each anion and the DCHA macrocycle with the formation of a ribbon developed along the [101] direction in the unit cell. Ternary complex (**3**) is built of the neutral species, diaza-18-crown-6, water molecules and dimers of OPD alternated in the chains and held together by OH···O and NH···O hydrogen bonds.

Introduction

Crown ethers and related macrocycles deserve the considerable attention for their host–guest chemistry as receptors for cations and neutral organic molecules [1]. These double-face spacers are capable to be included in the extended supramolecular networks formulated by the self-assembled neutral organic molecules, rich in both H-donor and acceptor centers with the final partial retention or rearrangement of H-bonds which sustain the supramolecular architecture [2].

We intended to prepare the novel dioxime, pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime (H_2-PTD) and study its ability to complex with 18-membered crown ethers. Another task was to elucidate in which of four possible tautomeric forms the (H_2-PTD) molecule is present in the crown ether complexes and what factors are decisive for the stabilization of the preferable tautomer.

The most widely used way of the preparation of pyrimidines containing exocyclic functional groups includes the attack of the corresponding nucleophiles on the chloropyrimidines [3, 4]. Essentially less attention has been devoted to the reactions of overamination [5, 6], notwithstanding that in several cases the aminopyrimidines are more accessible than the corresponding chloropyrimidines [3, 4].

It is known that 6-amine-5-nitrosopyrimidine-2,4-(1*H*,3*H*)-dione (**I**) easily participates in the acid catalysed metathesis reaction of the amine group by hydroxylamine.

The product of the reaction, 6-(hydroxyamino)-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dione (**II**) may also exist in three other tautomeric forms, (**III–V**), 6-

* **Supplementary Data** relevant to this article were deposited with the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 180269-180271.

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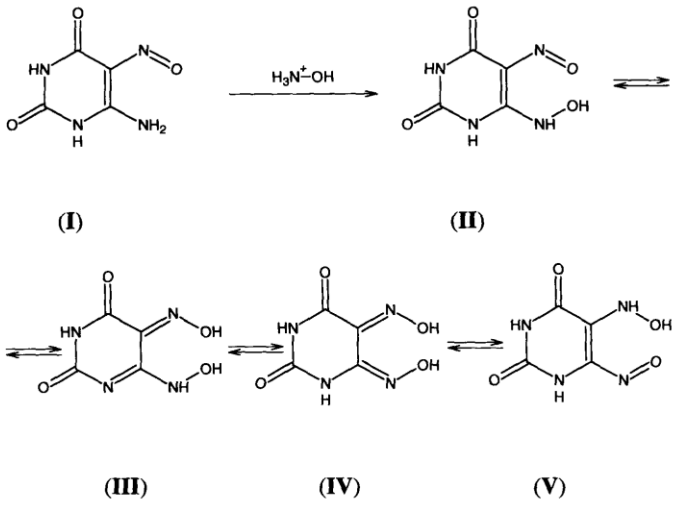


(I) (II)

(III) (IV) (V)

Scheme **I–V**.

(hydroxyamino) pyrimidine-2,4,5(3*H*)-trione-5-oxime, (**III**), pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime, (**IV**), 5-(hydroxyamino)-6-nitrosopyrimidine-2,4(1*H*,3*H*)-dione, (**V**). The absence of the color, that is the specific feature of the nitrosouracils, permits us with high probability to exclude the presence of tautomers (**II**) and (**V**). In its turn, the tautomer (**IV**) may exist in the form of one of four stable geometric isomers (**IVa–d**) or as their mixture.

X-ray data were obtained for the complexes of diazonia-18-crown-6 with (4*Z*,5*E*)-isomer of (H-PTD)$^-$ anion (**1**) (1 : 2), its ammonium salt with *cis-syn-cis* isomer of dicyclohexano-18-crown-6 (DCH6A) (**2**) (1 : 1), and diaza-18-crown-6 and water with (1,2,5)oxadiazolo-(3,4-*d*)pyrimidine-5,7(4*H*,6*H*)-dione, (**3**) (1 : 2 : 2).

Experimental

Synthesis

The thin layer chromatographic control of the substances purity was performed on the Silufol UV-254 plates. Mass-spectrum was obtained on the Varian MAT-112 instrument using 70 eV ionization radiation, and a temperature of 220 °C. The *IR* spectrum was recorded on a Specord-80 spectrometer of mulls in nujol.

Synthesis of (H_2-PTD)

A mixture of 1.4 g (0.009 mol) of 6-amino-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dione (**I**), 2 g (0.03 mol) of hydroxylamine hydrochloride, 1.6 g (0.02 mol) of sodium acetate in 50 mL of water was heated up to 65–70° and stirred until bleaching the reactive mixture. The precipitate was filtered off, washed by the cold water and air dried. The yield of (H_2-PTD) is 1.4 g (91%). M.P. > 250 °C with decomposition. Found, C, 27.92, H, 2.36, N, 32.40 for $C_4H_4N_4O_4$. Calculated, %: C, 27.90; H, 2.33; N, 32.56.

IR, ν, cm^{-1}: 3320, 3000, 1720, 1680, 1600. Mass-spectrum, m/z (I%): 154(39) – [M$^+$-H_2O], 111(12), 70(10), 68(15), 58(8), 54(10), 53(13), 43(100).

Synthesis of (**1**)

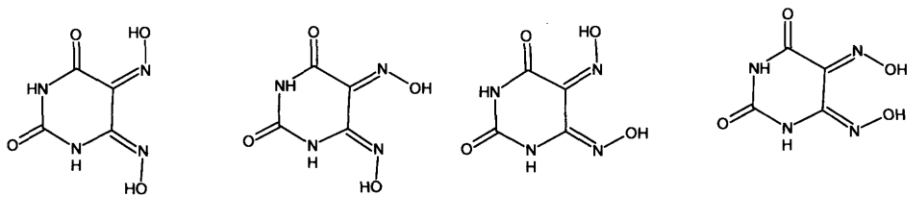
A mixture of 86 mg (0.5 mol) of (H_2-PTD) and 131 mg (0.5 mmol) of diaza-18-crown-6 was dissolved in 5 mL of distilled water and 10 mL of ethanol. The insoluble residue was filtered off and the solvent was allowed to evaporate in ambient conditions. Bright-yellow crystals with the M.P. 175–180 °C with decomposition. Found, C, 39.57, H, 5.69, N, 23.12 for $C_{20}H_{34}N_{10}O_{12}$. Calculated, %: C, 39.60; H, 5.65; N, 23.09.

Synthesis of (**2**)

86 mg (0.5 mmol) of (H_2-PTD) was dissolved in 5 mL of 25% aqueous ammonia solution, a solution of 186 mg (0.5 mmol) of DCH6A was added and the reactive mixture allowed to evaporate at room temperature. Red monocrystals of the complex were obtained. M.P. 176–177 °C. Found, C, 51.28, H, 7.77, N, 12.51 for $C_{24}H_{43}N_5O_{10}$. Calculated, %: C, 51.31; H, 7.72; N, 12.47.

Synthesis of (**3**)

(**3**) was obtained as a minor product in the synthesis of (**1**) via the cyclisation of (H_2-PTD) in (OPD). The insoluble residue remaining after the separation of complex (**1**) from the reaction mixture, was mixed with the triple excess of diaza-18-crown-6 and dissolved in the minimal amount of boiling water. Very poor quality colorless crystals were obtained by the recrystallization from water. M.P. 200 °C.



(IVa) **(IVb)** **(IVc)** **(IVd)**

Scheme **IVa–IVd**. (**IVa**) – (4*Z*,5*Z*)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime
(**IVb**) – (4*Z*,5E)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone-4,5-dioxime
(**IVc**) – (4E,5Z)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime
(**IVd**) – (4E,5E)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime

Found, C, 39.62, H, 5.63, N, 23.07 for $C_{20}H_{34}N_{10}O_{12}$. Calculated, %: C, 39.60; H, 5.65; N, 23.09.

Data collection and structure refinement

The X-ray intensity data for (**1**)–(**3**) were collected on a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo-Kα radiation using ω rotation with a sample-to-detector distance of 40 mm. Unit cell parameters were obtained and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO [7]. The scaling as well as the global refinement of crystal parameters were performed by SCALEPACK [7]. Reflections, which were partly measured on previous and subsequent frames, were used to scale these frames on each other. The structure solution and refinement proceeded similarly for all structures (SHELX-97 software [8]). Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were refined anisotropically (full-matrix least squares method on F^2). C-bound hydrogen atoms were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while the N-bound H-atoms were found from differential Fourier maps and refined without any constrains.

The X-ray data and the details of the refinement for (**1**)–(**3**) are given in Table 1, the selected geometric parameters are summarized in Table 2.

For (**3**) the intensity data set was obtained for a poor quality twinned crystal. Attempts were made to separate the twinned domains but abandoned, so the refinement was stopped at an *R*-value of 0.1394 and only main features of the supramolecular architecture of (**3**) are further discussed.

Crystallographic data for (**1**)–(**3**) were deposited with the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 180269-180271.

Results and discussion

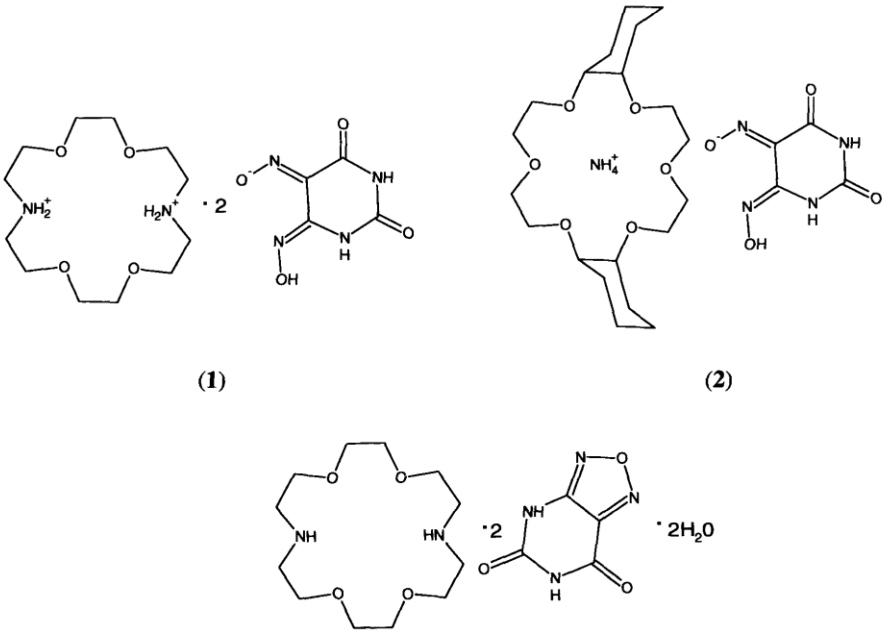
Structure of the (H-PTD)$^-$ anion in (1) and (2)

The molecule of (H_2-PTD) present in (**1**) and (**2**) in the form of the monoanion with one oxime group being deprotonated. The geometric parameters of the uracil heterocycle are very close to the literature data for the relative compounds [9–12]. Due to the conjugation with the *exo*-functional groups all the C—C and C—N interatomic distances are shortened in comparison with the standard values for the corresponding single bonds. All the bond angles at C-atoms approach essentially to 120° (the maximal deviation from this value is 5.1(1)°), while the angles at the N-atom adopt practically the same values in the both complexes equal 126.7(1)° and 126.6(1)°, respectively. The six-membered heterocycle both in (**1**) and (**2**) is practically planar, with the average deviation from complanarity of the six heteroatoms defined the uracil ring being 0.020(1) Å in (**1**) and 0.006(8) Å in (**2**). The deviations of the *exo*-cyclic atoms non-contributing in this plane scatter in the range 0.129(3) for N(4G) to −0.068(3) Å for O(2G) in (**1**) and from 0.079(2) for O(3G) to −0.015(2) Å for N(4G) in (**2**).

Structure of (1)

The crystal structure of (**1**) is built of the (H-PTD)$^-$ monoanions in general positions and $[H_2\text{-DA18C6}]^{2+}$ dications which occupy the positions around the inversion centers in the unit cell. The ORTEP diagram [13] of the independent part of the unit cell for (**1**) with the numbering scheme is shown in Figure 1. The components in (**1**) are mutually arranged in such a way, that the dihedral angle between the plane of 6-membered heterocycle of (H-PTD)$^-$ moiety and the plane of the six oxygen atoms of the crown ring is 74.6(1)°. The nitrogen and oxygen atoms of the deprotonated oxime group act as H-acceptors and bridge the symmetry related NH_2-groups of the diazonia-18-crown-6 macrocycle, N(4)···N(4G) 2.889(2), N(4)···O(4G)($-x$, $-$y, $-z-1$) 2.742(2) Å. The carbonyl oxygen O(1G) of (H-PTD)$^-$ as H-acceptor also contributes in H-bonding with the crown, N(4)···O(1G) 3.009(2) Å, the details of H-bonding geometry for (**1**) and (**2**) are given in Table 3.

Two (H-PTD)$^-$ anions are combined into the centrosymmetric planar dimer *via* the pair of bifurcated OH···N and OH···O hydrogen bonds with the participation of both oxime groups, protonated (as H-donor) and deprotonated (as H-acceptor) ones, O(3G)···N(3G)($-x+1$, $-$y, $-z$) 2.770(2) Å, $R_2^2(6)$ [14], O(3G)···O(4G)($-x+1$, $-y$, $-z$) 2.810(2)



(1) (2) (3)

Scheme **1–3**.

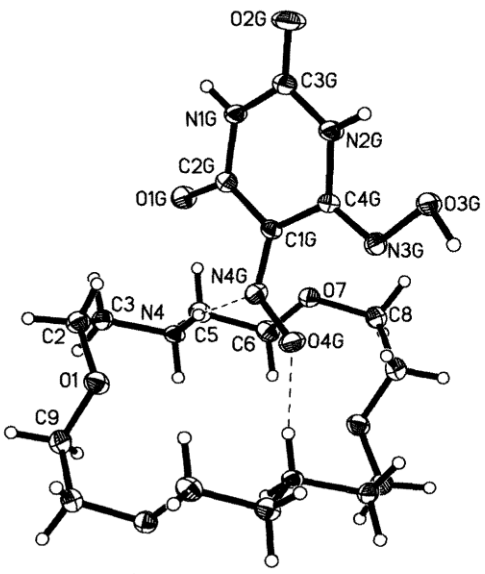


Figure 1. ORTEP drawing of (**1**) with atomic numbering scheme and hydrogen bonds shown as dotted lines. Non-hydrogen atoms are represented by thermal ellipsoids at 30% probability. The symmetry related (H-PTD)$^-$ anion is omitted for the sake of clarity.

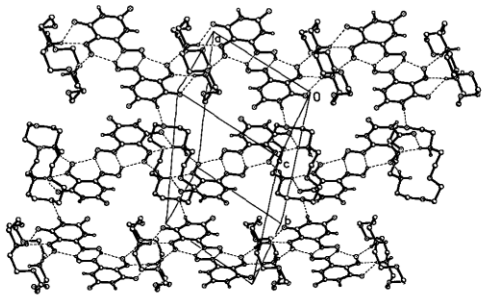


Figure 2. H-bonded chains in (**1**) running along [101] direction. Hydrogen atoms of the crown-molecules are omitted for the sake of clarity.

Å R_2^2 (14) graph sets. The $[(\text{H-PTD})^-]_2$ dimers alternate with the $[H_2\text{-DA18C6}]^{2+}$ cations in the chains running along [101] direction in the unit cell, Figure 2.

Side interactions between the N(1G) atom of the (H-PTDH)$^-$ anion and the O(7) oxygen atom of the crown molecule related with the basic one by glide plane, N(1G)$\cdots$O(7)(x, $-y + 1/2$, $z + 1/2$) 2.881(2) Å are responsible for the joining of these chains in the 3D network, as shown in Figure 3.

Complex (**1**) represents an example of the simple salt of the diazonia-18-crown-6 macrocycle with a bulky organic anion stabilized by H-bonds. Chekhlov et al. [15–17] stud-

Table 1. Crystal data and summary of intensity data collection and structure refinement for compounds (**1**)–(**3**)

Compound	(**1**)	(**2**)	(**3**)
CCDC number	180269	180270	180271
Empirical formula	$C_{20}H_{34}N_{10}O_{12}$	$C_{24}H_{43}N_5O_{10}$	$C_{20}H_{34}N_{10}O_{12}$
Formula weight	606.58	561.63	608.58
Temperature, K	293(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P-1$	$P-1$
Unit cell dimensions			
a, Å	9.969(3)	10.963(2)	7.178(4)
b, Å	18.673(8)	11.492(2)	7.755(4)
c, Å	7.441(4)	12.236(3)	13.125(1)
α, deg.	–	107.18(1)	74.40(2)
β, deg.	105.72(3)	98.43(1)	78.38(2)
γ, deg.	–	103.06(1)	79.82(3)
Cell volume, Å^3	1333.3(1)	1396.5(5)	683.4(7)
Formula units/unit cell	2	2	1
D_{calc}, g cm^{-3}	1.511	1.336	1.479
μ, mm^{-1}	0.126	0.104	0.123
F(000)	640	604	322
Crystal dimensions, mm	0.15 × 0.20 × 0.25	0.20 × 0.20 × 0.30	0.15 × 0.25 × 0.30
θ range for data collection, deg.	2.39 to 27.49	1.93 to 32.00	2.75 to 27.47
Limiting indices	$-11 < h < 12$,	$0 < h < 16$,	$-9 < h < 9$,
	$-24 < k < 24$,	$-17 < k < 16$,	$-10 < k < 10$,
	$-9 < l < 9$	$-18 < l < 17$	$-16 < l < 16$
Reflections collected/unique	4930/2869	9285/9285	5796/3097
	[R(int) = 0.0305]		[R(int) = 0.1076]
Reflections with $I > 2\sigma(I)$	1906	6776	2167
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	2869/0/207	9285/0/380	3097/9/203
Goodness-of-fit on F^2	1.029	1.020	1.260
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0474$,	$R_I = 0.0496$,	$R_1 = 0.1394$,
	$wR_2 = 0.0933$	$wR_2 = 0.1069$	$wR_2 = 0.1695$
R indices (all data)	$R_1 = 0.0857$,	$R_1 = 0.0809$,	$R_1 = 0.2104$
	$wR_2 = 0.1022$	$wR_2 = 0.1167$	$wR_2 = 0.1877$
Largest diff. peak and hole e A^{-3}	0.235 and −0.176	0.313 and −0.260	0.300 and −0.631

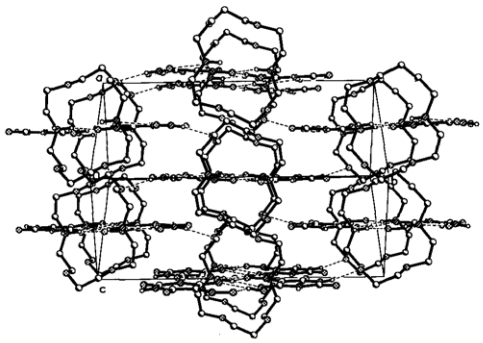


Figure 3. Crystal packing in (**1**). The chains are combined into 3D network along *b* axis *via* NH···O(crown) hydrogen bondings.

ied the complexes of diazonia-18-crown-6 of the salt type. He divided them into two main groups, simple salts having the composition $[H_2DA18C6]^{2+}\cdot 2An^-$ with the monoanions, An^-: Cl^-, Br^-, I^-, NO_3^-, SCN^-, $CF_3CO_2^-$ etc. [16], and dihydrates of the salts with the composition, $[H_2DA18C6]^{2+}\cdot 2An^-\cdot 2H_2O$, with the monoanions, An^-: HSO_4^-, $H_2PO_4^-$, HCO_3^-, $C_6H_5CO_2^-$ [17]. The anhydrous complexes are built in such a mode that the anions have short H-bonding contacts with the positively charged NH_2^+ centers of the diazonia cations with the formation of 1 : 2 complexes of the 'host–guest type'. Water molecules in the second type of complexes are bound with the anions and formulate the second coordination sphere of a macrocycle and expand the structure in two or three directions. The organization of some complexes is similar to (**1**). Thus, in the 3D structure of the complex of diazonia-18-crown-6 with tartarate tetrahydrate $[H_2DA18C6]^{2+}\cdot C_4H_4O_6^{2-}\cdot 4H_2O$ [16c], tartarate dianions, $C_4H_4O_6^{2-}$ and macrocyclic cations

Table 2. Selected bond distances (Å) and angles (deg) in (**1**)–(**3**)

Geometry of the (H-PTD)$^-$ in (**1**) and (**2**)	(**1**)	(**2**)	
O(1G)—C(2G)	1.223(2)	1.231(1)	
O(2G)—C(3G)	1.211(2)	1.220(1)	
O(3G)–N(3G)	1.413(2)	1.415(1)	
O(4G)—N(4G)	1.289(2)	1.300(1)	
C(1G)—N(4G)	1.320(2)	1.331(1)	
C(1G)—C(2G)	1.459(2)	1.461(2)	
C(1G)—C(4G)	1.461(2)	1.455(1)	
C(2G)—N(1G)	1.383(2)	1.391(1)	
C(3G)—N(2G)	1.361(2)	1.369(1)	
C(3G)—N(1G)	1.372(2)	1.378(2)	
C(4G)—N(3G)	1.282(2)	1.296(1)	
C(4G)—N(2G)	1.381(2)	1.395(1)	
N(4G)—C(1G)—C(2G)	113.9(1)	114.3(1)	
N(4G)—C(1G)—C(4G)	127.2(1)	126.8(1)	
C(2G)—C(1G)—C(4G)	118.9(1)	118.9(1)	
O(1G)—C(2G)—N(1G)	1119.0(2)	118.9(1)	
O(1G)—C(2G)—C(1G)	125.1(1)	124.7(1)	
N(1G)—C(2G)—C(1G)	115.9(1)	116.3(1)	
O(2G)—C(3G)—N(2G)	122.7(2)	122.4(1)	
O(2G)—C(3G)—N(1G)	122.2(2)	122.8(1)	
N(2G)—C(3G)—N(1G)	115.1(2)	114.9(1)	
N(3G)—C(4G)—N(2G)	121.3(1)	120.8(1)	
N(3G)—C(4G)—C(1G)	122.3(1)	122.6(1)	
N(2G)—C(4G)—C(1G)	116.4(1)	116.7(1)	
C(3G)—N(1G)—C(2G)	126.8(2)	126.7(1)	
C(3G)—N(2G)—C(4G)	126.7(2)	126.5(1)	
C(4G)—N(3G)—O(3G)	110.6(1)	110.1(1)	
O(4G)—N(4G)—C(1G)	118.7(1)	117.4(1)	
Geometry of the OPD molecule in (**3**)			
O(1G)—C(2G)	1.222(5)	N(4G)—O(3G)—N(3G)	112.1(3)
O(2G)—C(3G)	1.252(5)	C(2G)—N(1G)—C(3G)	128.0(3)
O(3G)—N(4G)	1.377(4)	C(3G)—N(2G)—C(4G)	116.1(4)
O(3G)—N(3G)	1.409(5)	C(4G)—N(3G)—O(3G)	103.9(3)
N(1G)—C(2G)	1.377(5)	C(1G)—N(4G)—O(3G)	104.0(3)
N(1G)—C(3G)	1.410(5)	N(4G)—C(1G)—C(4G)	111.0(4)
N(2G)—C(3G)	1.329(5)	N(4G)—C(1G)—C(2G)	128.4(4)
N(2G)—C(4G)	1.353(5)	C(4G)—C(1G)—C(2G)	120.6(4)
N(3G)—C(4G)	1.320(5)	O(1G)—C(2G)—N(1G)	123.9(4)
N(4G)—C(1G)	1.308(5)	O(1G)—C(2G)—C(1G)	126.7(4)
C(1G)—C(4G)	1.413(6)	N(1G)—C(2G)—C(1G)	109.4(4)
C(1G)—C(2G)	1.470(6)	O(2G)—C(3G)—N(2G)	124.0(4)
		O(2G)—C(3G)—N(1G)	115.1(4)
		N(2G)—C(3G)—N(1G)	120.9(4)
		N(3G)—C(4G)—N(2G)	126.0(4)
		N(3G)—C(4G)—C(1G)	108.9(4)
		N(2G)—C(4G)—C(1G)	125.0(4)

Table 2. Continued

Torsion angles along the heterocyclic framework in (**1**) and (**2**)			
	(**1**)		(**2**)
C(9)—O(1)—C(2)—C(3)	−71.7(2)	C(18)—O(1)—C(2)—C(3)	−173.5(1)
O(1)—C(2)—C(3)—N(4)	−50.8(2)	O(1)—C(2)—C(3)—O(4)	−72.0(1)
C(2)—C(3)—N(4)—C(5)	−161.3(1)	C(2)—C(3)—O(4)—C(5)	175.4(1)
C(3)—N(4)—C(5)—C(6)	−175.5(1)	C(3)—O(4)—C(5)—C(6)	176.5(1)
N(4)—C(5)—C(6)—O(7)	−68.0(2)	O(4)—C(5)—C(6)—O(7)	67.4(1)
C(5)—C(6)—O(7)—C(8)	173.4(1)	C(5)—C(6)—O(7)—C(8)	−177.3(1)
C(6)-O(7)—C(8)—C(9)^i	−91.8(2)	C(6)—O(7)—C(8)—C(9)	177.7(1)
O(7)—C(8)—C(9)^i—O(1)^i	65.4(2)	O(7)—C(8)—C(9)—O(10)	−56.3(1)
C(8)—C(9)^i—O(1)^i—C(2)^i	166.3(1)	C(8)—C(9)—O(10)—C(11)	64.5(1)
		C(9)—O(10)—C(11)—C(12)	−168.7(1)
		O(10)—C(11)—C(12)—O(13)	−67.0(1)
		C(11)—C(12)—O(13)—C(14)	171.0(1)
		C(12)—O(13)—C(14)—C(15)	172.9(1)
		O(13)—C(14)—C(15)—O(16)	67.7(1)
		C(14)—C(15)—O(16)—C(17)	176.1(1)
		C(15)—O(16)—C(17)—C(18)	71.3(1)
		O(16)—C(17)—C(18)—O(1)	57.5(1)
		C(17)—C(18)—O(1)—C(2)	−175.0(1)

Symmetry transformations used to generate equivalent atoms: $i\ -x, -y, -z-1$.

alternate in the chains, and water molecules combine them into a 3D network. The linear architecture is found in the complex of $[H_2DA18C6]^{2+}$ with the dimers of monoaquapentafluorogermanate anions where these dimers and macrocyclic cations alternate [18].

In (**1**) the $[H_2DA18C6]^{2+}$ adopts the C_i conformation described by the following set of torsion angles, $(-g, -g, a, a, -g, a, -g, g, a)_2$ (Table 2). In the centrosymmetric dication there are four symmetry related angular fragments [19], in two of them two *gauche* bonds of the same sign meet at C(2) and C(2)$(-x, -y, -z-1)$ atoms, while two *gauche*-bonds of the opposite sign meet at C(8) and C(8)$(-x, -y, -y, -z-1)$ atoms. This strained conformation may be explained by the bridge function of the deprotonated oxime group which links two symmetry related nitrogen atoms of the macrocycle. More often in its complexes $[H_2DA18C6]^{2+}$ adopts a D_{3d} or C_i-conformation with two angular fragments differing in their position along the macrocyclic framework [15–17]. The distorted shape of the macrocycle is characterized by the pronounced deviations of the heteroatoms from the average plane which they define, O(1) 0.366(4), N(4) −0.467(1), O(7) 0.340(6) Å and the shortened distances between the trans-annular nitrogen atoms N(4)···N(4)$(-x, -y, -z-1)$ 4.323(2) Å in comparison with the trans-annular distances between oxygen atoms, O(1)···O(1)$(-x, -y, -z-1)$ 5.727(2), O(7)···O(7)$(-x, -y, -z-1)$ 6.494(2) Å.

Structure of (**2**)

The independent part of the unit cell of (**2**) contains one macrocyclic cation [DCH6A···NH_4]+ and the (H-PTD)$^-$ monoanion linked together by H-bonds. The ORTEP drawing of (**2**) with the numbering scheme is depicted in Figure 4. The ammonium cation occupies the perching position and its nitrogen atom is displaced by 1.114(1) Å from the average plane of all oxygen atoms of the macrocycle. It affords three NH···O hydrogen bonds to three oxygen atoms, two of them, O(10) and O(16) being attached to the cyclohexyl rings, N···O distances N(1)···O(16) 2.909(1) Å, N(1)···O(10) 2.956(1) Å, and the central oxygen atom, N(1)···O(4) 2.950(1) Å. The ammonium cation is co-ordinated to the crown oxygens on the same side of the crown ether as two cyclohexyl substituents. A similar proximal arrangement was found for the metal and hydronium cations, K^+ [20], Tl^+ [21], Ba^{2+} [22], H_3O^+ [23], and for neutral molecules [24]. Some rare exceptions refer to complexes when bulky molecules such as the zwitter-ion of amidosulfuric acid, $^+NH_3SO_3^-$ [25], or the antimony trifluoride [26] molecule co-ordinates on the rear face of the macrocyclic cavity. The organization of each $[DCH6A{\cdot}NH_4]^+$ cation in (**2**) strictly resembles it in the complex $[DCHA{\cdot}NH_4)(H_2O)I]_2$ [27].

In the same H-bonding mode as in (**1**), in (**2**) two $(PTDH)^-$ anions are linked into the centrosymmetric planar dimer, O(3G)···N(3G)$(-x+1, -y+1, -z)$ 2.803(1), O(3G)···O(4G)$(-x+1, -y+1, -z)$ 2.774(1) Å. These dimers are also combined into the chain through the pair of symmetry related NH···O interactions typical for barbiturate derivatives [10–13], N(1G)···O(1G)$(-x+1, -y, -z-1)$ 2.870(1) Å, $R_2^2(8)$ graph set, Figure 5. *Via* its fourth hydrogen atom the ammonium cation is involved in the N(1)···O(4G) 2.720(1) Å interaction with the (H-PTD)$^-$ counterion and bridges the $[(PTDH)^-]_n$ chain and the attached macrocyclic molecules with the formation of the ribbon running along the [101] direction in the unit cell.

The DCHA conformation is described by the rather unusual set of torsion angles, *a*, *g*-, *g*-, *a*, *a*, *g*, *a*, *a*, *g*-, *g*-,

Table 3. Hydrogen bonds in (**1**) and (**2**)

D—H···A, Å	d(D—H), Å	d(D···A), Å	D(D···A), Å	∠(DHA), deg
Complex (**1**)				
O(3G)—H(3G)···N(3G)^{i}	0.96(3)	1.91(3)	2.770(2)	148(2)
O(3G)—H(3G)···O(4G)^{i}	0.96(3)	2.11(2)	2.810(2)	128(2)
N(4)—H(1N4)···N(4G)	0.91(2)	2.00(2)	2.889(2)	166(2)
N(4)—H(1N4)···O(1G)	0.91(2)	2.46(2)	3.009(2)	119(2)
N(4)—H(2N4)···O(4G)^{ii}	0.91(2)	1.88(2)	2.742(2)	159(2)
N(1G)—H(1G)···O(7)^{iii}	0.84(2)	2.04(2)	2.881(2)	171(2)
Complex (**2**)				
N(1)—H(1N1)···O(16)	0.87(2)	2.04(2)	2.909(1)	172(2)
N(1)—H(2N1)···O(10)	0.90(2)	2.06(2)	2.956(1)	176(1)
N(1)—H(3N1)···O(4G)	0.96(2)	1.76(2)	2.720(1)	173(2)
N(1)—H(4N1)···O(4)	0.85(2)	2.11(2)	2.950(1)	166(2)
O(3G)—H(3G)···O(4G)^{iv}	0.86(2)	2.06(2)	2.774(1)	140(2)
O(3G)—H(3G)···N(3G)^{iv}	0.86(2)	2.09(2)	2.803(1)	140(2)
N(1G)—H(1G)···O(1G)^{v}	0.87(2)	2.00(2)	2.870(1)	175(1)

Symmetry transformations used to generate equivalent atoms: $i\ -x+1, -y, -z$; $ii\ -x, -y, -z-1$; $iii\ x, -y+1/2, z+1/2$; $iv\ -x+1, -y+1, -z$; $v\ -x+1, -y, -z-1$.

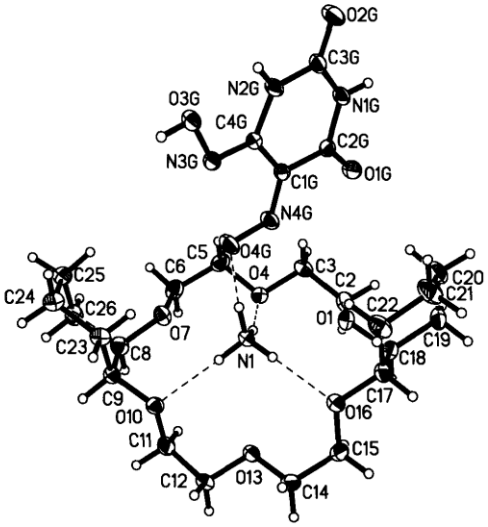


Figure 4. ORTEP drawing of (**2**) with atomic numbering scheme and hydrogen bonds shown as dotted lines. Non-hydrogen atoms are represented by thermal ellipsoids at 50% probability.

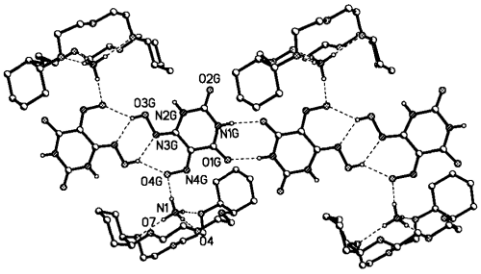


Figure 5. Ribbons in (**2**) running along [101] direction. Hydrogen atoms of the crown-molecules are omitted for the sake of clarity.

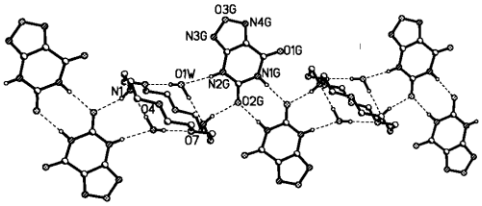


Figure 6. Chains in (**3**) running along *c* direction. Hydrogen atoms of the crown-molecules are omitted for the sake of clarity.

a, *g*-, *a*, *a*, *g*, *a*, *g*, *g*, with three angular *gauche*, *gauche* fragments along the heterocyclic framework. The oxygen atoms of the macrocycle deviate essentially from their best plane, O(1), −0.156(1), O(4), 0.480(1), O(7), −0.324(1), O(10), −0.356(1), O(13), 0.901(1), O(16), −0.544(1) Å.

Structure of (**3**)

Complex (**3**) is built of the neutral molecules DA18C6, OPD and water in the ratio 1 : 2 : 2, as shown in Figure 6. The OPD and DA18C6 molecules in (**3**) are arranged in such a way that the dihedral angle between the plane which includes all non-hydrogen atoms of the planar bicyclic OPD molecule and the plane of six oxygen atoms of the crown ring is 80.3(1)°.

A water molecule occupies the position above the macrocycle and acts as H-donor in two hydrogen bonds with the oxygen and nitrogen atoms of the crown-molecule, O(1w)···O(7)($-x+1, -y+1, -z+1$) 2.942(4), O(1w)···N(1) 3.023(5) Å, and as H-acceptor with OPD molecule, N(2G)···O(1w) 3.006(5) Å. The OPD molecule itself also has direct contact *via* the O(2G) carbonyl oxygen

atom with the NH-group of the macrocycle, N(1)···O(2G) 2.720(5) Å. Two OPD molecules are combined into the planar dimer *via* a couple of symmetry related N—H···O hydrogen bonds, N(1G)···O(2G)($-x+1, -y, -z$) 2.901(4) Å, which as mentioned above, are typical for this class of compounds. The molecules in (**3**) are assembled into chains developed along the *c* direction in the unit cell.

The OPD molecule is characterized by a planar skeleton with the dihedral angle between the six-membered and diazole heterocycles equal to 1.00°. The conformation of the DA18C6 molecule is described by the ordinal D_{3d} symmetry typical for this molecule in the complexes with metal cations and in the uncomplexed state [28] with the C—C torsion angles in the range 67.8(4)–73.9(4)° and the maximal deviation of the C—O torsion angles from the open one being 3.2°.

Conclusions

For the first time the (4*Z*,5*E*)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone-4,5-dioxime and the product of its cyclization, (1,2,5)-oxadiazolo(3,4-d)pyrimidine-5,7(4*H*,6*H*)-dione were prepared and the X-ray data obtained for their inclusion complexes with 18-membered crown ethers. H_2-PTD is stabilized in the form of the monoanion in the complex with diazonia-18-crown-6 and as ammonium salt in the complex with the *cis-syn-cis* isomer of dicyclohexano-18-crown-6.

The crucial factor in (**1**)–(**3**) is the mutual complementarity of donor and acceptor groups which provide the H-bonds responsible for the supramolecular architecture.

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Додаток 14

Копія доповіді

“Unusual way of preparation and crystal structure of oxonium hexafluorosilicate - the simplest "hydrate" of hexafluorosilicic acid”

14th European Symposium on Fluorine Chemistry, 11-16th July, Poznan, Poland

B-O-15

UNUSUAL WAY OF PREPARATION AND CRYSTAL STRUCTURE OF OXONIUM HEXAFLUOROSILICATE – THE SIMPLEST "HYDRATE" OF HEXAFLUOROSILICIC ACID

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As a part of our systematic investigations of the products of hexafluorosilicic acid (FSA) interaction with organic bases[1], we have tried to released the reaction of FSA and hydrazide $NCCH_2C(O)NHNH_2$. It has been found that evaporation of a reaction mixture of 45 % FSA and methanol solution of $NCCH_2C(O)NHNH_2$ (mole ratio 3 : 1) at room temperature leads to a colourless crystalline product with the small yeld. Crystals are melting at ≥ 60 °C with their decomposition. The composition and crystal structure of this compound has been established by X-ray analysis. Crystal data: $H_6F_6O_2Si$, $(H_3O)_2SiF_6$ (I), M = 180.14, rhombic, a = 5.928(1), b = 17.790(4), c = 25.152(2) Å, V = 2652.6(9) Å^3, Z = 18, space group Immm, $F(000)$ = 1620, R = 0.0846 (1344 observed reflections with $I > 2\sigma(I)$).

The components of high symmetrical structure I – oxonium cations and SiF_6^{2-} anions, are united by the numerous weak H-bonds of OH···F type in the 3D network (O···F 2.95 – 3.05 Å). The geometric parameters of SiF_6^{2-} anions are similar to those in other SiF_6^{2-} containing complexes[1]. The Si–F distances vary in the range 1.67(1) – 1.71(1) Å, the F–Si–F angles are in the range 89.1(4) – 91.1(4)°. It is interesting to note, that crystalline hydrates of FSA $H_2SiF_6 \cdot nH_2O$ (n = 4, 6, and 9.5) with well-known structures of oxonium hexafluorosilicates $(H_5O_2)SiF_6$, $(H_5O_2)SiF_6 \cdot 2H_2O$, $(H_5O_2)SiF_6 \cdot 4.5H_2O$ [2] and early described "dihydrate" $H_2SiF_6 \cdot 2H_2O$ are less stable (m.p. 20, –12, –54, 19 °C respectively) than the complex I. Probably, the "dihydrate" can exist in two different crystal modifications and we have obtained the more stable form.

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Додаток 15

Копія доповіді

“Extended supramolecular assemblages built on the Si, Sb, Hf fluoride bricks and macrocyclic spacers and sustained by the developed hydrogen bonding”

14th European Symposium on Fluorine Chemistry, 11-16th July, Poznań, Poland

B-O-24

EXTENDED SUPRAMOLECULAR ASSEMBLAGES BUILT ON THE Si, Sb, Hf FLUORIDE BRICKS AND MACROCYCLIC SPACERS AND SUSTAINED BY THE DEVELOPED HYDROGEN BONDING

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Novel hybrid organic/inorganic materials are the subjects of current challenge for supramolecular chemistry. The rational combination of inorganic cations and anions with organic macrocyclic ligands results in a lot of well-defined structures with desired properties. Macrocycles as O-crown ethers, N,O-crown-ethers, azamacrocycles (cyclen, cyclam, pyofan etc) are promising spacers to afford in the crystal 1D, 2D and 3D supramolecular architectures with Si, Sb, Hf fluorides and their hydrates. The system, H_2SiF_6 - macrocycle provides three types of dimensionalities, discrete adducts, chains, carcass, built on the octahedral $[SiF_4 \cdot 2H_2O$, $(SiF_5 \cdot H_2O)^-$, $SiF_6^{2-}]$ or pentagonal $[SiF_5^-]$, building blocks. The system, tetrahedral SbF_3 – macrocycle affords discrete adducts with O-containing macrocycles and 2D sheets with N,O-containing macrocycles (in the presence of HCl)[1]. The system HfO_2 – HF – H_2O – macrocycle affords the adducts $[(18\text{–crown-}6)(H_3O)_2(Hf_2F_{10} \cdot 2H_2O) \cdot 4H_2O]^2$, $[(H\text{–monoaza–}18\text{–crown–}6 \cdot H_3O)(M_2F_{10} \cdot 2H_2O) \cdot 2H_2O]$, $[(H_2\text{–diaza–}18\text{–crown–}6)(M_2F_{10} \cdot 2H_2O) \cdot 2H_2O]$ (M=Hf, Zr) with the very similar 3D grids built of the negative inorganic planar layers and macrocyclic cations folded between these layers *via* equatorial fluorine atoms due to OH···F or NH···F hydrogen bonds. These studies are still in the progress.

References :

1. M.S. Fonari et al., *Journal of Chemical Crystallography*, **1999**, *29*, 1245
2. V.O. Gelmboldt et al, *Russian Journal of Inorganic Chemistry*, **2001**, *46*, 1833

Додаток 16

Копія доповіді

“Реакция 6-амино-5-нитрозоурацилов с тиомочевиной”

РЕАКЦИЯ 6-АМИНО-5-НИТРОЗОУРАЦИЛОВ С ТИОМОЧЕВИНОЙ

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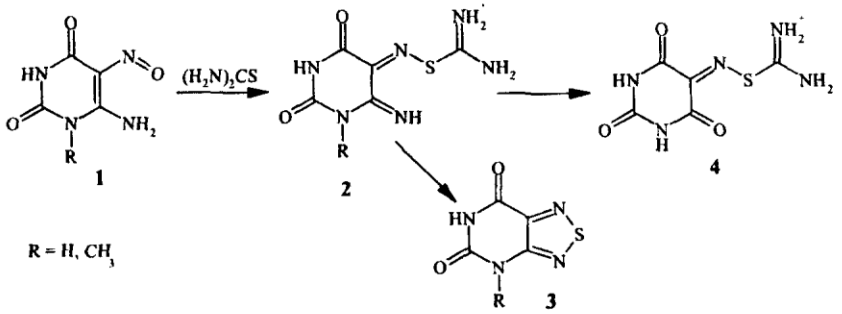
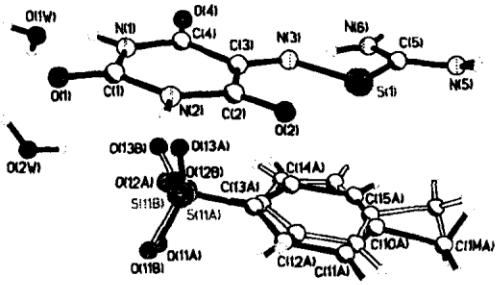
Известно несколько способов образования связи азот-сера путем гетероциклизации бифункциональных нитрозо- и изонитрозосоединений с рядом серусодержащих реагентов. Теоретически интересен метод состоящий в сплавлении 4-амино-5-нитрозопиримидинов с тиомочевиной и приводящий к пиримидо[1,2,5]тиадиазолам [1]. В ходе проведенных исследований, на примере взимодействия 6-амино-5-нитрозоурацилов (**1**) с тиомочевиной в водных растворах кислот установлено, что начальной стадией этой реакции является образование стабильной S-иминотиоурониевой соли (**2**).



Последующими продуктами реакции, в зависимости от строения и условий, могут быть как 1,2.5-тиадиазол (**3**), так и производное иминобарбитуровой кислоты (**4**).



Молекулярная структура соединения (**4**) в виде *p*-толуолсульфоната

1. C. Timmis // J.Chem. Soc. 1958. P. 804.

Додаток 17

Копія доповіді

“[1.5]Дибензо-18-краун-6, удобный темплат в построении супрамолекулярных ансамблей на основе классических и слабых водородных связей”

[1,5]ДИБЕНЗО-18-КРАУН-6, УДОБНЫЙ ТЕМПЛАТ В ПОСТРОЕНИИ СУПРАМОЛЕКУЛЯРНЫХ АНСАМБЛЕЙ НА ОСНОВЕ КЛАССИЧЕСКИХ И СЛАБЫХ ВОДОРОДНЫХ СВЯЗЕЙ

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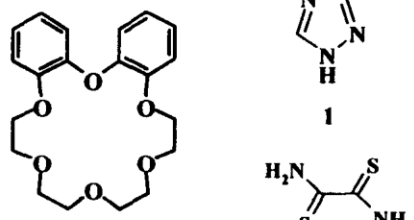
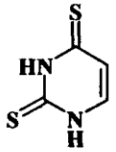
Впервые синтезированы, структурно охарактеризованы (РСА) и обсуждаются кристаллические Н-связанные супрамолекулярные комплексы [1,5]дибензо-18-краун-6 (**КЭ**) с NH-донорными нейтральными органическими молекулами (**1-5**):



КЭ

1



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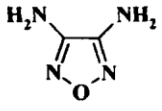
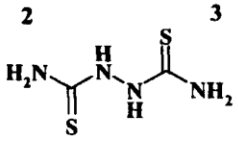


3

4



5

Комплексы **КЭ** с 3-нитро-1*H*-1,2,4-триазолом **1** и 2,4(1*H*,3*H*)-пиримидиндитионом **2** (1:1) являются дискретными молекулярными аддуктами, с моногидратом 1,2,5-оксадиазол-3,4-диамина **3** (1:1:1) и этандитиоамидом **4** (1:1) образуются своеобразные молекулярные ленты. В комплексе с 1,2-гидразиндикарботиоамидом **5** (2:3) компоненты (за счет многочисленных NH···O и NH···S взаимодействий) связаны в трехмерную сетку. Во всех случаях, при образовании сокристаллов, конкуренция О-содержащего макроциклического Н-акцептора с Н-акцепторными (О и S) центрами в нейтральных молекулах **1-5** приводит к замещению части Н-связанных супрамолекулярных гомосинтонов супрамолекулярными гетеросинтонами и изменению супрамолекулярной архитектуры.

Додаток 18

Копія статті

“The dihydropyrimidine-2,4-(1H,3H)-dione functionality: a suitable module for the novel crown-containing hydrogen-bonded supramolecular assemblies”

Supramolecular Chemistry, January–February 2004, Vol. 16 (1), pp. 23–30

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The Dihydropyrimidine-2,4-(1*H*,3*H*)-dione Functionality: a Suitable Module for Novel Crown-containing Hydrogen-bonded Supramolecular Assemblies

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Two novel pyrimidine derivatives, 2-(2-methylphenyl)-2*H*-[1,2,3]triazolo[4,5-*d*]pyrimidine-5,7(4*H*,6*H*)-dione 3-oxide (H-PD) and 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamic acid (H-PS), were synthesized and investigated as suitable ligands for co-crystallization with 1,10-diaza-18-crown-6 (DA18C6). Two solid compounds formulated as $[(H_2DA18C6)(PD)_2(H_2O)_4]$ (1) and $[(H_2DA18C6)(PS)_2(H_2O)_2]$ (2) have been shown by single-crystal structural analysis to be 2D and 3D networks, respectively, through extensive H-bonding intermolecular interactions. Both 1 and 2 incorporate the diaza-18-crown-6 units in the form of macrocyclic cations. In 1 the $(PD)^-$ anions deprotonated in the fourth position of the pyrimidine ring and water molecules are combined into 2D anionic sheets, the macrocyclic cations occupying the cavities in these sheets. In 2 the ensemble of donor and acceptor binding sites available in the 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamate anions $(PS)^-$ facilitates their self-assembly into a double layer via diverse hydrogen bonds. Water molecules and H_2-1,10-diazonia-18-crown-6 cations bridge the neighboring layers thus providing the final 3D supramolecular architecture.

Keywords: Pyrimidine derivatives; Self-assembly; Crown spacer; Hydrogen bonding

INTRODUCTION

The design of new supramolecular architectures [1–3] requires the identification of the suitable supramolecular modules and the usage of such connectors in the assembly of organic and metal-containing networks. So far, consolidation of metal complexes has been achieved through syntheses of coordination polymers, and several 2D and 3D metal-containing frameworks have resulted in porous solids with channels and cavities [4–6]. The creation of ordered hydrogen-bonded networks also has attracted attention, and some intermolecular connectors have been utilized successfully for the linking of building blocks into diverse types of hydrogen-bonded architecture [7–9]. The dihydropyrimidine-2,4-(1*H*,3*H*)-dione functionality represents a supramolecular module that can generate infinite two-dimensional networks through complementary hydrogen bonds with the formation of a dimeric N—H···O(=C) supramolecular synthon (synthon **I** in Chart 1) [10–15], $R_2^2(8)$ graph set [16,17]. If it is combined with the additional H-binding sites (oxime, amine or sulfonamide moieties), we obtain access to 3D supramolecular architectures.

Recently [18] the novel dioxime, (4*Z*,5*E*)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime (**H_2-PTD**) was obtained by the interaction of 6-amino-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dione with hydroxylamine hydrochloride. The structures of two complexes incorporating the corresponding monoanion, 6-hydroxyimino-2,4-dioxo-1,2,3,6-tetrahydropyrimidine-5(4*H*)-one oximate (Chart 2), deprotonated at one of the oxime groups, with H_2-1,10-diazonia-18-crown-6 (stoichiometry 1:2), and its ammonium salt in the complex with the *cis–syn–cis* isomer of dicyclohexano-18-crown-6

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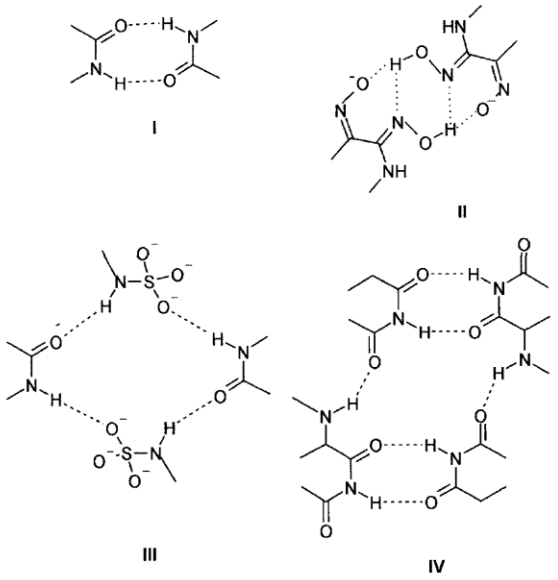


CHART 1 Supramolecular synthons found in dihydropyrimidine-2,4-(1*H*,3*H*)-dione derivatives.

(stoichiometry 1:1), were determined by X-ray analysis. In the first compound the **(H-PTD)**$^-$ anions are joined into dimers through O—H···N, and O—H···O hydrogen bonds, [synthon **II** in Chart 1, $R_2^2(6)$ and $R_2^2(14)$ graph sets], and alternate with macrocyclic cations in the chains sustained by N—H(crown)···O and N—H(crown)···N interactions. The chains are further consolidated into a 3D network via N—H···O(crown) hydrogen bonds. In the second complex the self-complementarity of the **(H-PTD)**$^-$ anions facilitates their assembly into chains via N—H···O [$R_2^2(8)$ graph set] (synthon **I** in Chart 1) O—H···N, $R_2^2(6)$ and O—H···O $R_2^2(14)$ (synthon **II** in Chart 1) interactions. The ammonium cations bridge each **(H-PTD)**$^-$ anion in the chain with the macrocycle, affording ribbons.

Two novel pyrimidine derivatives, 2-(2-methylphenyl)-2*H*-[1,2,3]triazolo[4,5-*d*]pyrimidine-5,7(4*H*,6*H*)-dione 3-oxide (**H-PD**) and 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamic acid (**H-PS**) were

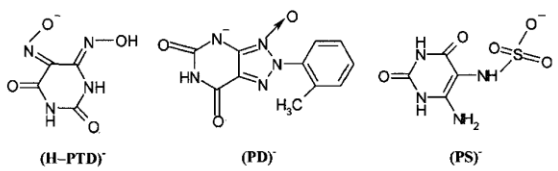


CHART 2 The anionic derivatives of dihydropyrimidine-2,4-(1*H*,3*H*)-dione incorporated in the co-crystals with crown ethers.

synthesized and explored in the design of polymeric networks with 1,10-diaza-18-crown-6 spacer, complexes **1** and **2**.

RESULTS AND DISCUSSION

The ternary complex **1** crystallizes in the monoclinic system, space group $P2_1/c$. Figure 1 displays an ORTEP drawing with the atom labels. The N(14) nitrogen atom in the **(PD)**$^-$ unit is deprotonated as was proved by the localization of two hydrogen atoms at the N(1) ammonium nitrogen of the crown molecule and an N(1)—H···N(14) 2.875(2) Å hydrogen bond. A search of the Cambridge Structural Database [19] for the deprotonated form of the barbital moiety identified six entries for barbital salts with metal ions or primary amines possessing similar geometry and conformation of the dioxopyrimidine ring [20–28]. In the **(PD)**$^-$ anion the triazole and pyrimidine rings and two carbonyl O-atoms, O(11) and O(12), form a practically planar system with a mean deviation of the atoms involved equal to 0.0264 Å. The dihedral angle between the least-squares plane through this bicyclic unit and the least-squares plane of the phenyl ring equals 106.5°. The dihedral angle between the least-squares planes through the heteroatoms of the macrocyclic cation and the pyrimidine ring equals 39.1°.

Two **(PD)**$^-$ anions and four water molecules are consolidated into a centrosymmetric association *via* four O(W)—H···O, two N—H···O(W), and two O—H(W)···O(W) hydrogen bonds, as shown in Fig. 2a. O(2W) behaves as an H-donor between two center-of-symmetry-related anions via O—H···O hydrogen bonds: O(2W)···O(13) 2.689(2), and O(2W)···O(11)($-x$, $-y$, $-z+2$) 2.826(2) Å (other interesting hydrogen bonded ring structures, even featuring crown-like architecture, exist [29–31]). The anions stack with an almost perfect overlap of the pyrimidine units with an interplane separation of 3.426 Å between the centers of the six-membered rings. Similar overlap has been observed for purine rings [32]. The O(1W) water molecule bridges the **(PD)**$^-$ anion and O(2W) molecule at distances of N(12)···O(1W) 2.943(2), and O(1W)···O(2W)($-x$, $-y$, $-z+2$) 2.874(3) Å. In Fig. 2a a nine-membered ring is observed, which is closed by three H-bonds. Water molecules themselves alternate in the chains running along the *c* direction, O(1W)···O(2W)($-x$, $y+1/2$, $-z+3/2$) 2.799(2) Å. Thus due to the (O1W) water molecules being shared between the neighboring $[(\mathbf{PD})_2(O2W)_2]^{2-}$ units, these associations are combined into infinite 2D anionic

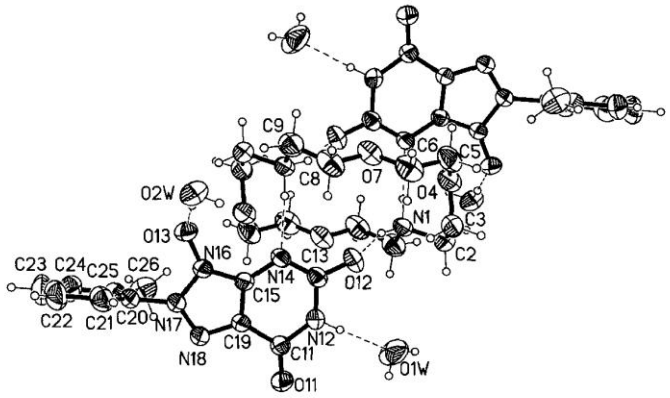


FIGURE 1 ORTEP drawing of **1** with atomic labelling; hydrogen bonds are represented by dashed lines. Thermal ellipsoids are scaled to the 50% probability level.

sheets developed parallel to the *bc* plane (Fig. 2b). The macrocyclic cations occupy the cavities within the sheets, and are held in position by ionic hydrogen bonds, $N(1)^{+}\cdots N(14)^{-}$ $(-x, -y, -z+1)$ 2.875(2) Å and $N(1)^{+}\cdots O(12)$ 2.764(2) Å (Fig. 3). The corrugated layers are packed along the *a* direction with only van der Waals contacts between them, the toluene substituents of $(\mathbf{PD})^{-}$

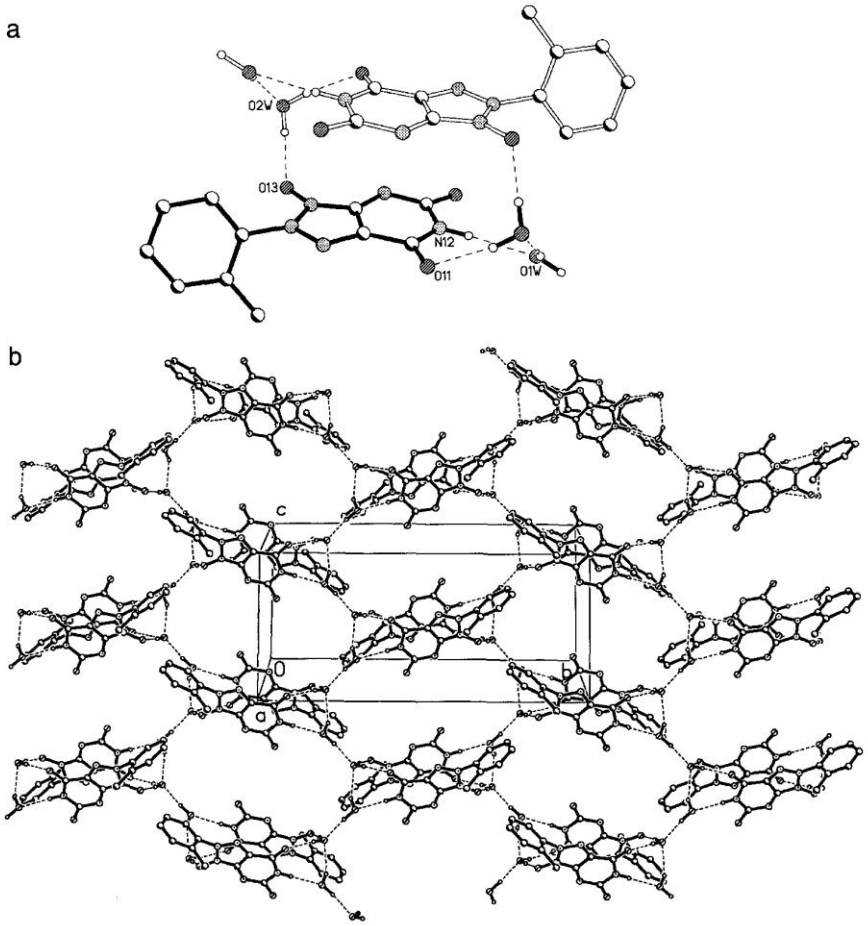


FIGURE 2 (a) Side view of the $[(\mathbf{PD})_2)H_2O)_4]^{2-}$ association in **1**. Non-functional hydrogen atoms are omitted for clarity. The darker lines indicate bonds in the molecule that are closer to the viewer. (b) View of the hydrogen-bonded anionic sheet in **1**. The cations of 1,10-diazonia-18-crown-6 are omitted.

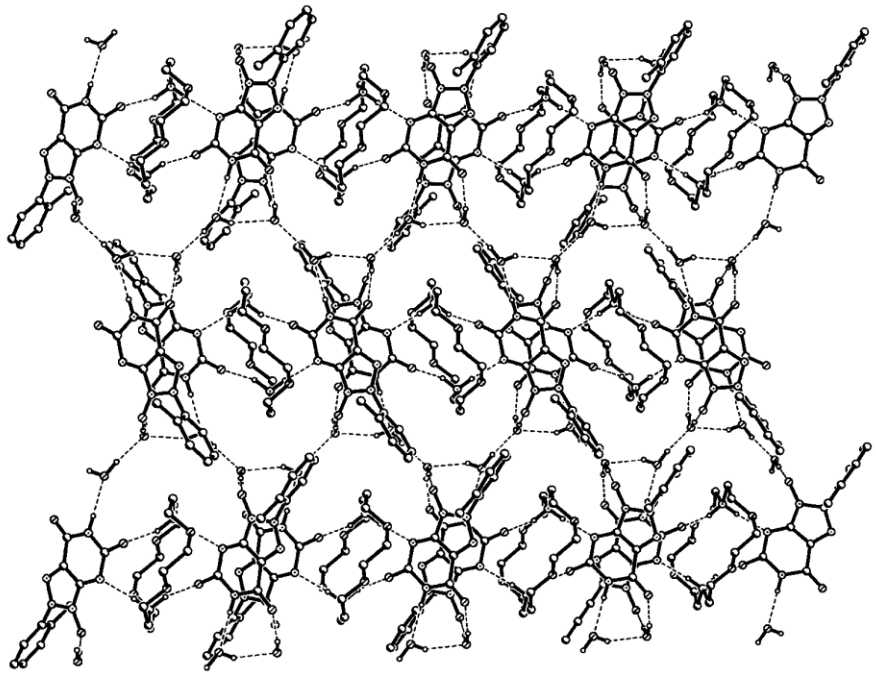


FIGURE 3 Layer in **1**. Macrocyclic cations are imprisoned in the cavities of the anionic network. Non-functional hydrogen atoms are omitted for clarity.

anions being oriented inside the voids between the layers.

The ternary complex **2** crystallizes in the triclinic system, space group $P\bar{1}$. Figure 4 displays an ORTEP drawing with atom labels. The components are held together by N—H···O and O—H···O ionic hydrogen bonds, $N(1)^{+}\cdots O(12)$ 2.927(2), and $O(1W)\cdots O(15)^{-}$ 2.844(4) Å. The hydrogen atoms of the ammonium functionalities of the macrocyclic cation are oriented outside the cavity and are involved in N—H(crown)···O(=C) hydrogen bonds with the four nearest $(\mathbf{PS})^{-}$ anions. A search of the CSD [19] for the protonated form of 1,10-diaza-18-crown-6, H_2-1,10-diazonia-18-crown-6, identified 37 entries with different orientations of ammonium hydrogen atoms with respect to the macrocyclic cavity. In only nine complexes was out-of-cavity coordination of ammonium functionalities found [33–41]. The mutual arrangement of the crown spacer and $(\mathbf{PS})^{-}$ anion in **2** is described by the dihedral angle between the least-squares plane of the crown heteroatoms and the pyrimidine ring, which is equal to 35.2(4)°.

Two $(\mathbf{PS})^{-}$ anions related by an inversion center are combined into a dimer of barrel-like

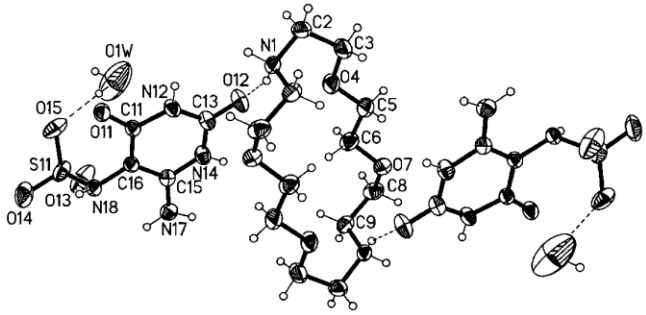


FIGURE 4 ORTEP drawing of **2** with atomic labelling; hydrogen bonds are represented by dashed lines. Thermal ellipsoids are scaled to the 50% probability level.

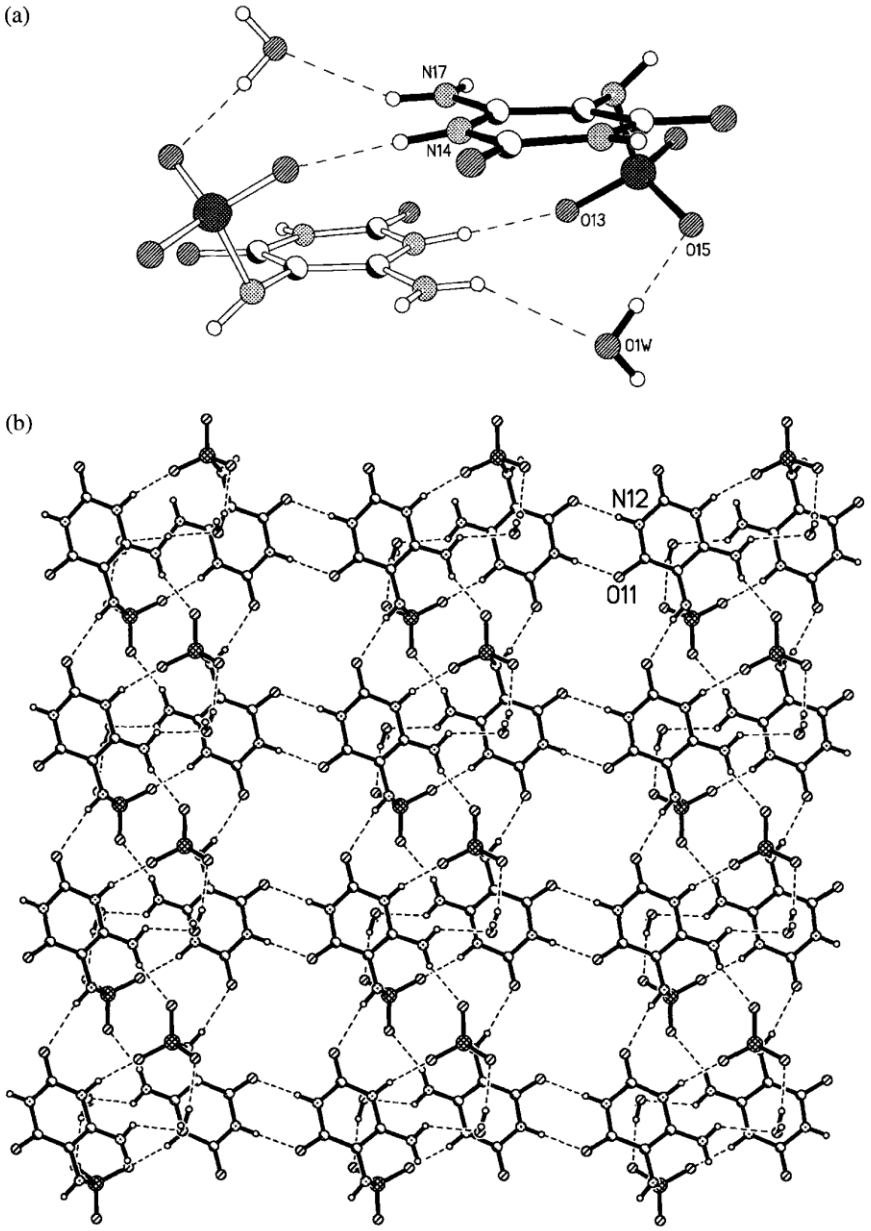


FIGURE 5 (a) View of the $[(\mathbf{PS})_2(H_2O)_2]^{2-}$ centrosymmetric heterotetramer in **2**. The darker lines indicate bonds in the molecule that are farther from the viewer. (b) Hydrogen-bonded anionic layer in **2**, parallel to the (011) plane.

shape, in which the 'top' and 'bottom' are formed by the planar pyrimidine rings, while the oppositely oriented N—SO_3^- covalent bonds, with the bond angle at N(18) equal to 116.1(1)°, serve as its 'walls'. The N—H···O hydrogen bond N(14)···O(13)($-x-1, -y+1, -z+3$) 2.776(2) Å, is situated practically in the plane of the pyrimidine unit (Fig. 5a). The $(\mathbf{PS}^-)_2$ dimer and two water molecules generate a special supramolecular entity, $[(\mathbf{PS})_2(O1W)_2]^{2-}$ (Fig. 5a) that is additionally stabilized by two H-bonds, N(17)···O(1W)($-x-1, -y+1, -z+3$) 3.187(3), and O(1W)···O(15) 2.844(3) Å. The resulting 10-membered H-bonded cycle with the participation of the O(1W) molecule is closed by three hydrogen bonds. The neighboring $[(\mathbf{PS})_2(H_2O)_2]^{2-}$ heterotetramers joined via shared SO_3^- groups form thick double chains propagated along the *b* direction

(Fig. 5b, synthon **III** in Chart 1) and are stabilized due to the interactions between the anions related by the translation, N(18)···O(12)(x, $y+1$, z) 3.155(2) Å, and by the inversion center, N(17)···O(14)($-x-1$, $y+2$, $-z+3$) 2.887(2) Å. The mode of the involvement of the SO_3^- group in the binding with the topologically non-complementary donor centers in **2** is rather different from that found for this group in the guanidinium alkene- (arene)sulfonates where both guanidinium cations and sulfonate anions possess a common threefold axis molecular topology [42,43]. These double chains are further interlinked into a 2D sheet (Fig. 5b) via the centrosymmetric N—H···O=C supramolecular synthon **I** [Chart 1, $R_2^2(8)$ graph set], N(12)···O(11)($-x$, $-y+1$, $-z+2$) 2.793(2) Å, which is realized in the plane of the pyrimidine ring and is traditional for barbiturates [24–32]. This synthon alternates with another centrosymmetric synthon **IV** [$R_4^4(18)$ graph set], where, besides the two above-mentioned H-bonds, two other symmetry-related interactions, N(14)···O(13)($-x-1$, $-y+1$, $-z+3$) 2.776(2) Å, close the 18-membered ring. The final anionic corrugated sheets are propagated parallel to the (111) plane. As is evident, only N—H···O interactions are responsible for the sheet organization. The sheets seem to be rather rigid, because both ionic and conventional hydrogen bonds contribute to their stability. Two water molecules, related by an inversion center and having a separation O(1W)···O(1W)($-x-1$, $-y+1$, $-z+2$) of 2.953(6) Å, join the neighboring sheets along the *a* direction. Crown spacers also behave as the bridges between the neighboring layers and participate in hydrogen bonds with the four $(\mathbf{PS})^-$ anions closest to them, N(1)···O(12) 2.927(2) (single H-bond), N(1)···O(11)($-x$, $-y+1$, $-z+2$) 2.870(2), N(1)···O(15)($-x$, $-y+1$, $-z+2$) 2.889(2) Å (bifurcated H-bond). Thus, each macrocyclic cation occupies the cavity that is restricted by four $(\mathbf{PS})^-$ anions and four water molecules.

In summary, modified pyrimidinedione functionalities represent suitable connectors, which, together with the diaza-18-crown-6 spacer, are capable of generating ordered networks: 2D sheets (**1**) or 3D network (**2**). The planar active moiety of the $(\mathbf{PD})^-$ anion is capable of ensuring only 2D architecture in the co-crystal with diaza-18-crown-6. The self-assembly of $(\mathbf{PS})^-$ anions, rich in donor and acceptor centers, provides thick double layers which are further combined into 3D networks via macrocyclic spacers and water molecules.

EXPERIMENTAL

H-PD was synthesized in accordance with the route suggested [44]. **H-PS** was obtained by boiling aqueous [1,2,5]thiadiazole[3,4-*d*]pyrimidine-5,7-dione 1-oxide [45]. *N*-Oxides of 1,2,5-thiadiazoles represent a rather unexplored family of the ligands. Under the conditions of the hydrolysis, rearrangement of the *N*-oxide [1,2,5]thiadiazole[3,4-*d*]pyrimidine-5,7-dione occurs. A possible mechanism includes transformation of the cyclic *N*-oxide into the six-membered cycle and subsequent rearrangement of the ester hydroxylamine in the sulfamine group in accordance with Scheme 1.

General Procedures for Synthesis of 1 and 2

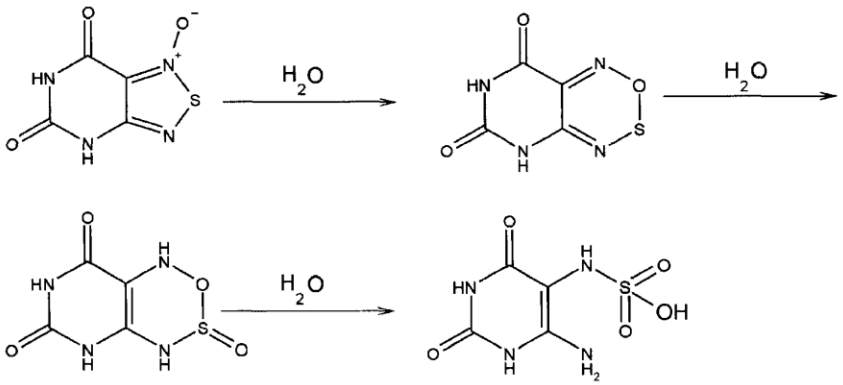
(**1**) **H-PD** (26 mg, 0.1 mmol) and diaza-18-crown-6 (26 mg, 0.1 mmol) were dissolved in the minimal amount of 50% methanol at the boiling temperature of the solution. The precipitate was filtered off, and recrystallized from 30% methanol. Long colorless crystals deposited from solution. Mp = 230°C (decomp.) (Found: C 47.92, H 6.12, N 19.76. Calc. for $C_{34}H_{52}N_{12}O_{14}$: C 47.88, H 6.15, N 19.71%)

(**2**) [1,2,5]Thiadiazole[3,4-*d*]pyrimidine-5,7-dione 2-oxide (186 mg, 1 mmol) was dissolved in the minimal amount of boiling water. The solution became purple and then bleached. The hot solution was filtered, and cooled till the crystals precipitated. The precipitate of 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamic acid (**H-PS**) was filtered off, mixed with diaza-18-crown-6 (262 mg, 1 mmol), dissolved in boiling water and filtered off. Long colorless crystals precipitated from solution. Mp = 227°C (Found: C 32.31, H 5.76, N 18.93, S 8.69. Calc. for $C_{20}H_{42}N_{10}O_{16}S_2$: C 32.34, H 5.70, N 18.86, S 8.63%).

X-ray Crystallography†

The X-ray data were collected on a Bruker AXS Smart single crystal diffractometer with CCD area detector at room temperature for **1** and 150 K for **2**. The structures were solved by direct methods with the software SHELXTL-NT V5.1 inserted into the Bruker AXS software [46]. The refinement of both structures proceeded similarly using SHELX-97 software [47]. The non-hydrogen atoms of the asymmetric unit were refined anisotropically (full-matrix least squares method on F^2). C-Bound H-atoms were placed in calculated positions with their isotropic displacement parameters riding on those of parent atoms, while the N- and O-bound H-atoms were found from

†Crystallographic files in CIF format for **1** and **2** are available free from the author. They have also been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 188811 and CCDC 188812.



SCHEME 1 The route of transformation of *N*-oxide [1,2,5]-thiadiazole-[3,4-*d*]pyrimidine-5,7-dione under hydrolysis conditions.

differential Fourier maps and refined without any constraints, except H-atoms of the O(1W) molecule in **2** which, because of their disorder, were refined in the rigid model. The ORTEP structures for **1** and **2** are shown in Figs. 1 and 4, the geometric parameters for the H-bonds are given in Table I. The crystal packing of **2** is shown in Fig. 6.

(**1**): Crystal data: $C_{34}H_{52}N_{12}O_{14}$, $M_r = 852.88$, monoclinic, space group $P2_1/c$, $a = 10.370(2)$, $b = 21.582(4)$, $c = 9.709(2)$ Å, $\beta = 108.00(3)°$, $V = 2066.6(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.374\,Mg/mm^{-3}$, $\mu = 0.108\,mm^{-1}$, $F(000) = 904$, wavelength 0.71073 Å. A colorless prism with dimensions $0.15 \times 0.20 \times 0.25\,mm^3$ was measured with a Bruker Smart AXS CCD, θ range for data collection 1.89–30.25°. A total of 28793 reflections were measured, of which 5776 were unique ($R_{int} = 0.0268$). Weighting scheme $w = 1/[S^2(F_o^2) + (0.0622P)^2 + 0.4615P]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness of fit on F^2 was 1.055. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0483$, $wR_2 = 0.1298$. Largest difference Fourier peak and hole 0.615 and $-0.287\,e\,Å^{-3}$.

(**2**): Crystal data: $C_{20}H_{42}N_{10}O_{16}S_2$, $M_r = 742.76$, triclinic, space group $P\bar{1}$, $a = 10.608(2)$, $b = 7.718(2)$, $c = 10.439(2)$ Å, $\alpha = 85.77(3)$, $\beta = 65.68(3)$, $\gamma = 82.41(3)°$, $V = 771.8(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.598\,Mg/mm^{-3}$, $\mu = 0.264\,mm^{-1}$, $F(000) = 392$, wavelength 0.71073 Å. A colorless prism with dimensions $0.20 \times 0.20 \times 0.30\,mm^3$ was measured with a Bruker Smart AXS CCD, θ range for data collection 2.12–30.34°. A total of 10852 reflections were measured, of which 4177 were unique ($R_{int} = 0.0156$). Weighting scheme $w = 1/[S^2(F_o^2) + (0.0703P)^2 + 0.1698P]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness of fit on F^2 was 1.060. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0406$, $wR_2 = 0.1141$. Largest difference Fourier peak and hole 0.400 and $-0.640\,e\,Å^{-3}$.

TABLE I Geometry of the selected hydrogen bonds in aggregates **1** and **2**

D—H···A	*r*(H···A) (Å)	*r*(D···A) (Å)	∠(DH···A) (°)	Symmetry transformation for H-acceptor
1				
N(1)—H(1N1)···O(12)	1.82(2)	2.765(2)	160(2)	*x*, *y*, *z*
N(1)—H(2N1)···N(14)	1.94(2)	2.866(2)	175(2)	$-x, -y, -z+1$
N(12)—H(12N)···O(1W)	2.06(2)	2.943(2)	178(2)	*x*, *y*, *z*
O(1W)—H(1W1)···O(2W)	1.87(4)	2.797(2)	171(3)	$-x, y+1/2, -z+3/2$
O(1W)—H(2W1)···O(2W)	2.16(4)	2.878(2)	153(4)	$-x, -y, -z+2$
O(2W)—H(1W2)···O(11)	1.99(3)	2.825(2)	165(2)	$-x, -y, -z+2$
O(2W)—H(2W2)···O(13)	1.82(3)	2.691(2)	177(2)	*x*, *y*, *z*
2				
N(1)—H(1N1)···O(12)	2.08(2)	2.928(2)	163(2)	*x*, *y*, *z*
N(1)—H(2N1)···O(11)	2.08(2)	2.870(2)	150(2)	$-x, -y+1, -z+2$
N(1)—H(2N1)···O(15)	2.32(2)	2.889(2)	123(2)	$-x, -y+1, -z+2$
N(12)—H(12A)···O(11)	1.92(2)	2.793(2)	177(2)	$-x, -y+1, -z+2$
N(14)—H(14A)···O(13)	1.88(2)	2.775(2)	167(2)	$-x-1, -y+1, -z+3$
N(17)—H(17A)···O(14)	2.08(2)	2.887(2)	152(2)	$-x-1, -y+2, -z+3$
N(17)—H(17B)···O(1W)	2.50(2)	3.183(3)	135(2)	$-x-1, -y+1, -z+3$
N(17)—H(17B)···O(13)	2.60(2)	3.307(2)	138(2)	$-x-1, -y+1, -z+3$
N(18)—H(18N)···O(12)	2.31(2)	3.155(2)	169(2)	$x, y+1, z$
O(1W)—H(1W1)···O(1W)	2.18(5)	2.958(6)	151(3)	$-x-1, -y+1, -z+2$
O(1W)—H(2W1)···O(15)	1.99(2)	2.842(4)	174(3)	*x*, *y*, *z*

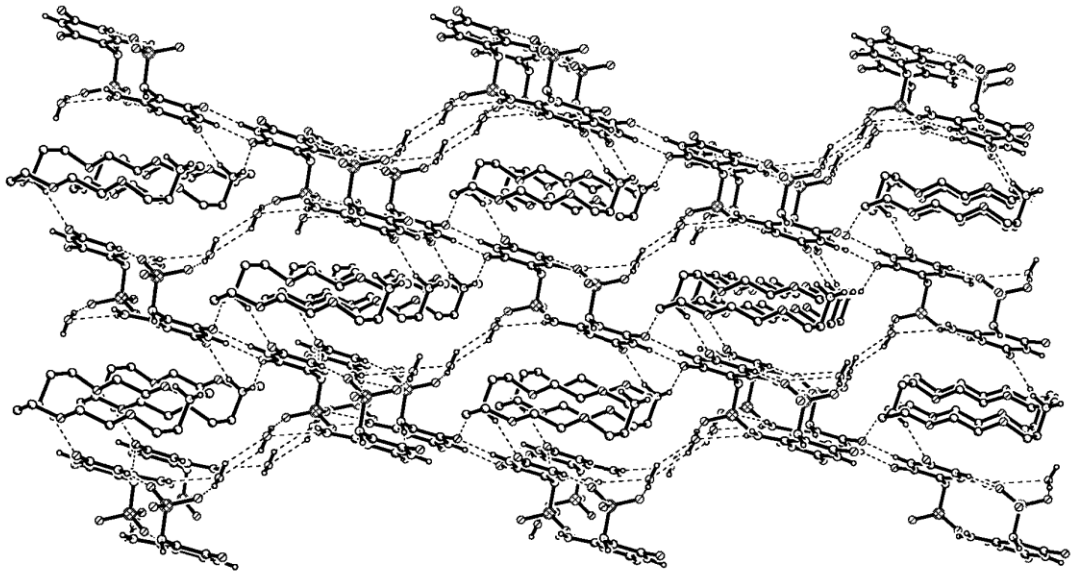


FIGURE 6 Crystal packing in **2**. Non-functional hydrogen atoms are omitted for clarity. Red: oxygen, blue: nitrogen, yellow: sulfur.

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Додаток 19

Копія статті

“Структурные аспекты взаимодействия кремнефтороводородной кислоты с органическими основаниями”

КООРДИНАЦИОННАЯ ХИМИЯ, 2004, том 30, № 3, с. 211–218

УДК 541.49

СТРУКТУРНЫЕ АСПЕКТЫ ВЗАИМОДЕЙСТВИЯ КРЕМНЕФТОРОВОДОРОДНОЙ КИСЛОТЫ С ОРГАНИЧЕСКИМИ ОСНОВАНИЯМИ

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Представлены результаты систематических структурных исследований продуктов взаимодействия кремнефтороводородной кислоты (КФК) с органическими основаниями, в составе которых удается стабилизировать различные гидролитически лабильные фторокомплексы кремния. В свете полученных данных обсуждается дискуссионная проблема состояния КФК в водных растворах.

Растворы кремнефтороводородной кислоты (**КФК**) различной концентрации являются крупнотоннажным побочным продуктом предприятий, перерабатывающих фтористое сырье, а также апатиты и фосфориты (производство фосфорных удобрений, фосфорной кислоты, элементного фосфора), и рассматриваются в качестве наиболее перспективного источника фтора для химической промышленности [1, 2]. Как и многие другие комплексные фторокислоты, КФК не существует в индивидуальном состоянии (последняя по времени неудачная попытка изолировать соединение состава H_2SiF_6 принадлежит авторам [3]). Несмотря на более чем полуторавековую историю изучения свойств КФК, вопросы состава присутствующих в ее растворах форм остаются предметом дискуссии [1, 2, 4–9]; до недавнего времени структурно изученными солями КФК оставались лишь гекса- и пентафторосиликаты. В настоящем сообщении представлены результаты систематических исследований строения продуктов взаимодействия КФК с органическими основаниями, в составе которых удается стабилизировать сосуществующие в растворах КФК гидролитически лабильные формы.

Для осуществления взаимодействия с КФК использовали основания следующих классов, отличающиеся природой донорных центров, строением и интервалом значений pK_a: 15- и 18-членные краун-эфиры; 15- и 18-членные азакраун-эфиры; 12- и 14-членные тетраазамакроциклы; гидразиды карбоновых кислот; тиосемикарбазиды.

Наиболее интересными и разнообразными в структурном отношении оказались продукты взаимодействия КФК с краун-эфирами и их частично замещенными аза-аналогами. Полученные соединения относятся к комплексам типа "гость–хозяин" (**Г–Х**) [10] (на основе межмолекулярных Н-связей), в составе которых в зависимости от строения макроциклического лиганда удается стабилизировать анион SiF_6^{2-} и все возможные продукты его гидролитических превращений: $[SiF_5 \cdot H_2O]^-$, SiF_5^-, $SiF_4 \cdot 2H_2O$. Автор [11] отметил дифференцирующее влияние строения краун-эфира на состав связываемого им фторокомплекса кремния: краун-эфиры с эквивалентно стерически экранированными сторонами плоскости макроцикла (15-краун-5 (**15К5**), 18-краун-6 (**18К6**)) селективно извлекают из растворов КФК аквакомплекс *транс*-$SiF_4 \cdot 2H_2O$ с образованием молекулярных соединений $[(транс\text{-}SiF_4 \cdot 2H_2O) \cdot 15K5 \cdot H_2O]$ (**I**) и $[(транс\text{-}SiF_4 \cdot 2H_2O) \cdot 18K6 \cdot 2H_2O]$ (**II**) [12].

По данным РСА, компоненты структуры II – *транс*-$SiF_4 \cdot 2H_2O$, 18К6 и молекулы H_2O – объединены системой Н-связей OH···O (O···O 2.599(3)–2.870(2) Å); внешнесферные молекулы воды являются мостиками между *транс*-$SiF_4 \cdot 2H_2O$ и 18К6 (рис. 1). Очевидно, аналогичное строение Н-связанного ассоциата имеет и комплекс I, а также описанный в [12] малоустойчивый продукт взаимодействия КФК с 12-краун-4 (**12К4**) вероятного состава $[(транс\text{-}SiF_4 \cdot 2H_2O) \cdot 2(12K4)]$ [13]. Стабилизация комплекса $SiF_4 \cdot 2H_2O$ в составе соединений Г–Х в форме *транс*-изомера согласуется с теоретическими оценками относительной стабильности геометрических изомеров 12-электронных комплексов *p*-элементов [14], учитывающи-

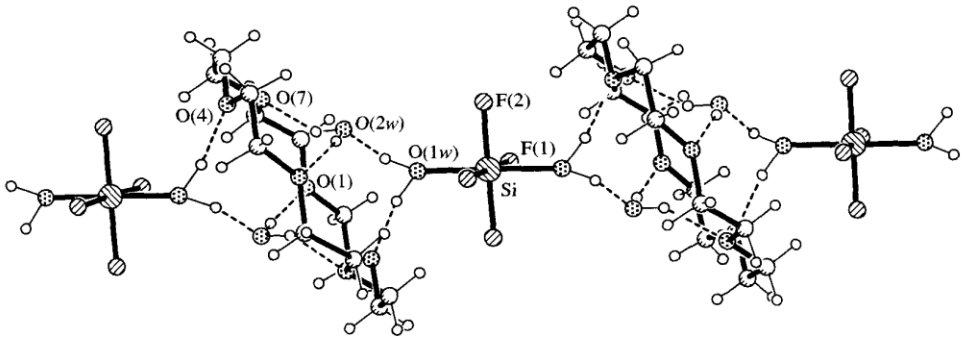
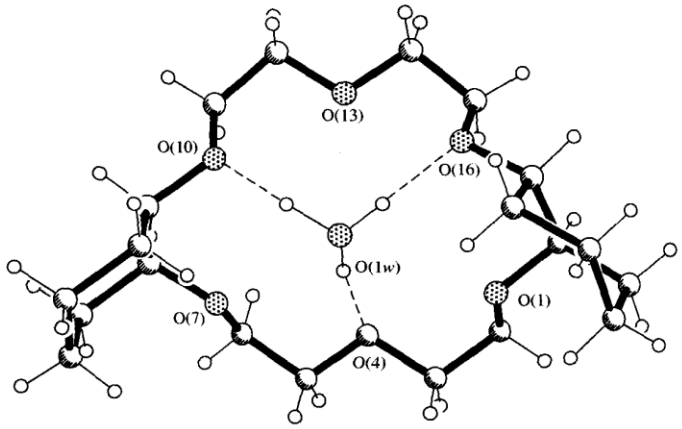


Рис. 1. Фрагмент цепочечной структуры комплекса II.



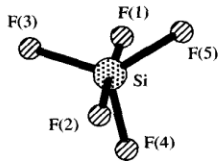


Рис. 2. Строение комплекса III.

ми специфику связывания в комплексах кремния(IV) как легкого непереходного элемента, подтверждается данными ЯМР ^{19}F [6], однако противоречит результатам расчетов *ab initio* комплекса в газовой фазе [15].

Цис-син-цис-изомер дициклогексано-18-краун-6 (**ДЦГ-6А**) с неэквивалентно стерически экранированной плоскостью макроцикла при взаимодействии с КФК образует ионный комплекс $[ДЦГ\text{-}6А \cdot H_3O]SiF_5$ (**III**) [16]. В структуре III (рис. 2) катион гидроксония объединен с каждым вторым атомом О лиганда тремя прочными Н-связями ОН···О (О···О 2.615(3)–2.637(3) Å); внешнесферный анион SiF_5^- связан с катионом лишь электростатическими взаимодействиями. По данным спектроскопии ЯМР ^{19}F, ^{29}Si [17], указанное строение соединения $[ДЦГ\text{-}6А \cdot H_3O]SiF_5$ с тригонально-бипирамидальной геометрией аниона сохраняется и в растворе ацетона. Отмеченная в [11] взаимосвязь между строением краун-эфира и составом связываемого им фторокомплекса (молекулярная или ионная форма) имеет, по-видимому, достаточно общий характер, что иллюстрируют данные РСА соединений $[(BF_3 \cdot H_2O)_2 \cdot 18К6 \cdot 2H_2O]$ [18], $[(BF_3 \cdot H_2O)_2 \cdot ДЦГ\text{-}6В]$ (ДЦГ-6В – *цис-анти-цис*-дициклогексано-18-краун-6 с симметрично экраниро-

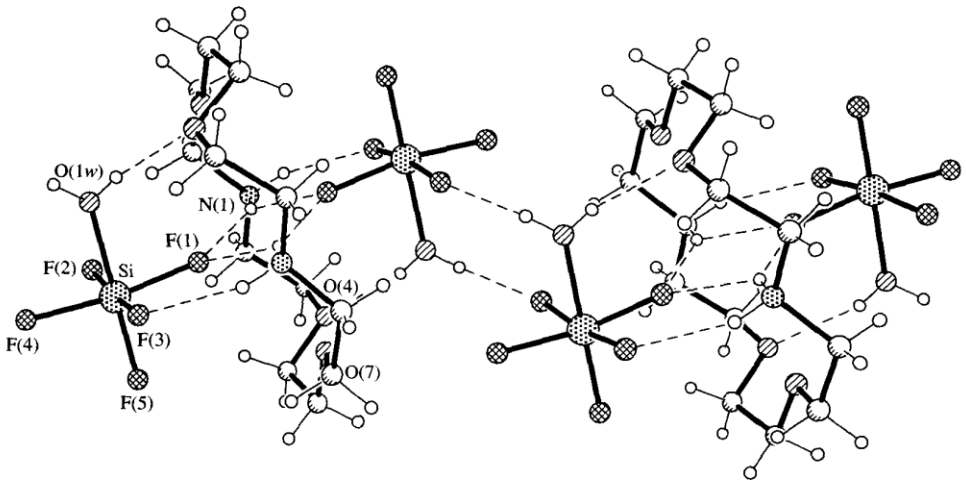


Рис. 3. Строение комплекса V.

ванной полостью макроцикла) [19] и [ДЦГ-6А · · H_3O]BF_4 [20], выделенных из реакционных смесей $BF_3 \cdot OEt_3$–H_2O–краун-эфир. Авторы [16] пришли к заключению, что склонность ДЦГ-6А к образованию комплексов с солями гидроксония однозарядных анионов обусловлена способностью пространственно объемных катионов [ДЦГ-6А · · H_3O]$^+$ формировать в кристалле устойчивый структурный мотив в форме зигзагообразных каналов, в которые могут встраиваться различные "гости" (SiF_5^- [16], BF_4^- [20], ClO_4^- [21]).

Протонирующиеся в кислых средах моноаза-18-краун-6 (**MA18K6**) и 1,10-диаза-18-краун-6 (**ДА18К6**) стабилизируют в составе ионных комплексов Г–Х [(MA18K6H · H_2O)($SiF_5 \cdot H_2O$) · H_2O] (**IV**) и [($ДА18К6H_2$)($SiF_5 \cdot H_2O$)$_2$] (**V**) аквапентафторосиликатные анионы [22], а 1,7-диаза-15-краун-5 (**ДА15К5**) образует комплекс с гексафторосиликатным анионом [($ДА15К5H_2$)SiF_6] (**VI**) [23]. Дополнительный вклад в стабилизацию структур комплексов IV–VI, наряду с электростатическими взаимодействиями, вносят системы водородных связей ГН···Х и ХН···Г.

Строение комплекса V показано на рис. 3. Помимо взаимодействий ОН···О (между атомами О макроцикла и координированными молекулами воды) и NH···F, в структуре V реализуются контакты Г···Г типа ОН···F между анионами [$SiF_5 \cdot H_2O$]$^-$ (О···F 2.680(4) Å). В структуре комплекса VI симметрия анионов SiF_6^{2-} понижена до C_{2v} вследствие участия трех из шести фторолигандов в Н-связях NH···F различной прочности (N···F 2.722(3)–2.823(2) Å) (рис. 4). Для сравнения укажем, что взаимодействие КФК с ациклическими аналогами азакраун-эфиров – 3-окса-1,5-диаминопентаном, 3-окса-1,5-N,N'-диметилдиаминопентаном и 3,6-диокса-1,8-диаминооктаном – приводит исключительно к гексафторосиликатам дипротонированных форм аминоподандов [24], охарактеризованных методами ИК-, КР и масс-спектроскопии.

Двенадцатичленные тетраазамакроциклы – 1,4,7,10-тетраазациклододекан (**L^1**), 1,4,7,10-тетрааза-2,6-пиридинофан[12] (**L^2**) – и четырнадцатичленный *мезо*-5,7,7,12,12,14-гексаметил-1,4,8,11-тетраазациклотетрадекан (**L^3**) образуют гидратные формы гексафторосиликатов состава (L^1H_4)$_2$(SiF_6)$_4$ · · $7H_2O$ (**VII**) [25], (L^2H_3)$_2$(SiF_6)$_3$ · $4H_2O$ (**VIII**) [26], (L^3H_4)$_2$(SiF_6)$_4$ · $4H_2O$ (**IX**) [27]. В структуре гептагидрата VII (рис. 5) пять молекул воды посредством прочных Н-связей (О···О 2.806(7)–2.834(6) Å) формируют линейный "кластер", что является редким случаем такого крупного водного ассоциата в гидратных комплексах КФК. Симметрия анионов SiF_6^{2-} в VII близка к C_{4v}.

На рис. 6 показано окружение катиона 1,4,7,10-тетрааза-2,6-пиридинофана [12] в комплексе VIII. Пиридиновый атом азота катиона не протонирован, однако участвует во внутримолекулярной Н-связи NH···N (N···N 2.827(4) Å) с эндоциклически ориентированным атомом водорода группы NH_2. Все эти группы вовлечены в межмолекулярные Н-связи, среди которых доминируют контакты NH···F. Гексафторосиликатные анионы в комплексе VIII имеют слегка искаженное октаэдрическое строение. Находящийся в более симметричном окружении органических катионов и молекул воды анион Si(2)F_6^{2-} симметрии C_2 отличается меньшей степенью искажения (длины связей Si–F в пределах 1.667(3)–1.683(3) Å; углы FSiF отличаются от идеальных не более чем на 0.7°). Для сравнения

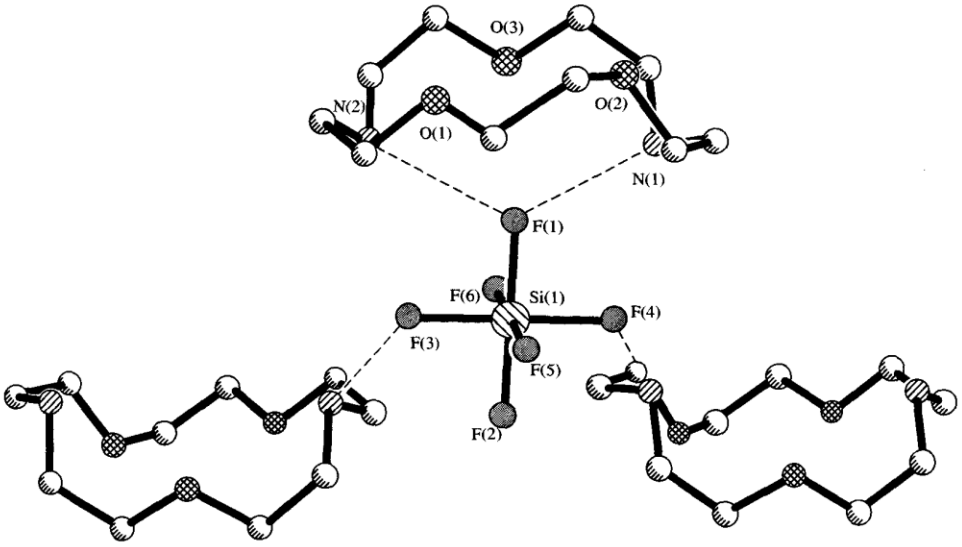


Рис. 4. Фрагмент кристаллической структуры комплекса VI.

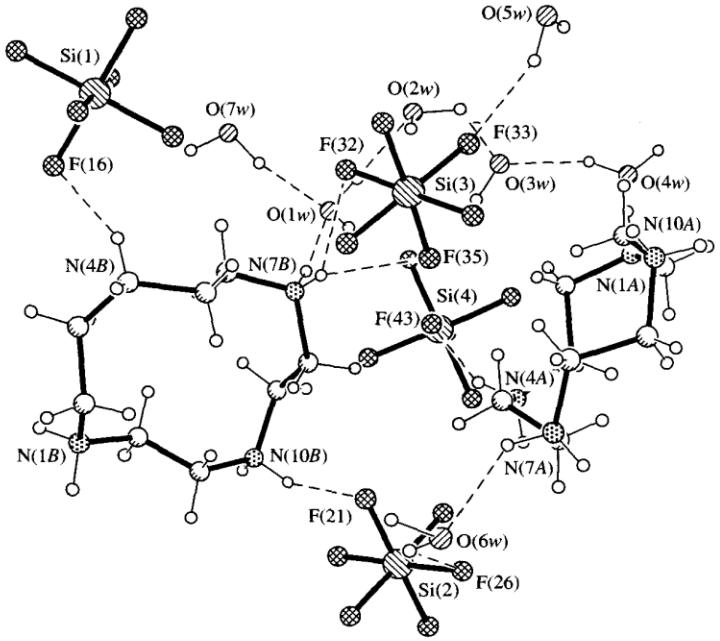


Рис. 5. Строение комплекса VII.

укажем, что в анионе $Si(1)F_6^{2-}$ расстояния Si–F составляют 1.677(2)–1.703(2) Å, а отличие валентных углов FSiF от идеальных значений достигает 2.8°. В целом для продуктов взаимодействия КФК с макроциклическими основаниями характерно образование гидратных форм; участвующие в системах Н-связей молекулы воды выполняют важную структурную функцию, зачастую являясь мостиками между различными фрагментами комплексов.

Взаимодействие КФК с N,O-амбидентатными гидразидами карбоновых кислот [28, 29] и N,S-амбидентатными тиосемикарбазидами [30, 31] приводит к гексафторосиликатам протонированных форм оснований. Центром протонирования явля-

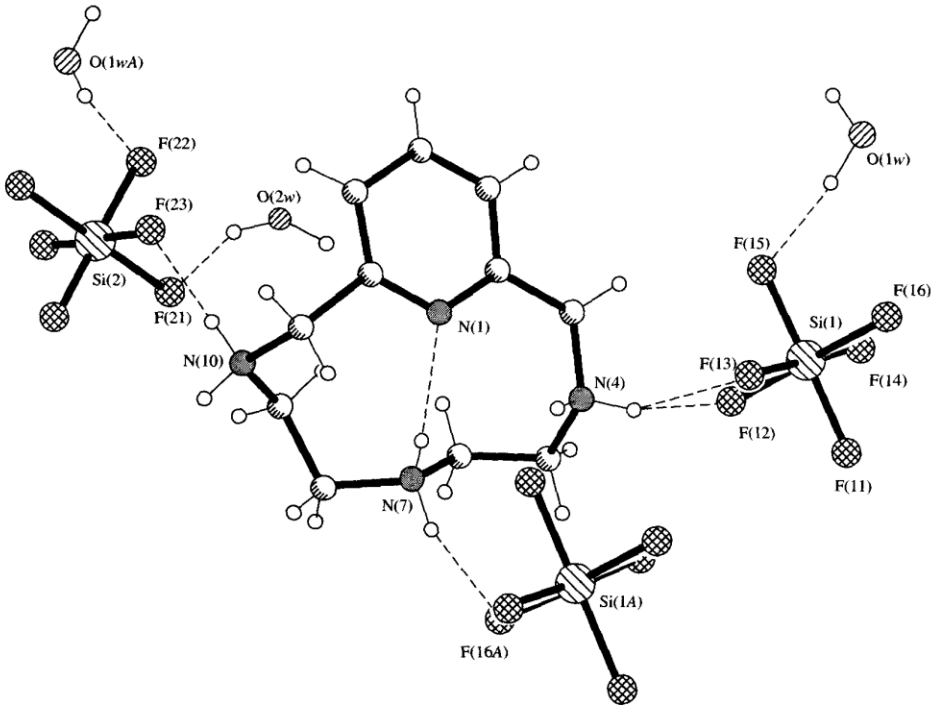


Рис. 6. Окружение катиона 1,4,7,10-тетрааза-2,6-пиридинофана [12] в комплексе VIII.

ется концевой атом азота гидразинового фрагмента, хотя расчеты распределения зарядов на атомах в молекулах гидразидов и тиосемикарбазидов полуэмпирическим методом PM3 указывают на локализацию максимального отрицательного заряда на атомах O и S оснований соответственно [32]. В структуре соединения КФК с гидразидом изоникотиновой кислоты ($\mathbf{L^4}$) состава $(L^4H_2)SiF_6$ (**X**) [28] протонирован и атом азота пиридинового цикла; все три N-протонодонорных центра катиона участвуют в H-связях с атомами фтора аниона. В то же время в комплексе КФК с гидразидом 5-амино-1-бензил-1,2,3-триазол-4-карбоновой кислоты ($\mathbf{L^5}$) состава $(L^5H)_2SiF_6 \cdot 3H_2O$ (**XI**), компоненты которого объединены множественными H-связями NH···F, NH···O, OH···F в трехмерный каркас (рис. 7), эндоциклический атом азота пиридинового типа не участвует в протонировании [29].

Особенностью реакции КФК с тиосемикарбазидом ($\mathbf{L^6}$) является вовлечение части лиганда в процесс циклизации с образованием протонированного по эндоциклическому атому азота 2,5-диамино-1,3,4- тиадиазола ($\mathbf{L^7H^+}$), стабилизирующего вместе с L^6H^+ структуру двойного гексафторосиликата $(L^6H^+)_2(L^7H^+)(SiF_6)_{1.5}$ (**XII**) [30]. Компоненты структуры объединены межмолекулярными H-связями NH···F и NH···S. Интересно отметить, что попытка осуществить циклизацию тиосемикарбазида в присутствии хлороводородной кислоты привела к получению продукта его линейной конденсации – гидразодитиоамида. 4-Фенилтиосемикарбазид ($\mathbf{L^8}$) при контакте с КФК циклизации не подвергается, а образует структурно охарактеризованное соединение $(L^8H)_2SiF_6$ (**XIII**, рис. 8) [31]. В то же время выделить какой-либо кристаллический продукт взаимодействия КФК с менее нуклеофильным 2-фенилтиосемикарбазидом не удалось.

В заключение необходимо сделать ряд общих замечаний. В формировании и стабилизации кристаллических структур соединений II–XIII – продуктов взаимодействия КФК с органическими основаниями различных классов – основная роль принадлежит водородным связям. Для всех структурно изученных комплексов наблюдается диспропорционирование длин связей Si–F фтороанионов в зависимости от того, участвует или нет соответствующий фторолиганд в H-связях и какова прочность последних. Наиболее короткие связи Si–F отмечены для атомов фтора, не вовлеченных в H-связи. В системах H-связей, реализующихся в соединениях N-протонированных органических оснований, превалируют взаимодействия NH···F.

Специфика поведения краун- и азакраун-эфиров при взаимодействии с КФК заключается в формировании систем множественных H-связей

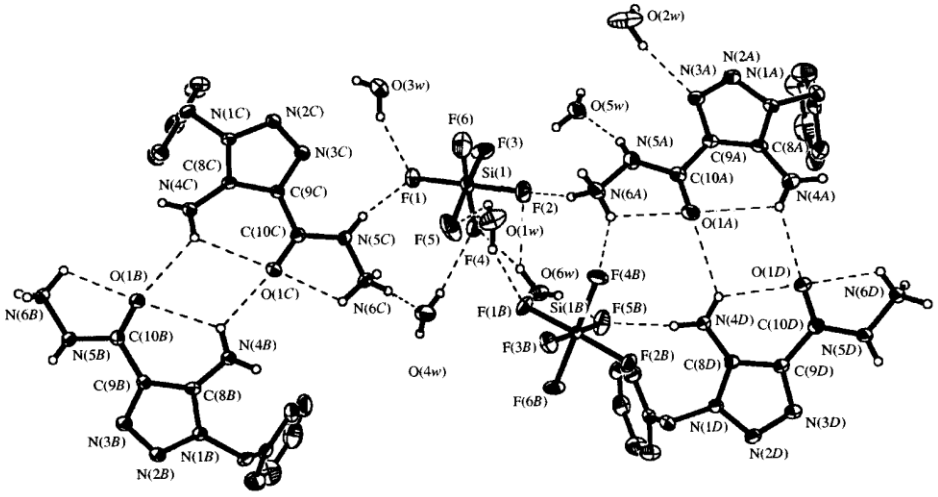


Рис. 7. Независимая часть элементарной ячейки для соединения XI.

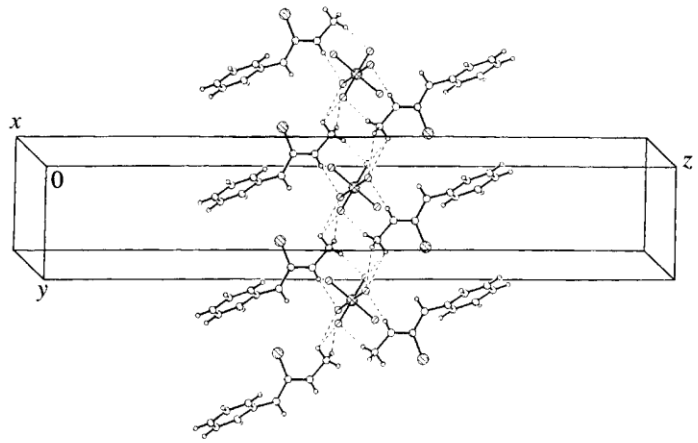


Рис. 8. Ленточная структура комплекса XIII.

между "органической" (X) и "неорганической" (Г) компонентами образующихся комплексов Г–X, позволяющих эффективно стабилизировать в твердой фазе менее симметричные по сравнению с гексафторосиликатным анионом и соответственно более лабильные в поле внешнесферных катионов анионы SiF_5^- и $[SiF_5 \cdot H_2O]^-$ [33], а также неизвестный в индивидуальном состоянии комплекс *транс*-$SiF_4 \cdot 2H_2O$. Приведенные результаты являются структурным аргументом в пользу представлений о растворах КФК как равновесной многокомпонентной системе, включающей анион SiF_6^{2-} и продукты его гидролитических превращений – комплексы $[SiF_5 \cdot H_2O]^-$ и *транс*-$SiF_4 \cdot 2H_2O$ [1, 2, 5, 6], причем комплексы SiF_6^{2-} и $[SiF_5 \cdot H_2O]^-$ присутствуют в КФК в соизмеримых количествах. Существование $[SiF_5 \cdot H_2O]^-$ и *транс*-$SiF_4 \cdot 2H_2O$ в растворах КФК обсуждалось ранее на основании данных спектральных (ЯМР ^{19}F, ИК-), кинетических, потенциометрических и кондуктометрических исследований.

Альтернативная точка зрения [7, 9], основанная преимущественно на данных потенциометрии и предусматривающая безусловное доминирование аниона SiF_6^{2-} в растворах КФК, представляется менее реалистичной. Следует также отметить, что среди продуктов взаимодействия КФК с органическими основаниями не обнаружены соединения полиядерных фторокремниевых анионов, возможность существования которых в растворах КФК обсуждалась в [34, 35]. В частности, авторы

[35] на основании данных гель-хроматографии пришли к выводу о присутствии в растворах технической и реактивной КФК в качестве основной формы соединения состава $H_2Si_2F_{10}$, хотя криоскопические измерения [36] не подтверждают приведенную формулу КФК.

Представленные в [4] результаты ИК-спектроскопического исследования экстрагируемой формы КФК в трибутилфосфате (**ТБФ**) (полосы колебаний ν(SiF) и δ(SiF_2) при 735 и 482 $см^{-1}$ соответственно, аналогичные поглощению в спектрах гексафторосиликатов) послужили одним из аргументов в пользу существования молекулярной формы КФК. Однако подобный характер поглощения наблюдается в ИК-спектрах соединений Г–X I и II, в которых проявляются колебания ν(SiF) и δ(SiF_2) "гостевого" комплекса *транс*-$SiF_4 \cdot 2H_2O$ [12], а также указанного комплекса в среде сольватирующего ацетона [37]. По мнению авторов [38], именно комплекс $SiF_4 \cdot 2H_2O$ переходит в фазу ТБФ при экстракции кремния из разбавленных растворов КФК. Существование молекулярной формы КФК не нашло подтверждения и в работе [39], авторы которой сравнивали зависимости кажущегося мольного объема и сжимаемости КФК и серной кислоты от концентрации кислоты.

Таким образом, если факт присутствия в растворах КФК гексакоординационных фторокомплексов кремния состава $[SiF_{6-n}(H_2O)_n]^{n-2}$ ($n = 0$–2) можно считать надежно подтвержденным, то возможность существования в таких системах полиядерных фторокомплексов и форм с $n > 2$ [6, 8] продолжает оставаться дискуссионной. Так в частности, в составе продуктов взаимодействия КФК с органическими основаниями не удалось изолировать комплекс предполагаемого состава $[SiF_3(OH) \cdot 2H_2O]$ [6], вклад которого в общий баланс фтора для раствора КФК с $\varphi = \Sigma F/Si \approx 5$, по данным ЯМР ^{19}F, составляет около 3% (для сравнения укажем, что вклад комплекса *транс*-$SiF_4 \cdot 2H_2O$ в это равновесие <5%). Однако нельзя исключить, что расширение ассортимента органических оснований, в частности использование в реакции с КФК функционализированных краун-эфиров с повышенным числом Н-акцепторных и Н-донорных центров, позволит стабилизировать новые малоустойчивые фторидные соединения кремния, реализующиеся в процессе гидролитических превращений гексафторосиликатного аниона.

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Додаток 20

Копія статті

“Комплексы краун-эфиров с 3-нитро-1,2,4-триазолом и пиримидин-2,4-дитионом”

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КОМПЛЕКСЫ КРАУН-ЭФИРОВ С 3-НИТРО-1,2,4-ТРИАЗОЛОМ И ПИРИМИДИН-2,4-ДИТИОНОМ

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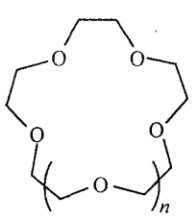
Непременным условием образования кристаллических молекулярных комплексов «хозяин–гость» [1, 2] краун-эфиров («хозяев») с «гостевыми» молекулами является присутствие в «госте» протонодонорных центров при одном атоме C, N или O (в частности, H_2N, H_2NSO_2, H_2NCS, H_2NHNCO, H_3N^+, $H_2C=$, H_3C, CH_3O и аналогичных групп или молекул воды [1, 2]), обеспечивающих стабилизацию компонент комплекса водородными связями. В связывании, как правило, участвует пара протонов донорной группы «гостя», причем стабильность комплексов падает в ряду $OH_2 > NH_2 > > CH_2$ [3]. Известны также немногочисленные примеры образования кристаллических комплексов «хозяин–гость» при участии лишь наиболее эффективных [3, 4] 18-членных краун-эфиров (Iб) [5] и (V) [6–8] с «гостевыми» молекулами, подвижные протоны которых расположены при соседних α-протонодонорных атомах, по одному при каждом, разделенных валентной связью (малеиновый ангидрид [5–7], 2-тиоурацил [8]).

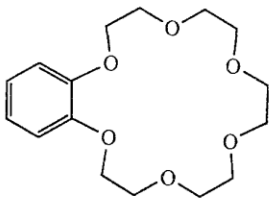
Целью работы являлось определение возможности синтеза кристаллических молекулярных комплексов краун-эфиров различного строения с «гостевыми» молекулами, имеющими по одному протону при двух α-протонодонорных атомах, разделенных валентной связью.

Установлено, что при самопроизвольном испарении растворителей из растворов краун-эфиров (I–V) с гетероциклами (VI, VII) образуются кристаллические молекулярные комплексы: [(Iа)·(VI)] – (VIII), [(Iб)·2 (VI)] – (IX), [(II)·2 (VI)] – (X), [(V)·2 (VI)] – (XI), [(Iб)·(VII)] – (XII), [(II)·(VII)] – (XIII), [(III)·(VII)] – (XIV), [(IV)·(VII)] – (XV), [(V)·(VII)] – (XVI) соответственно.

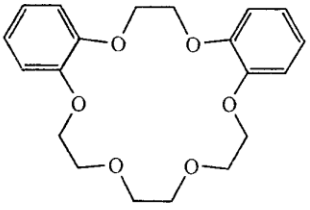
Таким образом, образование устойчивых кристаллических молекулярных комплексов нейтральных органических молекул (VI, VII) с краун-эфирами, имеющими различный размер макроциклической полости [соединения (Iа, б)], ароматические и алифатические заместители при ней [соединения (II, III) и (IV, V) соответственно], а также различно пространственно-экранированные стороны полости макроциклического кольца [соединения (IV, V)], позволяет полагать, что факты связывания краун-эфиров в соединения «хозяин–гость» молекулами, имеющими по одному протону при двух протонодонорных атомах, разделенных валентной связью, носят неслучайный характер, что может быть учтено при моделировании молекулярных взаимодействий природных молекул [1, 9], а также направленном синтезе комплексов «хозяин–гость» краун-эфиров с протонодонорными молекулами.



Iа, б

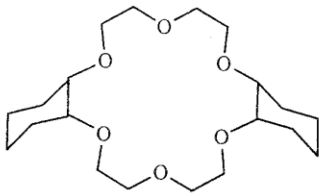


II

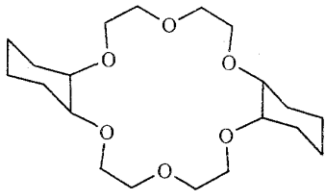


III

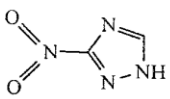
Поступило в Редакцию 28 февраля 2003 г.



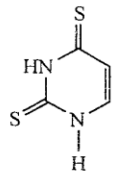
IV



V



VI



VII

I, n = 1 (а), 2 (б).

(Ia) – 1,4,7,10,13-пентаоксациклопентадекан, (Iб) – 1,4,7,10,13,16-гексаоксациклооктадекан, (II) – 2,3,5,6,8,9,11,12,14,15-декагидро-1,4,7,10,13,16-бензогексаоксациклооктадецин, (III) – 6,7,9,10,12,13,20,21-октагидродибензо[*b*,*h*][1,4,7,10,13,16]гексаоксациклооктадецин, (IV) – *цис-син-цис*-эйкосагидродибензо[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецин, (V) – *цис-анти-цис*-эйкосагидродибензо[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецин, (VI) – 3-нитро-1,2,4-триазол, (VII) – пиримидин-2,4-дитион.

Кристаллические молекулярные комплексы (VIII–XVI). К 1 ммолю краун-эфира (I–V) добавляли раствор 1 ммоля соединения (VI) в смеси ацетон–гексан, 1:1, или 1 ммоля соединения (VII) в смеси метанол–этилацет, 1:2, и оставляли испаряться при 20°C. Выделившийся монокристаллический осадок отделяли, промывали той же смесью растворителей и сушили на воздухе.

Комплекс 11,4,7,10,13-пентаоксациклопентадекана с 3-нитро-1,2,4-триазолом, 1:1 (VIII), выход 90%, т. пл. 110–112°C. Спектр ЯМР ^{1}H, δ, м. д.: 3.53 с (20H, CH_2O), 8.86 с (1H, CH). Найдено, %: C 43.15; H 6.61; N 16.84. $C_{12}H_{22}N_4O_7$. Вычислено, %: C 43.11; H 6.63; N 16.76.

Комплекс 1,4,7,10,13,16-гексаоксациклооктадекана с 3-нитро-1,2,4-триазолом, 1:2 (IX), выход 88%, т. пл. 184–186°C. Спектр ЯМР ^{1}H, δ, м. д.: 3.50 с (24H, CH_2O), 8.86 с (2H, CH). Найдено, %: C 39.11; H 5.76; N 22.84. $C_{16}H_{28}N_8O_{10}$. Вычислено, %: C 39.03; H 5.73; N 22.75.

Комплекс 2,3,5,6,8,9,11,12,14,15-декагидро-1,4,7,10,13,16-бензогексаоксациклооктадецина с 3-нитро-1,2,4-триазолом, 1:2 (X), выход 81%, т. пл. 94–96 °C. Спектр ЯМР ^{1}H, δ, м. д.: 3.58 м, 3.72 м, 4.05 м (20H, CH_2O), 6.88 м (4H, Ar–H), 8.86 с (2H, CH). Найдено, %: C 44.41; H 5.28; N 20.77. $C_{20}H_{28}N_8O_{10}$. Вычислено, %: C 44.45; H 5.22; N 20.73.

Комплекс *цис-анти-цис*-эйкосагидродибензо-[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецина с 3-нитро-1,2,4-триазолом, 1:2 (XI), выход 87%, т. пл. 178–180°C. Спектр ЯМР ^{1}H, δ, м. д.: 1.20–1.71 м, 3.52 м (36H, CH_2O, CH_2, CH), 8.86 с (2H, CH). Найдено, %: C 48.08; H 6.76; N 18.73. $C_{24}H_{40}N_8O_{10}$. Вычислено, %: C 47.99; H 6.71; N 18.66.

Комплекс 1,4,7,10,13,16-гексаоксациклооктадекана с пиримидин-2,4-дитионом, 1:1 (XII), выход 93%, т. пл. 164–166°C. Спектр ЯМР ^{1}H, δ, м. д.: 3.50 с (24H, CH_2O), 6.49 д, 7.24 д. с (2H, CH). Найдено, %: C 47.13; H 6.89; N 6.97. $C_{16}H_{28}N_2O_6S_2$. Вычислено, %: C 47.04; H 6.91; N 6.86.

Комплекс 2,3,5,6,8,9,11,12,14,15-декагидро-1,4,7,10,13,16-бензогексаоксациклооктадецина с пиримидин-2,4-дитионом, 1:1 (XIII), выход 85%, т. пл. >250°C (разл.). Спектр ЯМР ^{1}H, δ, м. д.: 3.55 м, 3.73 м, 4.05 м (20H, CH_2O), 6.90 м (4H, Ar–H), 6.49 д, 7.25 д (2H, CH). Найдено, %: C 52.56; H 6.13; N 6.24. $C_{20}H_{28}N_2O_6S_2$. Вычислено, %: C 52.61; H 6.18; N 6.14.

Комплекс 6,7,9,10,12,13,20,21-октагидродибензо[*b*,*h*][1,4,7,10,13,16]гексаоксациклооктадецина с пиримидин-2,4-дитионом, 1:1 (XIV), выход 80%, т. пл. 236–238°C. Спектр ЯМР ^{1}H, δ, м. д.: 3.59 м, 3.72 м, 4.07 м (16H, CH_2O), 6.96 м (8H, Ar–H), 6.49 д, 7.25 д (2H, CH). Найдено, %: C 57.08; H 5.63; N 5.58. $C_{24}H_{28}N_2O_6S_2$. Вычислено, %: C 57.12; H 5.59; N 6.22.

Комплекс *цис-син-цис*-эйкосагидродибензо-[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецина с пиримидин-2,4-дитионом, 1:1 (XV), выход 83%, т. пл. >260°C (разл.). Спектр ЯМР ^{1}H, δ, м. д.: 1.20–1.71 м, 3.55 м (36H, CH_2O, CH_2, CH), 6.49 д, 7.25 д (2H, CH). Найдено, %: C 55.82; H 7.84; N 5.45. $C_{24}H_{40}N_2O_6S_2$. Вычислено, %: C 55.79; H 7.80; N 5.42.

Комплекс *цис-анти-цис*-эйкосагидродибензо-[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецина с пиримидин-2,4-дитионом, 1:1 (XVI), выход 91%, т. пл. >250°C (разл.). Спектр ЯМР ^{1}H, δ, м. д.: 1.23–1.68 м, 3.53 м (36H, CH_2O, CH_2, CH), 6.49 д, 7.25 д,

(2H, CH). Найдено, %: C 55.76; H 7.83; N 5.49. $C_{24}H_{40}N_2O_6S_2$. Вычислено, %: C 55.79; H 7.80; N 5.42.

Спектры ЯМР ^{1}H регистрировали на приборе Varian VXR-300 (300 МГц) в ДМСО-d_6, внутренний стандарт – ТМС. Краун-эфиры (IV, V) получены согласно данным работы [10], использованы коммерческие (Aldrich) соединения (I–III, VI–VII) без дополнительной очистки.

Работа выполнена в рамках проекта NCS 90-2811-M-032.

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Додаток 21

Копія статті

“Synthesis and structure of fluorosilicic acid compounds with 4-aminobenzoic acid and with 4-aminobenzenesulfonamide”

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Synthesis and structure of fluorosilicic acid compounds with 4-aminobenzoic acid and with 4-aminobenzenesulfonamide The role of H-bonding in crystal structure formation

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Abstract

Preparation and characterization of the ammonium hexafluorosilicate salts, $2[R]^+[SiF_6]^{2-}$ (R = 4-(aminosulfonyl)benzenammonium) (**1**), and $2[R]^+[SiF_6]^{2-}.4H_2O$ (R = 4-carboxybenzenammonium), (**2**), are described. These salts, prepared from the reaction of the 4-aminobenzenesulfonamide or the 4-aminobenzoic acid with fluorosilicic acid, were characterized by IR, mass spectrometry and X-ray diffraction. **1** and **2** crystallize in monoclinic crystal system (space group $P2_1/c$ and $P2_1/n$, respectively), with $Z = 2$ in both cases. Compounds exhibit an extensive system of hydrogen bonding.
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Keywords: Hexafluorosilicate; Aromatic amines; Hydrogen bonding; Crystal structure

1. Introduction

Solutions of fluorosilicic acid (FSA) of different concentrations are the by-products in the production of phosphorus-containing fertilizers, phosphoric acid and elemental phosphorus and are considered as a possible alternative source of fluorine for chemical industry [1,2]. As for other complex fluoro-containing acids, FSA does not exist as the compound H_2SiF_6 [3], while its crystalline low stable hydrates of the composition $H_2SiF_6{\cdot}nH_2O$ (n = 4; 6; 9.5; m.p. 20, −12 and −54 °C respectively) have been shown from X-ray structural data to be oxonium salts of compositions $(H_5O_2)_2SiF_6$, $(H_5O_2)_2SiF_6{\cdot}2H_2O$ and $(H_5O_2)_2SiF_6{\cdot}4.5H_2O$ [4]. One possible application of hexafluorosilicate salts is the formation of ionic liquids [5] which generally associate nitrogen-containing organic cations and inorganic anions. A search in the Cambridge Structural Database [6] revealed 41 hits for complexes of amines, linear and aromatic, and macrocycles with the FSA. The family of hexafluorosilicates of aromatic bases is restricted to six compounds, in these compounds different numbers of fluorine atoms are involved in the system of hydrogen bonding. Thus, in bis(*N*,*N*′-bis(3-nitrophenyl)isophthalamide) tetra-*n*-butylammonium hexafluorosilicate [7], each $[SiF_6]^{2-}$ anion is connected via its equatorial fluorine atoms within the crown-like cavity formed by two *N*,*N*′-bis(3-nitrophenyl)isophthalamide residues. In co-crystals with acridinium [8] and quinolinium [9] cations, only two or five over six fluorine atoms participate in hydrogen bond network. Hydrates of *p*-bromoanilinium and *p*-toluidinium hexafluorosilicates [10] both formulate a thick layer with two hydrophobic surfaces formed by the aromatic

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Table 1
Crystal data and structure refinement parameters for **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{12}H_{18}F_6N_4O_4S_2Si$	$C_{14}H_{24}F_6N_2O_5Si$
Formula weight	488.51	490.44
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	9.747(5)	6.333(1)
b (Å)	9.444(4)	25.975(5)
c (Å)	9.850(5)	6.891(1)
β (degree)	98.14(2)	115.81(3)
Cell volume (Å^3)	897.56(8)	1020.5(3)
Z	2	2
D_{calc} (g/cm^3)	1.808	1.596
μ, (mm^{-1})	0.455	0.214
$F(000)$	500	508
θ range for data collection (degree)	2.11–25.03	3.14–25.35
Limiting indices	$-11 \le h \le 11$,	$0 \le h \le 7$
	$-11 \le k \le 10$	$0 \le k \le 30$
	$-10 \le l \le 11$	$-8 \le l \le 7$
Reflections collected/unique	5539/1569	1842/1842
Reflections with $I > 2\sigma(I)$	1204	1180
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1569/4/154	1842/6/194
Goodness-of-fit on F^2	1.013	1.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0320$,	
$wR_2 = 0.0780$	$R_1 = 0.0495$, $wR_2 = 0.1196$	
R indices (all data)	$R_1 = 0.0471$	
$wR_2 = 0.0826$	$R_1 = 0.0871$, $wR_2 = 0.1336$	
Extinction coefficient	0.118(6)	0.31(2)
Largest difference hole/peak (e.A^{-3})	−0.395/0.285	0.243/0.219

rings arranged perpendicular to the layer surface and the hexagonal H-bonded network inside the layer. The interaction of the hydrazine of 5-amino-1-benzyl-1,2,3-triazol-4-carbonic acid with fluorosilicic acid leads to a corresponding trihydrate [11] with a complex system of hydrogen bonding which combines the components into a 3D grid.

The present work is an exploration of the situation where fluorosilicic acid and aromatic amines with a second donor group (SO_2NH_2 and COOH) in the *para*-position to the amine group are combined. The preparation of the bis(4-(aminosulfonyl)benzenammonium) hexafluorosilicate $[C_6H_9N_2O_2S]_2[SiF_6]$ (**1**), and $[C_7H_8NO_2]_2[SiF_6].4H_2O$ (**2**) is described. The compounds were characterized by IR, mass spectrometry and by X-ray diffraction.

2. Results and discussion

Compounds **1**–**2** crystallize in the monoclinic crystal system (space groups $P2_1/c$ and $P2_1/n$) with $Z = 2$. Crystal structure and refinement data are given in Table 1. Bond lengths and angles are given in Table 2. The asymmetric units of **1** and **2** reveal half of the hexafluorosilicate anion in partial position on the inversion center, one 4-(aminosulfonyl)benzenammonium or 4-carboxybenzenammonium cation, and two water molecules in general positions. The 4-(aminosulfonyl)benzenammonium cation has an angular shape which is dictated by the N(2)–S(1)–C(1) bond angle equal to 108.2(1)°. The 4-carboxybenzenammonium cation has the planar skeleton with practically all non-hydrogen atoms in the plane of phenyl ring.

The Si–F bond lengths are practically equal and adopt the values 1.683(1) and 1.684(1) Å in compound **1**, and range from 1.660(2) to 1.675(2) Å in **2**. All fluorine atoms are involved in strong N–H(NH_3^+)...F (**1**, **2**) and O–H(water)...F hydrogen bonds (**2**). In **1** and **2** the $[SiF_6]^{2-}$ anion shows very small deviations from ideal octahedral geometry. The F(*trans*)–Si–F(*trans*) angles are 180.0(3)° for **1** and **2**, the F(*cis*)–Si–F(*cis*) angles deviate from the right angle of 0.5(1)° in **1** and of 1.2(1)° in **2**. Such a practically ideal octahedral geometry for the $[SiF_6]^{2-}$ anion is rather unusual; usually, its complete involvement in hydrogen bonding causes a higher distortion of $[SiF_6]^{2-}$ octahedron. In compound **1**, the hydrogen bonds are formed between the hexafluorosilicate anion and 4-(aminosulfonyl)benzenammonium cations. Each of $[SiF_6]^{2-}$ octahedra is linked to eight 4-(aminosulfonyl)benzenammonium cations via twelve N–H...F hydrogen bonds with the participation of terminal NH_3^+ and NH_2 groups; N...F distances lie from 2.778(3) to 3.334(3) Å (Fig. 1, Table 3).

In **1**, along the a axis, the 4-(aminosulfonyl)benzenammonium cation bridges two $[SiF_6]^{2-}$ anions, that leads to the formation of centrosymmetric heterotetramers which are closed by six N–H...F hydrogen bonds. The 4-(aminosulfonyl)-benzenammonium cations related by the two-fold

Table 2
Selected intermolecular distances (Å) and angles (degree) for **1** and **2**

1			
Si(1)–F(1)	1.684(1)	F(1)–Si(1)–F(2)	89.8(1)
Si(1)–F(2)	1.683(1)	F(1)–Si(1)–F(3)	90.5(1)
Si(1)–F(3)	1.684(1)	F(2)–Si(1)–F(3)	90.5(1)
S(1)–O(1)	1.426(2)	F(1)–Si(1)–F(1)#1	180.0(1)
S(1)–O(2)	1.430(2)	F(2)–Si(1)–F(2)#1	180.0(1)
S(1)–N(2)	1.590(2)	F(3)–Si(1)–F(3)#1	180.0(1)
S(1)–C(1)	1.778(2)		
N(1)–C(4)	1.467(3)		
C(1)–C(2)	1.382(3)		
C(1)–C(6)	1.384(3)		
C(2)–C(3)	1.387(3)		
C(3)–C(4)	1.371(3)		
C(4)–C(5)	1.377(3)		
C(5)–C(6)	1.378(3)		
2			
Si(1)–F(1)	1.675(2)	F(1)–Si(1)–F(2)	90.45(7)
Si(1)–F(2)	1.658(2)	F(1)–Si(1)–F(3)	90.71(9)
Si(1)–F(3)	1.665(2)	F(2)–Si(1)–F(3)	90.5(1)
Si(1)–F(2A)	1.62(2)	F(1)–Si(1)–F(1)#2	180.0(1)
Si(1)–F(3A)	1.64(1)	F(2)–Si(1)–F(2)#2	180.0(2)
O(1)–C(7)	1.210(3)	F(3)#2–Si(1)–F(3)	180.0(2)
O(2)–C(7)	1.325(3)		
N(1)–C(4)	1.456(4)		
C(1)–C(7)	1.483(4)		
C(1)–C(6)	1.389(3)		
C(1)–C(2)	1.393(3)		
C(2)–C(3)	1.364(3)		
C(3)–C(4)	1.379(3)		
C(4)–C(5)	1.377(3)		
C(5)–C(6)	1.373(4)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x+2, -y, -z$.

screw axis are separated by N–H...O hydrogen bonds (N(1)...O(2) 2.894(3) Å) and lead to 'tail-to-head' chains running along the *c* direction (Fig. 2). The cations in the chains are arranged in a T-shape with the dihedral angle between the aromatic rings equal to 88.3°. A similar N–H...O hydrogen bond exists in 4-aminobenzenesulphonamide [12] and in 4-(aminosulfonyl)benzenammonium nitrosalycilate [13].

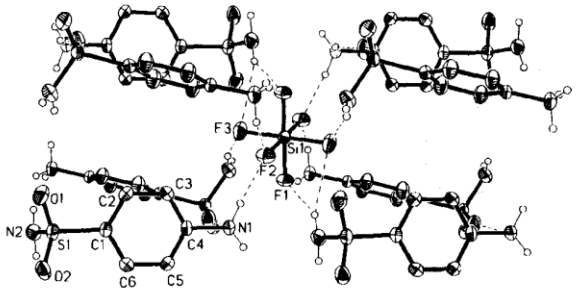

Fig. 1. ORTEP view of $[SiF_6]^{2-}$ anion surrounded by eight 4-(aminosulfonyl)-benzenammonium cations (**1**). Only the asymmetric unit is numbered. H-atoms of C groups are omitted for clarity.

Structure of **1** may also be described as the alternation of rows of $[SiF_6]^{2-}$ anions and rows of organic cations along the *a* direction, interconnected by hydrogen bonds into a 3D network (Fig. 3). Each cation bridges four neighboring $[SiF_6]^{2-}$ anions and two organic cations.

Compound **2** has the most extensive hydrogen bond network which involves $[SiF_6]^{2-}$ anions, 4-carboxybenzenammonium cations and water molecules. In a similar way to **1**, the $[SiF_6]^{2-}$ anion serves as a powerful connector. It is linked to four 4-carboxybenzenammonium cations and four water molecules via six N–H...F and four O–H...F hydrogen bonds (Fig. 4).

The fluorine atoms in the equatorial plane of $[SiF_6]^{2-}$ anion are disordered over two positions, F2, F3 and F2A, F3A; both sets of fluorine atoms are involved in the hydrogen-bonding system (Table 3). Each ammonium group bridges two anions related by the inversion center via three N–H...F interactions which range from 2.834(3) to 2.948(3) Å. Only one water molecule, O(1w) is connected with ammonium group (2.835(3 Å)).

The 4-carboxybenzenammonium cations and water molecules are assembled into positive layers via three O–H...O and one N–H...O hydrogen bonds. The water molecules are bonded into dimer with O(1w)...O(2w) separation equal to 2.839(3) Å. The organic cations are connected by their carboxyl tails with the water dimers, giving rise to chains. The neighboring chains, related by the inversion center, are H-bonded via one hydrogen of ammonium group and O(2w) lone pair in the wave-like layer propagated in the *ac* plane. The cations are stacked in parallel and arranged so, that the planar carboxylic group of

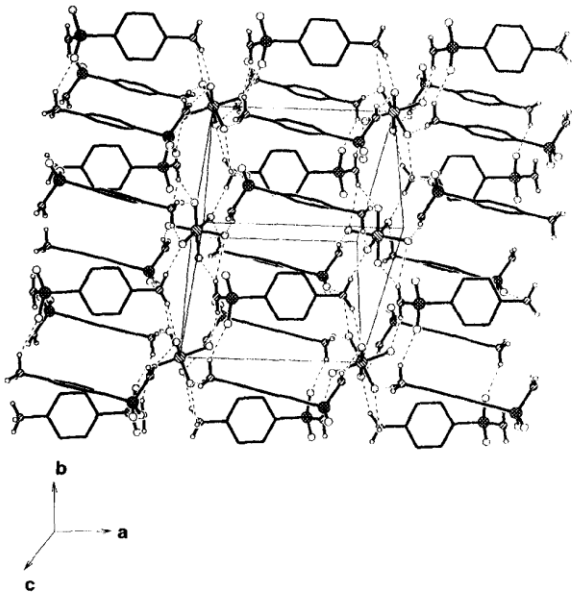

Fig. 2. View of the rows of $[SiF_6]^{2-}$ anions alternating with chains of 4-(aminosulfonyl)benzenammonium cations in **1**.

Table 3
Geometry of hydrogen bonds for **1** and **2**

D–H...A	d(D–H) Å	d(H...A) Å	d(D...A) Å	∠(DHA) (degree)	Symmetry transformation for acceptor
1					
N(1)–H(1A)...F(1)	0.91(2)	2.06(2)	2.907(3)	153(3)	x, y, z
N(1)–H(1B)...F(2)	0.92(2)	2.42(3)	2.851(3)	109(2)	x, y, z
N(1)–H(1B)...O(2)	0.92(2)	2.07(2)	2.894(3)	149(3)	x + 1, y + 1/2, −z + 1/2
N(1)–H(1C)...F(2)	0.93(2)	1.86(2)	2.778(2)	170(2)	x, −y + 1/2, z + 1/2
N(2)–H(2A)...F(3)	0.93(2)	1.99(2)	2.894(3)	162(3)	x + 1, y, z
N(2)–H(2B)...F(1)	0.93(2)	2.04(2)	2.903(3)	154(2)	x + 1, −y + 1/2, −z + 1/2
N(2)-H(2B)...F(3)	0.93(2)	2.55(2)	3.334(3)	142(2)	x + 1, −y + 1/2, z + 1/2
2					
O(2)–H(1O)...O(2W)	0.87(2)	1.77(2)	2.628(3)	171(3)	x, y, z
N(1)–H(1A)...F(2)	0.83(2)	2.09(3)	2.889(3)	160(4)	x + 2, y, z
N(1)–H(1A)...F(3A)	0.83(2)	2.01(3)	2.80(2)	157(4)	x, y, z
N(1)–H(1A)...F(1)	0.83(2)	2.51(4)	2.948(3)	114(3)	x, y, z
N(1)–H(1B)...F(1)	0.83(2)	2.04(3)	2.834(3)	155(4)	−x + 1, y, −z
N(1)–H(1B)...F(2A)#2	0.85(2)	2.34(4)	2.807(15)	115(3)	x + 1, y, z
N(1)–H(1C)...O(1W)	0.84(2)	2.04(2)	2.835(3)	157(4)	x, y, z
O(1W)–H(1W1)...F(3)	0.83(3)	2.31(3)	3.139(3)	174(4)	x − 1, y, z − 1
O(1W)–H(1W1)...F(3A)	0.83(3)	1.96(3)	2.741(13)	156(4)	x − 1, y, z − 1
O(1W)–H(1W1)...F(2)	0.83(3)	2.60(3)	3.180(3)	127(4)	x + 1, y, z − 1
O(1W)–H(2W1)...O(1)	0.84(3)	1.95(3)	2.789(3)	178(3)	x − 1/2, −y + 1/2, z − 1/2
O(2W)–H(1W2)...F(3)	0.84(3)	2.07(3)	2.905(3)	172(4)	x + 3/2, y + 1/2, −z + 1/2
O(2W)–H(1W2)...F(2A)	0.84(3)	2.02(3)	2.744(15)	144(3)	x + 3/2, y + 1/2, −z + 1/2
O(2W)–H(2W2)...O(1W)	0.84(3)	2.01(3)	2.839(3)	173(4)	x − 1/2, −y + 1/2, z + 1/2

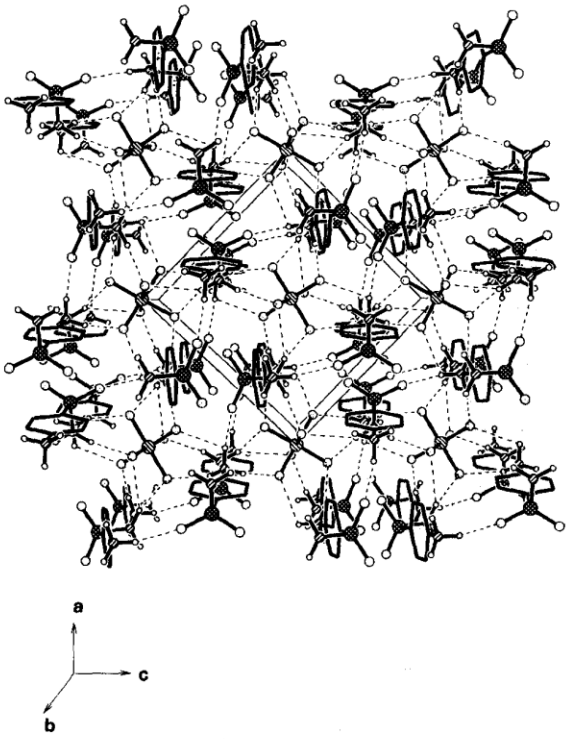

Fig. 3. Crystal packing for **1**.

one cation is displayed above the phenyl ring of its closest neighbor, the distances between the closest aromatic rings range from 3.449 to 3.514 Å. Along *b* axis, the alternation close to that encountered in **1** of the rows of $[SiF_6]^{2-}$ anions and 4-carboxybenzeneammonium cations is observed (Fig. 5). The positive and negative rows run along the *c* direction. The $[SiF_6]^{2-}$ anions bind the positive layers via a lot of N–H...F and O–H...F hydrogen bonds with the formation of 3D grid (Fig. 6).

The significant IR frequencies for **1** and **2** in comparison with the corresponding free bases are summarized in Table 4. In the IR spectrum of **1**, the $\nu(NH_2)$ and $\nu(NH_3^+)$ frequencies represent the wide bands with several maxima in the range 3350–2600 cm^{-1}. Intense bands at 1320 and 1175 cm^{-1}, which can be attributed to $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$, are slightly shifted in comparison with the free base. The

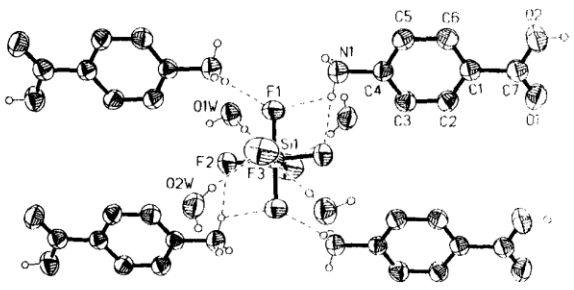

Fig. 4. ORTEP view of $[SiF_6]^{2-}$ anion surrounded by four 4-carboxybenzeneammonium cations and four water molecules in **2**. Only the asymmetric unit is numbered. H-atoms of C-groups are omitted for clarity.

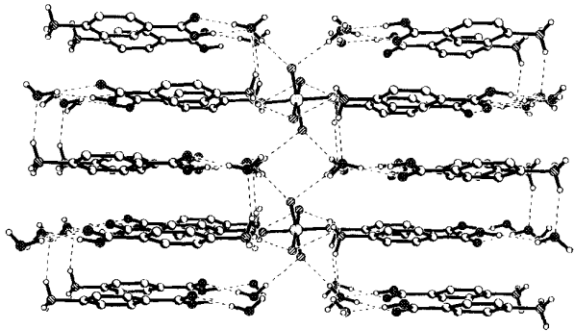

Fig. 5. The alternation of rows of $[SiF_6]^{2-}$ anions and positive layers in **2**.

diffused character of the maxima of the bands $\nu(NH_3^+)$ and $\nu(OH)$ in the range 3500–2600 cm^{-1} in the spectrum of **2** is probably correlated to the participation of the corresponding functional groups in the system of intermolecular hydrogen bonding. Deformation vibrations, $\delta(NH_3^+)$ and $\delta(H_2O)$, present under complicated large intense bands with the maximum at 1625 cm^{-1}. The intense bands at 740 and 745 cm^{-1} and the band at 720 cm^{-1} more intense in **1** are connected with the $\nu(SiF)$ vibrations of the $[SiF_6]^{2-}$ anions. The $\delta(SiF_2)$ vibrations are registered in the form of doublet and triplet bands at 470, 460, 430 cm^{-1} and 480, 440 cm^{-1} respectively. It must be noted that the multiple character of the vibrations of $[SiF_6]^{2-}$ anions in **1** and **2** is correlated with the deviation very small in **1** of the hexafluorosilicate anion geometry from the ideal octahedral one, the distortion being more pronounced in **2**.

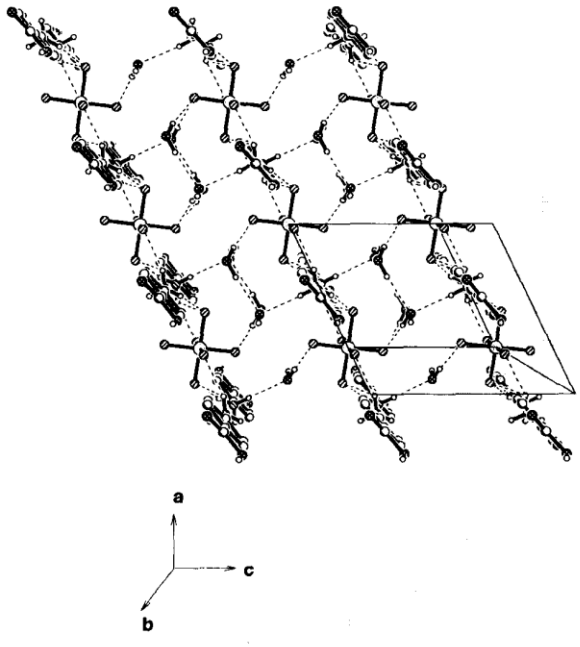

Fig. 6. Section of the crystal packing in **2** parallel to the *ac* plane.

In conclusion, some general remarks could be made. The linear and aromatic amines, alkylamines [9,14], propargilamine [15], nitrogen-containing heterocycles of piperidine or quinoline types [9], the derivatives of guanine [16,17], hydrazides, thiosemicarbazides, protonated by the FSA, form co-crystals exclusively with highly symmetric hexafluorosilicate anion, $[SiF_6]^{2-}$. The most interesting products with diversified structures were formed in the reactions of FSA with crown ethers and their partially substituted aza analogs. The authors managed to stabilize the $[SiF_6]^{2-}$ anion and all products of its hydrolytic transformations, *trans*-$SiF_4{\cdot}2H_2O$, $[SiF_5{\cdot}H_2O]^-$, $[SiF_5]^-$, in these complexes [18,19]. According to X-ray diffraction data, the neutral components of structure [(18-crown-6) (*trans*-$SiF_4{\cdot}2H_2O){\cdot}2H_2O$] are linked by a system of O–H...Ocrown hydrogen bonds, the outersphere water molecule acts as a bridge between *trans*-$SiF_4{\cdot}2H_2O$ and 18-crown-6 (L1). When the *cis–syn–cis* isomer of dicyclohexano-18-crown-6 (L2), whose macrocyclic plane is unequivalently screened sterically, reacts with FSA, it gives the ionic complex $[(L2{\cdot}H_3O)(SiF_5)]$, where the outer-sphere $[SiF_5]^-$ anion is bonded to the macrocyclic cation $(L2{\cdot}H_3O)^+$ only by electrostatic interactions [20]. Monoaza-18-crown-6 (L3) and 1,10-diaza-18-crown-6 (L4) are protonated in acid medium, and in the ionic complexes $[(L3H{\cdot}H_2O)(SiF_5{\cdot}H_2O){\cdot}H_2O]$ and $[(L4H_2)(SiF_5{\cdot}H_2O)_2]$ they stabilize monoaquapentafluorosilicate anion, $[SiF_5{\cdot}H_2O]^-$, while 1,7-diaza-15-crown-5 (L5) and hexafluorosilicate anion give the complex $[(L5H_2)(SiF_6)]$. In all of these complexes the components are held together by a complicated system of hydrogen bonds. The 14- and 12-membered tetraazamacrocycles, (cyclam, cyclen and pyofan) [21], similarly to arylamines, give the crystalline complexes exclusively with hexafluorosilicate anion due to the formation of numerous N–H...F and N–H...Owater hydrogen bonds.

4-aminobenzoic acid and 4-aminobenzenesulfonamide as all previously studied arylamines give the highly stable hexafluorosilacates sustained by the very diverse system of hydrogen bonds.

3. Experimental

IR spectra were recorded on a Specord 75 IR spectrophotometer (range 4000–400 cm^{-1}, samples as a suspensions in Nujol mulls between KRS-5 windows). Fluorine content was determined with a fluoride ion selective electrode. Mass spectra were obtained on a MX-1321 instrument (the ionizing energy was 70 eV, samples were directly introduced into the ion source).

3.1. Synthesis of (4-ammoniumbenzenesulfonamide) hexafluorosilicate (1)

A solution of 1.72 g (0.01 mol) of 4-aminobenzenesulfonamide in a mixture of 25 mL of methanol and of 20 mL of water was added to 9 mL of 45% FSA and evaporated at

Table 4
IR spectral data for **1** and **2** and free organic ligands

$H_2NC_6H_4SO_2NH_2$	**1**	Assignment	$H_2NC_6H_4COOH$	**2**	Assignment
3470 m				3520 m	
3430 m			3460 m		
3340 s	3350 s		3385 s	3380 sbr	
3300 s					
3200 s	3230 s	ν(NH)			ν(NH) ν(OH)
	3120 s		3150 sbr		
				3080 sbr	
	2735 m				
	2620 m			2630 mbr	
			1720 sh		
			1700 sh	1690 sh	ν_{as}(COO)
1615 s	1626 sh	$\delta(NH_2)$,		1625 s	$\delta(NH_3)$
	1600 sh	$\delta(NH_3^+)$	1585 s	1590 sh	$\delta(NH_3^+)$
1585 s	1570 sh				
1565 sh		ν(CC)			
1550 sh	1550 sh		1560 sh	1550 sh	ν(CC)
1500 s	1500 sh		1500 sh	1500 sh	
1335 sh	1320 vs	$\nu_{as}(SO_2)$		1330 w	ν_s(COO)
	1300 sh			1300 sh	
1280 vs			1270 m	1270 vs	
1180 m	1175 s	$\nu_s(SO_2)$		1190 sh	
1130 vs	1125 s		1130 m	1135 m	
1090 m					
	1025 w	$\rho(NH_2)$		1040 sh	
990 sh	990 w		980 sh	985 sh	
960 v	960 sh			926 v	$\rho(NH_3^+)$
	930 m	$\rho(NH_3^+)$			ρ(CNH)
880 m		ρ(CNH)	880 sh	880 sh	
840 sh	855 sh		840 sh	840 sh	
830 m	835 m				
	740 sh	ν(SiF)		745 s	ν(SiF)
720 sh	720 s		720 sh	720 sh	
670 s	670 m	$\delta(SO_2)$			
640 sh	640 sh			640 s	$\tau(NH_2)$ $\tau(NH_3^+)$
	620 sh	$\tau(NH_2)$, $\tau(NH_3^+)$ δ(CCH)			δ(CCH) δ(COO)
560 sh					$\rho(H_2O)$
540 s	545 s		540 m	545 sh	
	470 m			480 m	
	460 s	$\delta(SiF_2)$			$\delta(SiF_2)$
	430 sh			440 m	

Note: w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad.

room temperature. Colourless transparent crystals, of a qualitative yield, soluble in water, m.p. 250–252 °C. Anal. found, %: F 23.5, Si 5.9, N 11.7 Calcd. for $C_{12}H_{18}F_6N_4O_4S_2Si$, F 23.33, Si 5.8, N 11.5.

Mass spectrum: $[C_6H_8N_2O_2S]^+$ (m/z = 172, I = 100%), $[C_6H_6NO_2S]^+$ (m/z = 156, I = 88%), $[C_6H_6N]^+$ (m/z = 92, I = 72%), $[SiF_3]^+$ (m/z = 85, I = 19%).

3.2. Synthesis of bis(4-ammoniumbenzoic acid) hexafluorosilicate tetrahydrate (2)

A solution of 1.37 g (0.01 mol) of 4-aminobenzoic acid in a mixture of 40 mL of methanol and of 60 mL of water was added to 9 mL of 45% FSA and evaporated at room temperature. Crystals of complex, suitable for X-ray investigation, were obtained by recrystallization from water. Colourless transparent crystals, of a qualitative yield, soluble in water, m.p. 240–241 °C. Anal. found, %: F 23.2, Si 5.9, N 5.5; Calcd. for $C_{14}H_{24}F_6N_2O_8Si$, F 23.2, Si 5.7, N 5.7.

Mass spectrum: $[C_7H_7NO_2]^+$ (m/z = 137, I = 97%), $[C_7H_6NO]^+$ (m/z = 120, I = 100%), $[C_6H_6N]^+$ (m/z = 92, I = 33%), $[SiF_3]^+$ (m/z = 85, I = 70%).

3.3. Structure determination

The X-ray intensity data were collected at room temperature on a Nonius Kappa CCD diffractometer

equipped with graphite monochromated Mo-Kα radiation using ω rotation with a sample-to-detector distance of 40 mm. Unit cell parameters were obtained and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO [22]. The scaling as well as the global refinement of crystal parameters were performed by SCALEPACK [22]. Reflections, which were partly measured on previous and subsequent frames, were used to scale these frames on each other. The structure solution and refinement proceeded similarly for both structures using SHELX-97 program package [23]. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were treated anisotropically (full-matrix least squares method on F^2). In **2** the fluorine atoms F2 and F3 are disordered over two orientations in the equatorial plane. The occupancy factors refined to 0.898(5) for the major component (F2, F3) and 0.102(5) for the minor component (F2A and F3A), only major position was treated anisotropically. The disorder was justified by the reasonable system of hydrogen bonding (Table 3). Hydrogen atoms of C groups were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while H-atoms of ammonium group and water molecules were found from differential Fourier maps at an intermediate stage of the refinement and were treated isotropically using SADI restraints.

Crystallographic data (cif files) for the structural analysis of complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. **232837** and **232838**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44 1233 336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Додаток 22

Копія статті

“Супрамолекулярные соединения цис-син-цис дициклогексано-18-краун-6 с фторокомплексными кислотами ниобия и тантала”

Журнал общей химии. 2004. Т. 74. Вып. 5

УДК 547.89

СУПРАМОЛЕКУЛЯРНЫЕ СОЕДИНЕНИЯ *цис-син-цис*-ДИЦИКЛОГЕКСАНО-18-КРАУН-6 С ФТОРОКОМПЛЕКСНЫМИ КИСЛОТАМИ НИОБИЯ И ТАНТАЛА

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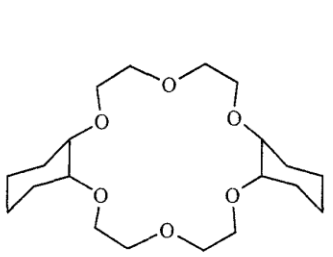
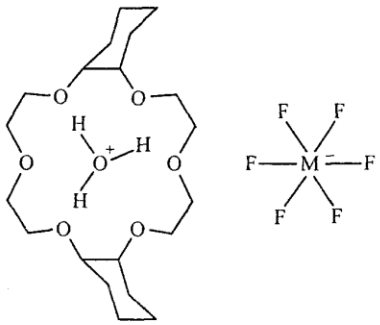
Известно, что галогениды металлов, таких как олово, цирконий, ванадий, ниобий, тантал, находящихся в высших степенях окисления, в безводных условиях либо расщепляют полиэфирные кольца краун-эфиров с образованием линейных продуктов, либо, как в случае использования пентахлорида тантала, происходит расширительная рециклизация 15-краун-5 (1,4,7,10,13-пентаоксациклопентадекан) в 18-краун-6 (1,4,7,10,13,16-гексаоксациклооктадекан) с образованием комплекса $[H_3O^+ \cdot (18\text{-краун-}6)]TaCl_6^-$ с выходом ~10% [1]. Из работы [2] видно, что растворы ниобия и тантала во фтористоводородной кислоте представляют собой лабильную смесь фторокомплексных кислот HMF_6 и H_2MF_7, где M = = Nb, Ta.

В рамках одного из приоритетных направлений супрамолекулярной химии по выявлению селективных взаимодействий и стабилизации краун-эфирами малоустойчивых соединений в стабильные кристаллические соединения включения [3, 4] в данной работе изучена возможность селективной экстракции и синтеза супрамолекулярных комплексов краун-эфира с гекса- или гептафторокомплексами ниобия и тантала из их растворов во фтористоводородной кислоте.

При испарении растворителей из растворов ниобия или тантала и *цис-син-цис*-изомера дициклогексано-18-краун-6 (I) во фтористоводородной кислоте селективно образуются кристаллические супрамолекулярные комплексы (IIа, б) с гексафторониобатом или гексафторотанталатом гидроксония соответственно. С учетом данных работы [1], а также характерной способности *цис-син-цис*-пергидродибензо[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецина (I) стабилизировать «закрытой» стороной полости макроциклического кольца катионы гидроксония [5–7] для синтезированных объектов можно предложить строение (II).



I



IIа, б

II. M = Nb (а), Ta (б).

Полученные кристаллические супрамолекулярные соединения являются первым примером селективной экстракции краун-эфиром фторокомплексных кислот ниобия и тантала из кислотных растворов, они стабильны и могут представлять интерес в качестве контейнеров [3] этих кислот.

Поступило в Редакцию 28 июля 2003 г.

Кристаллические супрамолекулярные комплексы (IIа, б). В 5 мл 45%-ной фтористоводородной кислоты растворяли 1 ммоль пентафторида ниобия или тантала, к полученному раствору прибавляли 1.01 ммоля *цис-син-цис*-пергидродибензо-[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецина и реакционную смесь помещали в тефлоновый эксикатор над серной кислотой. После полного испарения растворителей с количественным выходом получали монокристаллы комплексов (IIа, б).

Комплекс *цис-син-цис*-пергидродибензо[*b*,*k*]-[1,4,7,10,13,16]гексаоксациклооктадецина с гексафторониобатом гидроксония, 1:1 (IIа), т. пл. 105–107°C. Спектр ЯМР ^{1}H, δ, м. д.: 1.29–1.85 м и 3.64 м (36H, CH, CH_2, CH_2O). Найдено, %: C 40.18; H 6.65; F 19.12. $C_{20}H_{39}F_6NbO_7$. Вычислено, %: C 40.13; H 6.57; F 19.05.

Комплекс *цис-син-цис*-пергидродибензо[*b*,*k*]-[1,4,7,10,13,16]гексаоксациклооктадецина с гексафторотанталатом гидроксония, 1:1 (IIб), т. пл. 103–104°C. Спектр ЯМР ^{1}H, δ, м. д.: 1.28–1.85 м и 3.65 м (36H, CH, CH_2, CH_2O). Найдено, %: C 35.04; H 5.80; F 16.67. $C_{20}H_{39}F_6O_7Ta$. Вычислено, %: C 34.98; H 5.73; F 16.61.

Спектры ЯМР ^{1}H регистрировали на приборе Varian VXR-300 (300 МГц) в метаноле-d_4, внутренний стандарт – ТМС.

Работа финансировалась в рамках проекта NCS 90-2811-M-032.

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Додаток 23

Копія доповіді

“Полиэтиленгликоли и краун-эфиры – перспективные модели хемосорбентов тетрафторида кремния”

May 20-21

2005

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INTERNATIONAL CONFERENCE

ECOLOGICAL CHEMISTRY

ABSTRACTS

Chisinau, Moldova

On the base of EPXMA, it can be presumed that some of the trace e
(Ba, Sr, Pb, Zr, Y, Ag, La, Ce, Cu) trend to be concentrated in discrete particl
existence of very fine particles, enriched in such toxic elements in available
suggests that fly ash might have a more deleterious impact on environm
health than it could be suggested from bulk analytical data.

Key words: coal fly ash, magnetic separation, analysis, EPXMA, solid w

ПОЛИЭТИЛЕНГЛИКОЛИ И КРАУН-ЭФИРЫ – ПЕРСПЕКТИВНЫ МОДЕЛИ ХЕМОСОРБЕНТОВ ТЕТРАФТОРИДА КРЕМНИЯ

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Высокотоксичный тетрафторид кремния (I класс опасности, ПДК мг/м^3) – один из основных компонентов технологических газов предприя перерабатывающих фторидное сырье, а также апатиты и фосфориты (пр водства фосфорных удобрений, фосфорной кислоты, элементного фосф Улавливание и утилизация SiF_4 из отходящих газов является актуальной за тарно-гигиенической и экологической задачей, а также представляет инте для экономики основного производства [1].

Установлено, что полиэтиленгликоли $HO(CH_2CH_2O)_nCH_2CH_2OH$ (n = 3) поглощают тетрафторид кремния с образованием жидких молекуляр комплексов состава $SiF_4 \cdot 6L$. Судя по данным ЯМР^{1}H и ИК-спектроско два лиганда координированы *транс*-монодентатно, а остальные закреп внешнесферно за счет межмолекулярных H-связей типа OH···O. Продукт взаимодействия SiF_4 с гексановыми растворами краун-эфиров (12К4, 1 18К6) в присутствии влаги воздуха являются кристаллические комп типа «гость-хозяин» [(*транс*-$SiF_4 \cdot 2H_2O$)$\cdot n$L$\cdot m H_2O$] (L = 12К4, n = 2, m L = 15К5, $n = m$ = 1; L = 18К6, n = 1, m = 2) [2]. Согласно данным РСА, и Раман-спектроскопии, компоненты комплексов объединены систе межмолекулярных H-связей типа OH···O. Специфика строения комп полиэтиленгликолей и краун-эфиров на основе преимущественно «сл взаимодействий находит свое отражение в их термохимическом по

термолиз комплексов с выделением в газовую фазу SiF_4 или SiF_4 в смеси с парами воды реализуется в исключительно мягких условиях при 100 – 140 °С. Существенно, что в отличие от комплексов моноатомных спиртов $SiF_4 \cdot 4ROH$, термическое разложение комплексов полиэтиленгликолей не сопровождается побочными реакциями деструкции лигандов. С учетом вышесказанного полиэтиленгликоли и краун-эфиры могут рассматриваться как перспективные модели О-донорных хемосорбентов SiF_4, способных к легкой термической регенерации.

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UTILIZATION OF DIFFERENT RETENTION SYSTEMS IN ORDER TO DIMINISH THE SUSPENDED SOLIDS CONTENT IN THE WASTE WATERS FROM PAPER MANUFACTURING

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The paper presents some comparative data concerning the effects of using different retention systems (single component, dual polymer, with micro particles) over the suspended solids content and turbidity in the waste waters from different paper grades manufacturing.

BIOTECHNOLOGICAL METHOD FOR THE WASTE WATER FROM THE PULP AND PAPER INDUSTRY TREATMENT

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The paper presents the results obtained with the product BIOLEN IS 80. BIOLEN IS 80 represents a biological activator, based on selected bacteria used in the treatment of waste waters from the pulp and paper industry.

The conclusion of the trials is that a better result is obtained for BIOLEN IS 80 application on waste waters from paper manufacturing (diminishing of BOD with

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Копія доповіді

“Гексафторосиликаты ариламмония: синтез, кристаллические структуры, физико-химические свойства”

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XXII МЕЖДУНАРОДНАЯ ЧУГАЕВСКАЯ КОНФЕРЕНЦИЯ ПО КООРДИНАЦИОННОЙ ХИМИИ

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Тридентатную координацию [AlL_3] мы наблюдали для изоструктурных соединений состава [$Cd\{AlL_3\}(CH_3OH)\{NO_3\}_2$] · $2CHCl_3$ и [$Cd\{AlL_3\}Br_2$] · $2CHCl_3$. В них компактные гетерометальные квадраты соседствуют с открытыми областями с размерами 7×12 Å, и их стабилизируют. Образование плотных гетерометальных квадратов не происходит при замене октаэдрического ц.а. на тетраедрический, например, в структуре [$(CdJ_2)_3\{AlL_3\}_2$], организованы восьмиугольники, которые обобщаются по двум ребрам.

Таким образом, использованный нами постадийный подход позволяет осуществить синтез гетерометальных координационных полимеров оригинального строения, в том числе открытых координационных каркасов, содержащих поры значительного размера.

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ГЕКСАФТОРОСИЛИКАТЫ АРИЛАММОНИЯ: СИНТЕЗ, КРИСТАЛЛИЧЕСКИЕ СТРУКТУРЫ, ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА

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Соединения кремнефтороводородной кислоты (КФК) с органическими основаниями – фторосиликаты соответствующих «ониевых» катионов, представляют интерес как фунгициды, противокариесные препараты, реагенты в синтезе комплексов тетрафторида кремния, «контейнеры» фтороводорода и тетрафторида кремния; обсуждается возможность их использования в качестве ионных жидкостей [1]. В отличие от алкиламмонийных аналогов, гексафторосиликаты ариламмония изучены в заметно меньшей степени. Цель настоящей работы – синтез, изучение структурных характеристик и свойств гексафторосиликатов 2- и 4-замещенных производных фениламмония.

Продуктами взаимодействия 45 %-ной КФК и метанольных растворов $RC_6H_4NH_2$ (R = 2-CH_3, L^1; 2-CH_3O, L^2; 2-Cl, L^3; 2-Br, L^4; 2-NO_2, L^5; 2-COOH,

L^n; **2-COOCH$_3$**, L^7; 2-NH_2, L^8; 4-COOH, L^9; 4-SO_2NH_2, L^{10}) являются кристаллические гексафторосиликаты состава $(LH)_2SiF_6$, за исключением соединений $(L^8H_2)SiF_6$ и $(L^9H)_2SiF_6 \cdot 4H_2O$. В масс-спектрах синтезированных соединений регистрируются пики молекулярных ионов M^+_L и продуктов их фрагментации, а также иона SiF_3^+ (*m/z* = 85). Строение комплексов $(L^7H)_2SiF_6$ (I), $(L^8H_2)SiF_6$ (II), $(L^9H)_2SiF_6 \cdot 4H_2O$ (III) и $(L^{10}H)_2SiF_6$ (IV) установлено методом РСА.

Структура I состоит из центросимметричных анионов SiF_6^{2-} и катионов L^7H^+; каждая NH_3^+-группа катиона является донором трех Н-связей: внутрикатионной NH···O (N···O 2.773(2), 3.192(2) Å) и двух межионных NH···F (N···F 2.763(2), 2.855(2) Å). Интервал расстояний Si–F – 1.659(1)–1.700(1) Å, причем проявляется известная тенденция: более короткие расстояния Si–F наблюдаются для атомов фтора, вовлеченных в более слабые Н-связи [1, 2].

В структуре II катионы $L^8H_2^{2+}$ и анионы SiF_6^{2-} объединены Н-связями NH···F вилочного типа (N···F 2.865(2)–2.967(2) Å). Общая топология структуры представляет собой двумерную сетку, в узлах которой чередуются катионы $L^8H_2^{2+}$ и анионы SiF_6^{2-}; каждая из структурных единиц взаимодействует с пятью соседями. Длины связей Si–F находятся в пределах 1.6709(12)–1.6958(12) Å. Как и в случае комплекса I, обнаружена корреляция между расстояниями Si–F и прочностью Н-связей NH···F.

Структуры III и IV состоят из катионов L^9H^+, $L^{10}H^+$ и анионов SiF_6^{2-} (в III входят также молекулы воды). Геометрия анионов SiF_6^{2-} в III и IV необычно мало отличается от правильной октаэдрической (расстояния Si–F равны 1.660(2)–1.675(2) и 1.683(1), 1.684(1) Å соответственно, углы $F_{транс}$–Si–$F_{транс}$ – 180.0(3) ° в III и IV, углы $F_{цис}$–Si–$F_{цис}$ отклоняются от 90 ° на 1.2(1) ° в III и на 0.5(1) ° в IV), несмотря на участие, как и в II, всех атомов фтора в сильных Н-связях типа NH···F (III, IV) и OH···F (III) [3]. Катионы L^9H^+ и объединенные в димеры молекулы воды (O···O 2.893(3) Å) образуют цепочки посредством Н-связей OH···O; аналогичную цепочечную структуру формируют катионы $L^{10}H^+$ на основе Н-связей NH···O.

Судя по данным ИК-спектроскопии, аналогичное ионное строение имеют соединения КФК с L^1–L^6. Колебания $\nu_{as,s}(NH_3^+)$ проявляются в области 3190–2600 см$^{-1}$, ν(SiF) – 770–700 см$^{-1}$, $\delta(SiF_2)$ – 480–415 см$^{-1}$; заметное низкочастотное смещение полос $\nu_{as,s}(NH_3^+)$ по сравнению с положением полос $\nu_{as,s}(NH_2)$ в ИК-спектрах исходных L^1–L^6 может указывать на включение NH_3^+-групп в прочные Н-связи NH···F, а мультиплетный характер поглощения ν(SiF) и $\delta(SiF_2)$ – на понижение симметрии анионов SiF_6^{2-} относительно правильной O_h.

Значения растворимости солей в воде при 25 °С в мас. % составляют (в скобках указано соответствующее основание): 19,1 (L^1); 56,6 (L^2); 27,9 (L^3); 32,4 (L^4); 2,7 (L^5); 10,3 (L^6); 25,6 (L^8); 1,8 (L^9); 1,5 (L^{10}). Растворимость соединения II в системе КФК – L^8 – H_2O при 25 °С изменяется вдоль линии кристаллизации в пределах 50,15–14,65 мас. %. Очевидно, соли подверга-

ются гидролизу, что подтверждается данными pH-метрии и наглядно обнаруживается при растворении в воде $(L^7H)_2SiF_6$ – образуется вторая жидкая фаза, L^7:

$$(L^7H)_2SiF_6 + 5H_2O \rightarrow 2L^7 + 3H_3O^+ + 3HF_2^- + SiO_2.$$

Результаты термогравиметрии указывают на одностадийную схему термолиза гексафторосиликатов $(LH)_2SiF_6$ (L = L^1–L^4, L^6) с полным выделением компонентов в газовую фазу:

$$(LH)_2SiF_{6\,(тв)} \rightarrow SiF_{4\,(г)} + 2HF_{(г)} + 2L_{(г)}.$$

Разложение соли $(L^5H)_2SiF_6$ сопровождается выделением жидкого 2-нитроанилина с его последующей окислительной деструкцией; термолиз соли фенилендиаммония $(L^8H_2)SiF_6$ протекает ступенчато с последовательным элиминированием в газовую фазу фтороводорода (140–175 °C), SiF_4 (210–225 °C) и паров L^8 (260 °C):

$$(L^8H_2)SiF_{6\,(тв)} \rightarrow SiF_4 \cdot L^8_{(тв)} + 2HF_{(г)},$$
$$SiF_4 \cdot L^8_{(тв)} \rightarrow SiF_{4\,(г)} + L^8_{(ж)}; L^8_{(ж)} \rightarrow L^8_{(г)}.$$

Относительная термическая устойчивость солей уменьшается в следующем ряду (L^* – анилин [4]; в скобках указаны температуры начала термолиза t_0, °C):

$(L^*H)_2SiF_6$ (190) > $(L^2H)_2SiF_6$ (175) > $(L^6H)_2SiF_6$ (140) ≈ $(L^1H)_2SiF_6$ (135) > $(L^3H)_2SiF_6$ (125) ≈ $(L^4H)_2SiF_6$ (125) > $(L^5H)_2SiF_6$ (100),

который в целом согласуется с порядком изменения показателей основности pK_a соответствующих аминов:

L^* (4,58) > L^2 (4,49) > L^1 (4,39) > L^3 (2,64) ≈ L^4 (2,60) > L^6 (2,11) > L^5 (–0,29).

Аналогичная взаимосвязь между температурами начала термолиза t_0 солей и pK_a аминов проявляется и в случае соединений КФК с 4-замещенными производными анилина [4].

Обсуждается эффект H-связей в термохимических и гидролитических превращениях «ониевых» гексафторосиликатов.

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Копія доповіді

“Состав и структура фторокомплексов ниобия(V) и тантала(V) с [0.6]- и [1.5]дибензокраун-6-эфирами”

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XXII МЕЖДУНАРОДНАЯ ЧУГАЕВСКАЯ КОНФЕРЕНЦИЯ ПО КООРДИНАЦИОННОЙ ХИМИИ

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г. Кишинёв
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Тезисы докладов.

СОСТАВ И СТРУКТУРА ФТОРОКОМПЛЕКСОВ НИОБИЯ(V) И ТАНТАЛА(V) С [0.6]- И [1.5]ДИБЕНЗОКРАУН-6-ЭФИРАМИ

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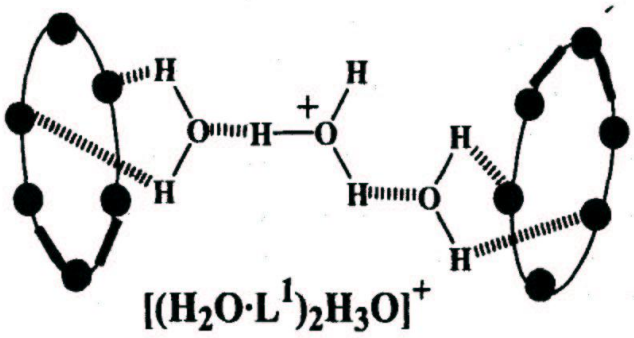
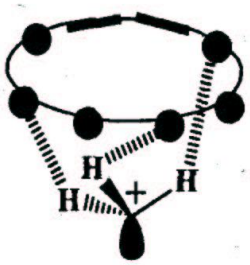
Процессы комплексообразования в системах HMF_6 (M = Nb, Ta)- краун-эфир - H_2O интересны как модели экстракционного выделения (концентрирования) указанных элементов из кислых фторидных растворов. В докладе обсуждаются состав и структура гексафторидных комплексов Nb(V) и Ta(V) с [1.5]дибензо-18- (L^1) и [0.6]дибензо-20-краун-6 (L^2), отличающихся не только строением и размером макроцикла, но и соотношением «алифатических» и «ароматических» атомов кислорода – 3:3 и 4:2, соответственно. Кристаллические комплексы $[(H_2O{\cdot}L^1)_2(H_3O)MF_6]$ (M = Nb, **I**; Ta, **II**) и $[(H_3O{\cdot}L^2)MF_6]$ (M = Nb, **III**; Ta, **IV**) получены взаимодействием растворов оксидов M_2O_5 в 45%-ной HF с метанольными растворами L^1 и L^2.



$[(H_2O{\cdot}L^1)_2H_3O]^+$



$[L^2{\cdot}H_3O]^+$

Согласно данным РСА, катионы комплексов **I** и **II** являются ассоциатами двух макроциклов, центрированных молекулами воды и мостиковым ионом гидроксония посредством Н-связей. В катионах комплексов **III** и **IV** реализуется характерная триподная Н-связь иона H_3O^+ с макрогетероциклом.

Во всех четырех комплексах геометрия фторометаллатных анионов MF_6^- лишь незначительно отличается от правильной октаэдрической, а CH···F взаимодействия ответственны за трехмерную архитектуру.

Додаток 26

Копія доповіді

“Супрамолекулярные соединения фторокомплексов бора(III) с макроциклическими лигандами”

Российская Академия наук
Институт общей и неорганической химии им.Н.С.Курнакова

Академия наук Молдовы
Институт химии

XXII МЕЖДУНАРОДНАЯ ЧУГАЕВСКАЯ КОНФЕРЕНЦИЯ ПО КООРДИНАЦИОННОЙ ХИМИИ

20-24 июня 2005 года

ТЕЗИСЫ ДОКЛАДОВ

г. Кишинёв
XXII Международная Чугаевская конференция по координационной химии.
20-24 июня г. Кишинёв.
Тезисы докладов.

СУПРАМОЛЕКУЛЯРНЫЕ СОЕДИНЕНИЯ ФТОРОКОМПЛЕКСОВ БОРА(III) С МАКРОЦИКЛИЧЕСКИМИ ЛИГАНДАМИ

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Эфират трифторида бора – реагент, широко используемый в практике органического синтеза, взаимодействует с краун-эфирами в незащищенной от влаги атмосфере с образованием кристаллических комплексов «гость-хозяин», состав которых зависит от строения лиганда. Краун-эфиры с симметрично экранированными сторонами плоскости макроцикла (15-краун-5, L^1; 18-краун-6, L^2; *цис-анти-цис*-дициклогексано-18-краун-6, L^3) образуют молекулярные соединения $[(BF_3 \cdot H_2O) \cdot 2L^1]$ (I), $[(BF_3 \cdot H_2O)_2 \cdot L^2 \cdot 2H_2O]$ (II), $[(BF_3 \cdot H_2O)_2 \cdot L^3]$ (III), в которых в качестве «гостя» стабилизирован малоустойчивый $BF_3 \cdot H_2O$ ($t_{пл.}$ 6 °C). Продукт реакции $BF_3 \cdot OEt_2$ и *цис-син-цис*-дициклогексано-18-краун-6 (L^4) с несимметричным расположением заместителей представляет собой ионный комплекс $[(H_3O \cdot L^4)BF_4]$ (IV). По данным РСА, компоненты комплексов II, III и катиона комплекса IV объединены системами Н-связей типа OH···O (O···O 2,65–2,85; 2,589–2,642; 2,624–2,650 Å соответственно).

Протонирующиеся в кислой среде азамакроциклы – рацемат 5,7,7,12,12,14-гексаметил-1,4,8,11-тетраазоциклотетрадекана (L^5), 1,4,7,10,13,16,19,22,25,28-декаазациклотриаконтан (L^6) и N,N′-дибензильное производное 1,10-диаза-18-краун-6 (L^7) образуют ионные тетрафтороборатные комплексы $[(L^5H_2)(BF_4)_2 \cdot H_2O]$ (V), $[(L^6H_{10})(BF_4)_{10} \cdot 10H_2O]$ (VI), $[(L^7H_2)(BF_4)_2 \cdot 3H_2O]$ (VII) с двух- и десятизарядными катионами. Структуры V-VII стабилизированы системами Н-связей с участием атомов фтора, молекул воды, NH_n-групп (n = 1, 2) и O-атомов макроцикла (VII). В VI восемь молекул воды формируют гидратную оболочку азамакроцикла за счет Н-связей типа NH···O (N···O 2,689–2,930 Å), конкурируя с анионами BF_4^- за место в его второй координационной сфере. Обсуждаются детали строения и термохимических превращений комплексов.

Додаток 27

Копія доповіді

“The composition and structure of the niobium (V)and tantalum (V) fluoride complexes with [1.5]- and [0.6]dibenzocrown-6 ethers”

DRESDEN, GERMANY • JULY 17 – 21, 2005



XXX International Symposium on Macrocyclic Chemistry

PROGRAMME AND ABSTRACTS



TECHNISCHE UNIVERSITÄT DRESDEN

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B 45

The composition and structure of the niobium (v) and tantalum (v) fluoride complexes with [1.5]- and [0.6]dibenzocrown-6 ethers

Ed. V. Ganin[1], V.O. Gelmboldt[2], A.A. Ennan[2], M.S. Fonari[3], Yu.A. Simonov[3], J. Lipkowski[4], S.A. Kotlyar[5] and G.L. Kamalov[5]

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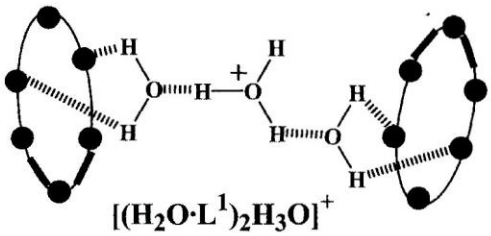
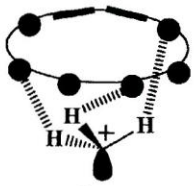
The processes of the complex formation in the systems of HMF_6 (M = Nb, Ta) – crown ether - H_2O are interesting as the models of the extraction (separation) or concentration of the listed elements from the acid fluoride solutions.

In this report the composition and structure of the Nb(V) and Ta(V) hexafluoride complexes with [1.5]dibenzo-18-crown-6 (L^1) and [0.6]dibenzo-20-crown-6 (L^2) are discussed. These ligands distinguish not only by the composition and size of the macrocycle, but also by the ratio of "aliphatic" and "aromatic" oxygen atoms, i.e. 3:3 and 4:2, correspondingly. The crystalline complexes $[(H_2O{\cdot}L^1)_2(H_3O)MF_6]$ (M = Nb, **I**; Ta, **II**) and $[(H_3O{\cdot}L^2)MF_6]$ (M = Nb, **III**; Ta, **IV**) were obtained by the interaction of the M_2O_5 oxide solutions in the 45 % HF with methanol solutions of L^1 and L^2.



$[(H_2O{\cdot}L^1)_2H_3O]^+$



$[L^2{\cdot}H_3O]^+$

According to the X-ray data, the complex cations **I** and **II** represent themselves the five-member associates of two macrocycles, centered by the means of H-bonds by water molecules and the hydroxonium bridge ion. In the complex cations **III** and **IV** the typical "tripod" arrangement of the H_3O^+ ion within the macrocyclic cavity is realized. In all complexes discussed herein the geometry of the MF_6^- fluorometallate anions is just slightly distinguishing from the ideal octahedral, and the C-H...F interactions are responsible for the supramolecular architecture.

Додаток 28

Копія доповіді

“"[1.5]dibenzo-18-crown-6, convenient template for the supramolecular assemblages sustained by Classic and weak H-bonds”

DRESDEN, GERMANY • JULY 17 – 21, 2005



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TECHNISCHE UNIVERSITÄT DRESDEN

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B 54

[1.5]dibenzo-18-crown-6, convenient template for the supramolecular assemblages sustained by Classic and weak h-bonds

M.S. Fonari[1], Ed.V. Ganin[2], Yu.A. Simonov[1], G. Bocelli[3], S.A. Kotlyar[4] and G.L. Kamalov[4]

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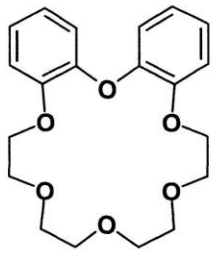
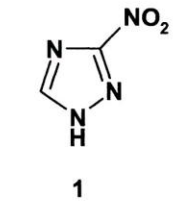
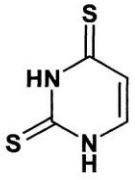
[1.5]Dibenzo-18-crown-6 (**CE**) forms the H-bonded supramolecular complexes with 3-nitro-1,2,4-triazole (**1**, ratio 1:1), pyrimidine-2,4(1*H*,3*H*)-dithione (**2**, ratio 1:1), 1,2,5-oxadiazole-3,4-diamine (**3**, monohydrate of 1:1:1 ratio), dithiooxamide (**4**, ratio 1:1), hydrazine-1,2-dicarbothioamide (**5**, ratio 2:3), all of which are complementary to **CE** in terms of hydrogen bonding and can therefore act as co-crystal formers.



CE



1



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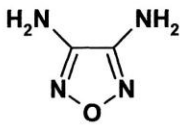

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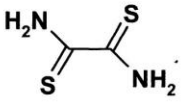

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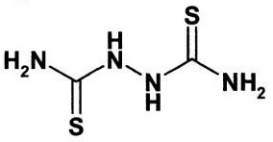

5

The **CE** complexes with **1** and **2** both are discrete molecular adducts, while in **CE** – **3** – water and **CE** – **4** complexes the components are combined in the different tapes. In the **CE** complex with **5**, the components (due to numerous NH...O and NH...S interactions) are bonded into the 3D network.

In all cases, the competition of the O-containing macrocyclic H-acceptor with H-acceptor (O and S) centers in the neutral molecules **1-5** results in the substitution of the part of H-bonded supramolecular homosynthons by the supramolecular heterosynthons and change of the supramolecular architecture.

Додаток 29

Копія доповіді

“Oxonium complexes of biphenyl-20-crown-6 and [1.5]dibenzo-18-crown-6 ”

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International Laboratory of Superconductivity and Solid State Electronics
Institute of Applied Physics of the Academy of Sciences of Moldova
Institute of Chemistry of the Academy of Sciences of Moldova
Institute of Physical Chemistry, Polish Academy of Sciences
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Moldavian Physical Society



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Program & Abstracts

Chişinău, R. Moldova, October 10-12, 2005

P13 **OXONIUM COMPLEXES OF BIPHENYL–20–CROWN–6 AND [1.5]DIBENZO–18–CROWN–6**

M.S.Fonari[1], Yu.A.Simonov[1], Ed.V.Ganin[2], V.O.Gelmboldt[3], L.V.Koroeva[3], A.A.Ennan[3], S.A.Kotlyar[4], G.L.Kamalov[4]

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As a part of our systematic investigations of the crown ethers in the complex formation with inorganic fluorides we obtained the crystalline products of interaction in the systems Me_2O_5 (Me = Nb, Ta) – HF – H_2O – L, where L – 20- or 18-membered crown ether, diphenyl-20-crown-6 (L^1) and [1.5]dibenzo-18-crown-6 (L^2). The new compounds with the composition $[(H_3O\cdot L^1)MeF_6]$ (Me = Nb, **I**; Ta, **II**) and $[(H_2O\cdot L^2)_2(H_3O)MeF_6]$ (Me = Nb, **III**; Ta, **IV**) were characterized by microanalysis, IR spectroscopy and X-ray structure analysis.

According to the X-ray data, compounds **I** and **II** are isostructural. Complexes **III** and **IV** are crystallized in the same space group, but with the different unit cell dimensions. The oxonium cation in **I** and **II** centers the crown cavity through a near-ideal "tripod" arrangement of OH···O H-bonding to alternate crown oxygen atoms. In the case of **III** and **IV** the $H_7O_3^+$ oxonium cation is enclosed inside the case formed by two crown ethers. The presence of oxonium ions in **I–IV** explains the appearance in the IR spectra ν(OH) and δ(HOH) bands in the ranges 3480 – 3030 and 1685 – 1620 cm^{-1} correspondingly, which diffused contour reflect the realization of the system of H-bonds of the OH···O type The vibrations ν(MeF) in the spectra **I** and **II** exhibit in the form of the very intense bands at 588 and 565 cm^{-1} correspondingly, and in the spectra of **III** and **IV** they are registered at 595 and 560 cm^{-1} Being poor H-bond acceptors, NbF_6^- and TaF_6^-, do not compete with the crown oxygen atoms for the oxonium hydrogen atoms, but are involved in the numerous C–H· · · F short contacts responsible for the expended supramolecular architectures in all the cases.

Додаток 30

Копія доповіді

“Host-Guest” compounds of germanium(IV) fluorocomplexes with macrocyclic ligands”

Academy of Sciences of R. Moldova
International Laboratory of Superconductivity and Solid State Electronics
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Institute of Chemistry of the Academy of Sciences of Moldova
Institute of Physical Chemistry, Polish Academy of Sciences
Institute of Organic Chemistry of the National Academy of Sciences of Ukraine
L. V. Pisarzhevsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine
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Chişinău, R. Moldova, October 10-12, 2005

P9 "HOST-GUEST" COMPOUNDS OF GERMANIUM(IV) FLUOROCOMPLEXES WITH MACROCYCLIC LIGANDS

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According to the ^{19}F NMR data, the GeO_2 solutions in hydrofluoric acid (formally "H_2GeF_6" acid) are characterized by the equilibrium between GeF_6^{2-}, $[GeF_5(H_2O)]^-$, *cis*-, *trans*-$GeF_4 \cdot 2H_2O$, and probably $[GeF_3(OH) \cdot 2H_2O]$ forms [1]. The crystalline complexes $[(trans\text{-}GeF_4 \cdot 2H_2O) \cdot L^1 \cdot H_2O]$(I), $[(trans\text{-}GeF_4 \cdot 2H_2O) \cdot L^2 \cdot 2H_2O]$ (II), $(L^3H_2)[GeF_5(H_2O)]_2$ (III), $(L^4H_2)GeF_6 \cdot 4H_2O$ (IV) have been obtained by the interaction in systems GeO_2 – HF – H_2O – L (L^1, 15-crown-5; L^2, 18-crown-6; L^3, 1,10-diaza-18-crown-6; L^4, *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). The complexes where characterized by chemical analysis, IR-spectroscopy and X-ray single crystal analysis (II – IV).

The structures of the complexes are stabilised by the systems of OH· · · O, NH· · · F, NH· · · O, and OH· · · F hydrogen bonds. For the [*trans*-$GeF_4 \cdot 2H_2O$] fragment in II the polyhedron symmetry is close to D_{4h} (Ge–F 1.763(2), 1.764(2) Å; Ge–O 1.927(2) Å). In complex III the shortest Ge–F distance, 1.738(2) Å, is observed for the Ge–F bond located *trans* to a water molecule (Ge–O 1.966(3) Å). The ν(GeF) vibrations in the IR spectra of I, II and III are identified at 630, 585 cm^{-1} and 630, 582, 560 cm^{-1} respectively. Complex IV was obtained in two polymorph forms, triclinic (space group $P\bar{1}$) and monoclinic (space group $P2_1/c$). In both forms the slightly distorted GeF_6^{2-} octahedron is characterized by Ge–F distances in the range 1.732(5) – 1.825(1) Å. Complexes II, III and IV (triclinic form) are isostructural with their silicon analogues. It is interesting to note that the observed stereospecific isolation of the *trans*-diaquatetrafluorocomplex from the mixture of *cis*-, *trans*-isomers in the form of compound II takes place also in the case of system SnF_4 – HF – H_2O – L^2, which contain *cis*-, *trans*- $SnF_4 \cdot 2H_2O$.

1. Buslaev Yu.A., Petrosyants S.P., Tarasov V.P. Zh. Strukt. Khim. 1969. V. 10. № 3. P. 411.

Додаток 31

Копія доповіді

“Closed and open conformations of N,N’-dibenzyl-4,13-diaza-18-crown-6 molecule in the complexes with charged and neutral species”

Academy of Sciences of R. Moldova
International Laboratory of Superconductivity and Solid State Electronics
Institute of Applied Physics of the Academy of Sciences of Moldova
Institute of Chemistry of the Academy of Sciences of Moldova
Institute of Physical Chemistry, Polish Academy of Sciences
Institute of Organic Chemistry of the National Academy of Sciences of Ukraine
[illegible]ogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine
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P1 CLOSED AND OPEN CONFORMATIONS OF *N,N'*-DIBENZYL 4,13 DIAZA-18-CROWN-6 MOLECULE IN THE COMPLEXES WITH CHARGED AND NEUTRAL SPECIES

S.S. Basok[1], L. Croitoru[2], M.S. Fonari[3], Ed.V. Ganin[4], J. Lipkowski[5], Yu A. Simonov[1]

[1]*A.V. Bogatsky Physico-Chemical Institute, National Academy of Science of Ukraine, Odessa, Ukraine,*
[2]*Tiraspol State University, Chisinau, R. Moldova*
[3]*Institute of Applied Physics Academy of Sciences of R. Moldova, Chisinau, R. Moldova*
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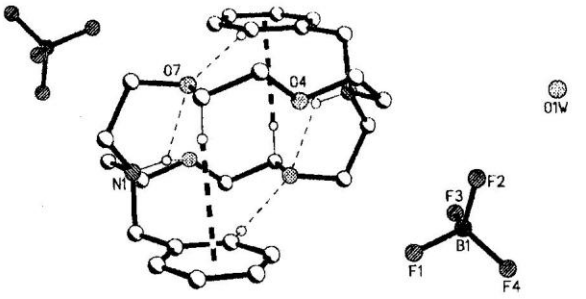
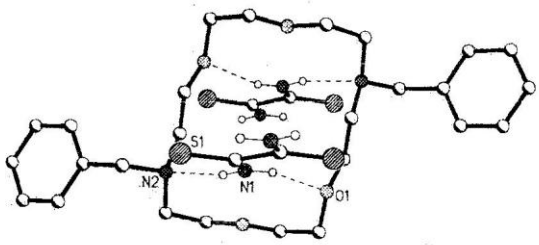
The crown ether family of macrocyclic compounds has attracted a huge amount of interest since their discovery in 1967[1,2], especially in the fields of host–guest and coordination chemistry. In the course of studying the coordination properties of macrocyclic ligands, and in particular *N,N'*-disubstituted diaza-18-crown-6, the exciting interactions have surfaced. For example, in *N,N'*-dibenzyl-diaza-18-crown-6 (DD18C6) complexes, a range of C–H···O and C–H···N interactions significantly affect the conformation of the macrocyclic ring and the ability of the crown to bind ions and neutral molecules.

Recently reported the X-ray crystal structure of $(H_2\text{-DD18C6})^{2+}2(BF_4)^-H_2O$ (I)[3], revealed the unusual C–H···π interactions between the phenyl substituents and two macrocyclic methylene protons that govern the overall conformation of the macrocycle. The geometry of the azacrown ring is close to planar and exhibits a degree of rigidity not normally observed for non-coordinated crown ether molecules such as this. This rigidity stems from the presence of C–H···π interactions between two methylene hydrogens and the aromatic substituents (Fig. 1), which effectively anchor the ring into its present conformation and inhibits flexing, which has often been observed with macrocycles of this type. This type of interaction is quite unusual in that a methylene hydrogen is participating in this interaction, rather than the hydrogen of a water molecule.



As a part of our investigation, the X-ray crystal structures of 1:2 complexes of DD18C6 host with dithioxamide, $H_2NC(=S)C(=S)NH_2$ (complex II) and *p*-nitrobenzenesulphamide, $O_2NPhSO_2NH_2$ as the guests (complex III) were obtained, revealing the hydrogen bonding between the components. The conformation of the azacrown ether in II (Fig. 2) and in III differs significantly from the previous example. The four oxygen heteroatoms lie in the same general plane, however, the two nitrogens extend out in a trans fashion from this plane, distorting the ends of the macrocycle to such an extent that they almost fold back over the azacrown ring. The two benzyl substituents extend horizontally away from the macrocyclic ring, and are coplanar in a similar fashion to the uncoordinated ligand[3].



1. Pedersen, C. J. *J. Am. Chem. Soc.*, **1967**, *89*, 7017.
2. Pedersen, C. J. *J. Am. Chem. Soc.*, **1967**, *89*, 2495.
3. S.S. Basok, L. Croitoru, M.S. Fonari, Ed.V. Ganin, V.O. Gelmboldt, J. Lipkowski, Yu.A. Simonov *Acta Cryst.* **2005**. *C61*, o188–o192.

Додаток 32

Копія доповіді

“Supramolecular archetecture in the co-crystal of azacrown ether and azamacrocycle with salicilic acide”

Academy of Sciences of R. Moldova
International Laboratory of Superconductivity and Solid State Electronics
Institute of Applied Physics of the Academy of Sciences of Moldova
Institute of Chemistry of the Academy of Sciences of Moldova
Institute of Physical Chemistry, Polish Academy of Sciences
Institute of Organic Chemistry of the National Academy of Sciences of Ukraine
[illegible]ogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine
Moldavian Physical Society



MOLDAVIAN - POLISH - UKRAINIAN

SYMPOSIUM

ON SUPRAMOLECULAR CHEMISTRY

Program & Abstracts

Chişinău, R. Moldova, October 10-12, 2005

P12 SUPRAMOLECULAR ARCHITECTURE IN THE CO-CRYSTALS OF AZACROWN ETHERS AND AZAMACROCYCLE WITH SALICYLIC ACID

M.S. Fonari[1], V.Ch. Kravtsov[1], Yu.A. Simonov[1] S.S. Basok[2], Ed.V. Ganin[3]

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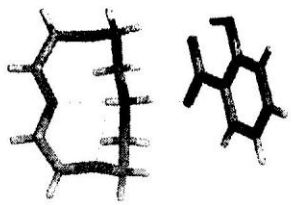
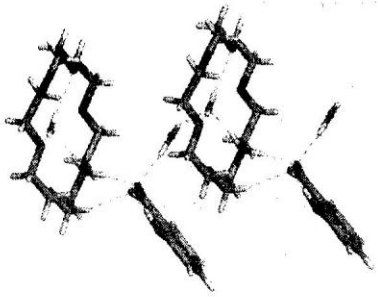
Crystalline self-assemblies represent promising delivery modularity for improving drug solubility, dissolution rate, stability and bioavailability. Supramolecular synthesis may be explored to obtain new pharmaceuticals from known active pharmaceutical ingredients and pharmaceutically accessible co-crystal formers. The interaction of monoaza-12-crown-4 (**1**), monoazamonobenzo-15-crown-5 (**2**), monoaza-18-crown-6 (**3**), diaza-18-crown-6 (**4**) and *meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**5**) with salicylic acid (**SA**) results in the protonation of amine functionality of the macrocycles by **SA** and formation in the crystals of anhydrous salt-like adducts of 1:1 ratio for **1** and **2** and of 1:2 ratio for **5**. The macrocycles **3** and **4** form di- and tri-hydrates, respectively.

In the *binary adducts* the components are held together by charge-assisted $NH^+\cdots O(COO^-)$ hydrogen bonds between ammonium and carboxylate functionalities. The supramolecular architecture is sustained by the combination of N-H· · · O and C-H· · · O interactions. In the *ternary complexes* two membered water cluster joins the neighboring azonia-salicylate supramolecular associates in the chains *via* OH(water)· · · O(COO^-) hydrogen bonds.



1·**SA** supramolecular complex



3·**SA**·**2H$_2$O** supramolecular complex

Acknowledgement: Authors from Moldova are indebted to MRDA(Moldova) – CRDF(USA) (MRDA-008 : BGP-III award MOC2-3063-CS-03) for financial support.

Додаток 33

Копія доповіді

“[1.5]Dibenzo-18crown-6 convenient template fpr the supramolecular assemblages sustained by classic and weak H-bonds”

Academy of Sciences of R. Moldova
International Laboratory of Superconductivity and Solid State Electronics
Institute of Applied Physics of the Academy of Sciences of Moldova
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Moldavian Physical Society



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SYMPOSIUM

ON SUPRAMOLECULAR CHEMISTRY

Program & Abstracts

Chişinău, R. Moldova, October 10-12, 2005

P11 [1.5]DIBENZO-18-CROWN-6, CONVENIENT TEMPLATE FOR THE SUPRAMOLECULAR ASSEMBLAGES SUSTAINED BY CLASSIC AND WEAK H-BONDS

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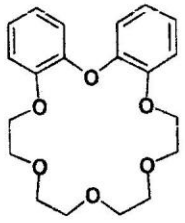
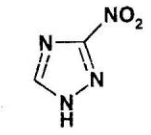
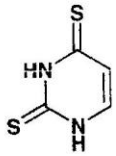
[1.5]Dibenzo-18-crown-6 (**CE**) forms the H-bonded supramolecular complexes with 3-nitro-1,2,4-triazole (**1**, ratio 1:1), pyrimidine-2,4(1*H*,3*H*)-dithione (**2**, ratio 1:1), 1,2,5-oxadiazole-3,4-diamine (**3**, monohydrate of 1:1:1 ratio), dithiooxamide (**4**, ratio 1:1), hydrazine-1,2-dicarbothioamide (**5**, ratio 2:3), all of which are complementary to **CE** in terms of hydrogen bonding and can therefore act as co-crystal formers.



CE



1



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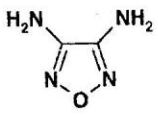

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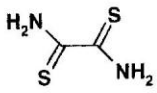

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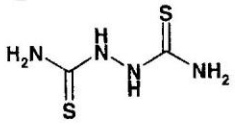

5

The **CE** complexes with **1** and **2** both are discrete molecular adducts, while in **CE** – **3** – water and **CE** – **4** complexes the components are combined in the different tapes. In the **CE** complex with **5**, the components (due to numerous NH...O and NH...S interactions) are bonded into the 3D network.

In all cases, the competition of the O-containing macrocyclic H-acceptor with H-acceptor (O and S) centers in the neutral molecules **1-5** results in the substitution of the part of H-bonded supramolecular homosynthons by the supramolecular heterosynthons and change of the supramolecular architecture.

Додаток 34

Копія статті

“Структурные аспекты взаимодействия кремнефтороводородной кислоты с органическими основаниями”

КООРДИНАЦИОННАЯ ХИМИЯ, 2004, том 30, № 3, с. 211–218

УДК 541.49

СТРУКТУРНЫЕ АСПЕКТЫ ВЗАИМОДЕЙСТВИЯ КРЕМНЕФТОРОВОДОРОДНОЙ КИСЛОТЫ С ОРГАНИЧЕСКИМИ ОСНОВАНИЯМИ

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Поступила в редакцию 18.08.03 г.

Представлены результаты систематических структурных исследований продуктов взаимодействия кремнефтороводородной кислоты (КФК) с органическими основаниями, в составе которых удается стабилизировать различные гидролитически лабильные фторокомплексы кремния. В свете полученных данных обсуждается дискуссионная проблема состояния КФК в водных растворах.

Растворы кремнефтороводородной кислоты (**КФК**) различной концентрации являются крупнотоннажным побочным продуктом предприятий, перерабатывающих фтористое сырье, а также апатиты и фосфориты (производство фосфорных удобрений, фосфорной кислоты, элементного фосфора), и рассматриваются в качестве наиболее перспективного источника фтора для химической промышленности [1, 2]. Как и многие другие комплексные фторокислоты, КФК не существует в индивидуальном состоянии (последняя по времени неудачная попытка изолировать соединение состава H_2SiF_6 принадлежит авторам [3]). Несмотря на более чем полуторавековую историю изучения свойств КФК, вопросы состава присутствующих в ее растворах форм остаются предметом дискуссии [1, 2, 4–9]; до недавнего времени структурно изученными солями КФК оставались лишь гекса- и пентафторосиликаты. В настоящем сообщении представлены результаты систематических исследований строения продуктов взаимодействия КФК с органическими основаниями, в составе которых удается стабилизировать сосуществующие в растворах КФК гидролитически лабильные формы.

Для осуществления взаимодействия с КФК использовали основания следующих классов, отличающиеся природой донорных центров, строением и интервалом значений pK_a: 15- и 18-членные краун-эфиры; 15- и 18-членные азакраун-эфиры; 12- и 14-членные тетраазамакроциклы; гидразиды карбоновых кислот; тиосемикарбазиды.

Наиболее интересными и разнообразными в структурном отношении оказались продукты взаимодействия КФК с краун-эфирами и их частично замещенными аза-аналогами. Полученные соединения относятся к комплексам типа "гость–хозяин" (**Г–Х**) [10] (на основе межмолекулярных Н-связей), в составе которых в зависимости от строения макроциклического лиганда удается стабилизировать анион SiF_6^{2-} и все возможные продукты его гидролитических превращений: $[SiF_5 \cdot H_2O]^-$, SiF_5^-, $SiF_4 \cdot 2H_2O$. Автор [11] отметил дифференцирующее влияние строения краун-эфира на состав связываемого им фторокомплекса кремния: краун-эфиры с эквивалентно стерически экранированными сторонами плоскости макроцикла (15-краун-5 (**15К5**), 18-краун-6 (**18К6**)) селективно извлекают из растворов КФК аквакомплекс *транс*-$SiF_4 \cdot 2H_2O$ с образованием молекулярных соединений [(*транс*-$SiF_4 \cdot 2H_2O$) · 15К5 · H_2O] (**I**) и [(*транс*-$SiF_4 \cdot 2H_2O$) · 18К6 · $2H_2O$] (**II**) [12].

По данным РСА, компоненты структуры II – *транс*-$SiF_4 \cdot 2H_2O$, 18К6 и молекулы H_2O – объединены системой Н-связей OH···O (O···O 2.599(3)–2.870(2) Å); внешнесферные молекулы воды являются мостиками между *транс*-$SiF_4 \cdot 2H_2O$ и 18К6 (рис. 1). Очевидно, аналогичное строение Н-связанного ассоциата имеет и комплекс I, а также описанный в [12] малоустойчивый продукт взаимодействия КФК с 12-краун-4 (**12К4**) вероятного состава [(*транс*-$SiF_4 \cdot 2H_2O$) · 2(12К4)] [13]. Стабилизация комплекса $SiF_4 \cdot 2H_2O$ в составе соединений Г–Х в форме *транс*-изомера согласуется с теоретическими оценками относительной стабильности геометрических изомеров 12-электронных комплексов *p*-элементов [14], учитывающи-

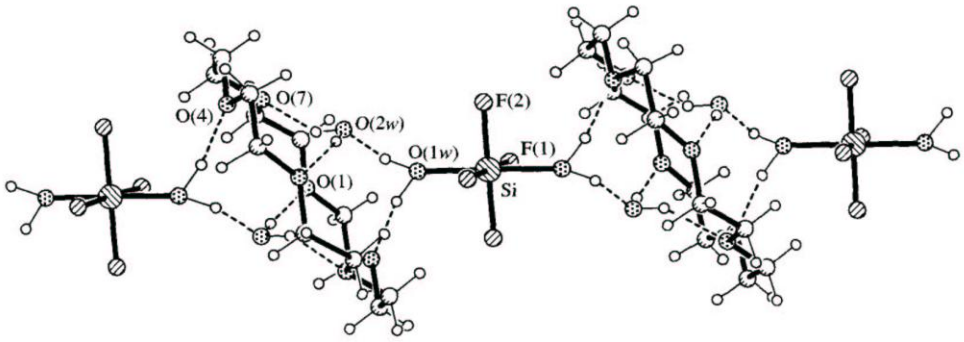
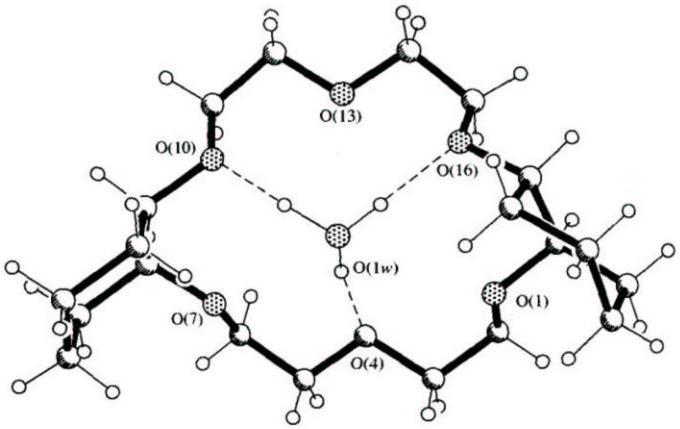


Рис. 1. Фрагмент цепочечной структуры комплекса II.



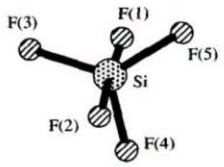


Рис. 2. Строение комплекса III.

ми специфику связывания в комплексах кремния(IV) как легкого непереходного элемента, подтверждается данными ЯМР ^{19}F [6], однако противоречит результатам расчетов *ab initio* комплекса в газовой фазе [15].

Цис-син-цис-изомер дициклогексано-18-краун-6 (**ДЦГ-6А**) с неэквивалентно стерически экранированной плоскостью макроцикла при взаимодействии с КФК образует ионный комплекс $[ДЦГ\text{-}6А \cdot H_3O]SiF_5$ (**III**) [16]. В структуре III (рис. 2) катион гидроксония объединен с каждым вторым атомом О лиганда тремя прочными Н-связями OH···O (O···O 2.615(3)–2.637(3) Å); внешнесферный анион SiF_5^- связан с катионом лишь электростатическими взаимодействиями. По данным спектроскопии ЯМР ^{19}F, ^{29}Si [17], указанное строение соединения $[ДЦГ\text{-}6А \cdot H_3O]SiF_5$ с тригонально-бипирамидальной геометрией аниона сохраняется и в растворе ацетона. Отмеченная в [11] взаимосвязь между строением краун-эфира и составом связываемого им фторокомплекса (молекулярная или ионная форма) имеет, по-видимому, достаточно общий характер, что иллюстрируют данные РСА соединений $[(BF_3 \cdot H_2O)_2 \cdot 18К6 \cdot 2H_2O]$ [18], $[(BF_3 \cdot H_2O)_2 \cdot ДЦГ\text{-}6В]$ (ДЦГ-6В – *цис-анти-цис*-дициклогексано-18-краун-6 с симметрично экраниро-

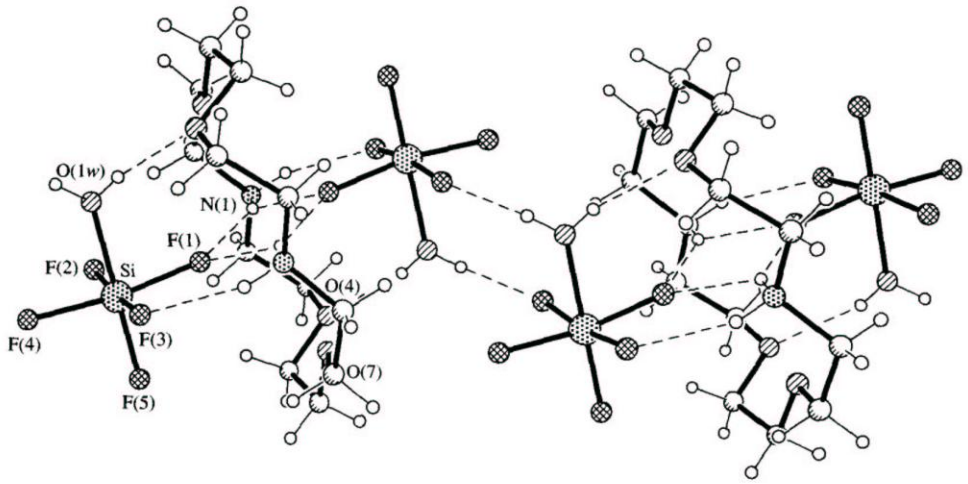


Рис. 3. Строение комплекса V.

ванной полостью макроцикла) [19] и [ДЦГ-6А · · H_3O]BF_4 [20], выделенных из реакционных смесей $BF_3 \cdot OEt_3$–H_2O–краун-эфир. Авторы [16] пришли к заключению, что склонность ДЦГ-6А к образованию комплексов с солями гидроксония однозарядных анионов обусловлена способностью пространственно объемных катионов [ДЦГ-6А · · H_3O]$^+$ формировать в кристалле устойчивый структурный мотив в форме зигзагообразных каналов, в которые могут встраиваться различные "гости" (SiF_5^- [16], BF_4^- [20], ClO_4^- [21]).

Протонирующиеся в кислых средах моноаза-18-краун-6 (**МА18К6**) и 1,10-диаза-18-краун-6 (**ДА18К6**) стабилизируют в составе ионных комплексов Г–Х [(МА18К6Н · H_2O)($SiF_5 \cdot H_2O$) · H_2O] (**IV**) и [(ДА18К6H_2)($SiF_5 \cdot H_2O$)$_2$] (**V**) аквапентафторосиликатные анионы [22], а 1,7-диаза-15-краун-5 (**ДА15К5**) образует комплекс с гексафторосиликатным анионом [(ДА15К5H_2)SiF_6] (**VI**) [23]. Дополнительный вклад в стабилизацию структур комплексов IV–VI, наряду с электростатическими взаимодействиями, вносят системы водородных связей ГН···Х и ХН···Г.

Строение комплекса V показано на рис. 3. Помимо взаимодействий ОН···О (между атомами О макроцикла и координированными молекулами воды) и NH···F, в структуре V реализуются контакты Г···Г типа ОН···F между анионами [$SiF_5 \cdot H_2O$]$^-$ (О···F 2.680(4) Å). В структуре комплекса VI симметрия анионов SiF_6^{2-} понижена до C_{2v} вследствие участия трех из шести фторолигандов в Н-связях NH···F различной прочности (N···F 2.722(3)–2.823(2) Å) (рис. 4). Для сравнения укажем, что взаимодействие КФК с ациклическими аналогами азакраун-эфиров – 3-окса-1,5-диаминопентаном, 3-окса-1,5-N,N'-диметилдиаминопентаном и 3,6-диокса-1,8-диаминооктаном – приводит исключительно к гексафторосиликатам дипротонированных форм аминоподандов [24], охарактеризованных методами ИК-, КР и масс-спектроскопии.

Двенадцатичленные тетраазамакроциклы – 1,4,7,10-тетраазациклододекан (**L^1**), 1,4,7,10-тетрааза-2,6-пиридинофан[12] (**L^2**) – и четырнадцатичленный *мезо*-5,7,7,12,12,14-гексаметил-1,4,8,11-тетраазациклотетрадекан (**L^3**) образуют гидратные формы гексафторосиликатов состава (L^1H_4)$_2$(SiF_6)$_4$ · · $7H_2O$ (**VII**) [25], (L^2H_3)$_2$(SiF_6)$_3$ · $4H_2O$ (**VIII**) [26], (L^3H_4)$_2$(SiF_6)$_4$ · $4H_2O$ (**IX**) [27]. В структуре гептагидрата VII (рис. 5) пять молекул воды посредством прочных Н-связей (О···О 2.806(7)–2.834(6) Å) формируют линейный "кластер", что является редким случаем такого крупного водного ассоциата в гидратных комплексах КФК. Симметрия анионов SiF_6^{2-} в VII близка к C_{4v}.

На рис. 6 показано окружение катиона 1,4,7,10-тетрааза-2,6-пиридинофана [12] в комплексе VIII. Пиридиновый атом азота катиона не протонирован, однако участвует во внутримолекулярной Н-связи NH···N (N···N 2.827(4) Å) с эндоциклически ориентированным атомом водорода группы NH_2. Все эти группы вовлечены в межмолекулярные Н-связи, среди которых доминируют контакты NH···F. Гексафторосиликатные анионы в комплексе VIII имеют слегка искаженное октаэдрическое строение. Находящийся в более симметричном окружении органических катионов и молекул воды анион $Si(2)F_6^{2-}$ симметрии C_2 отличается меньшей степенью искажения (длины связей Si–F в пределах 1.667(3)–1.683(3) Å; углы FSiF отличаются от идеальных не более чем на 0.7°). Для сравнения

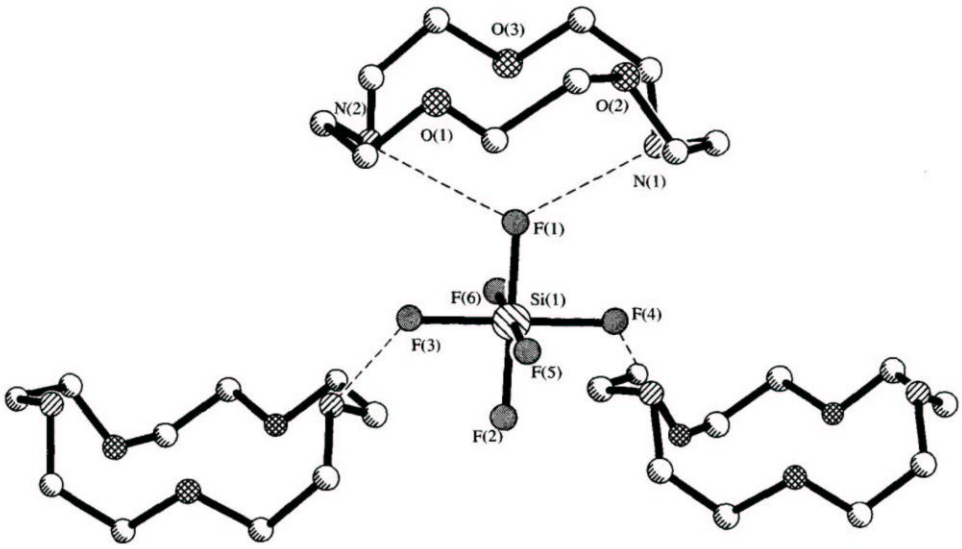


Рис. 4. Фрагмент кристаллической структуры комплекса VI.

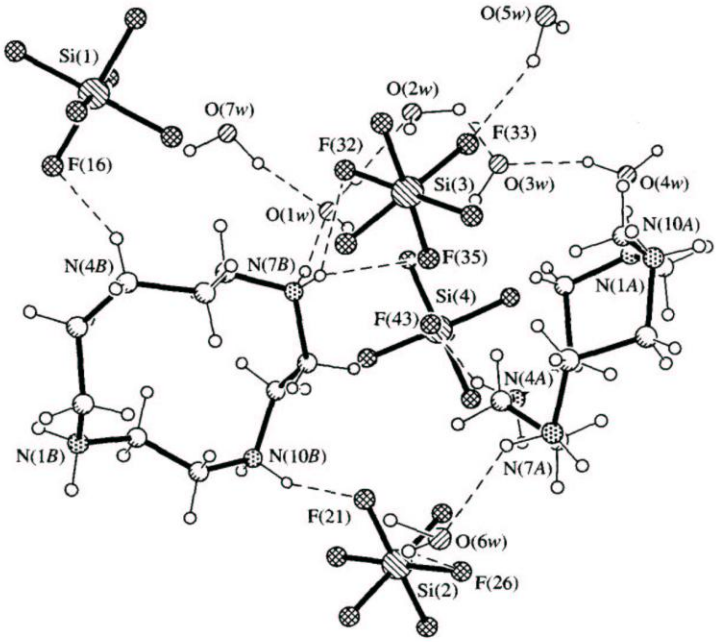


Рис. 5. Строение комплекса VII.

укажем, что в анионе $Si(1)F_6^{2-}$ расстояния Si–F составляют 1.677(2)–1.703(2) Å, а отличие валентных углов FSiF от идеальных значений достигает 2.8°. В целом для продуктов взаимодействия КФК с макроциклическими основаниями характерно образование гидратных форм; участвующие в системах Н-связей молекулы воды выполняют важную структурную функцию, зачастую являясь мостиками между различными фрагментами комплексов.

Взаимодействие КФК с N,O-амбидентатными гидразидами карбоновых кислот [28, 29] и N,S-амбидентатными тиосемикарбазидами [30, 31] приводит к гексафторосиликатам протонированных форм оснований. Центром протонирования явля-

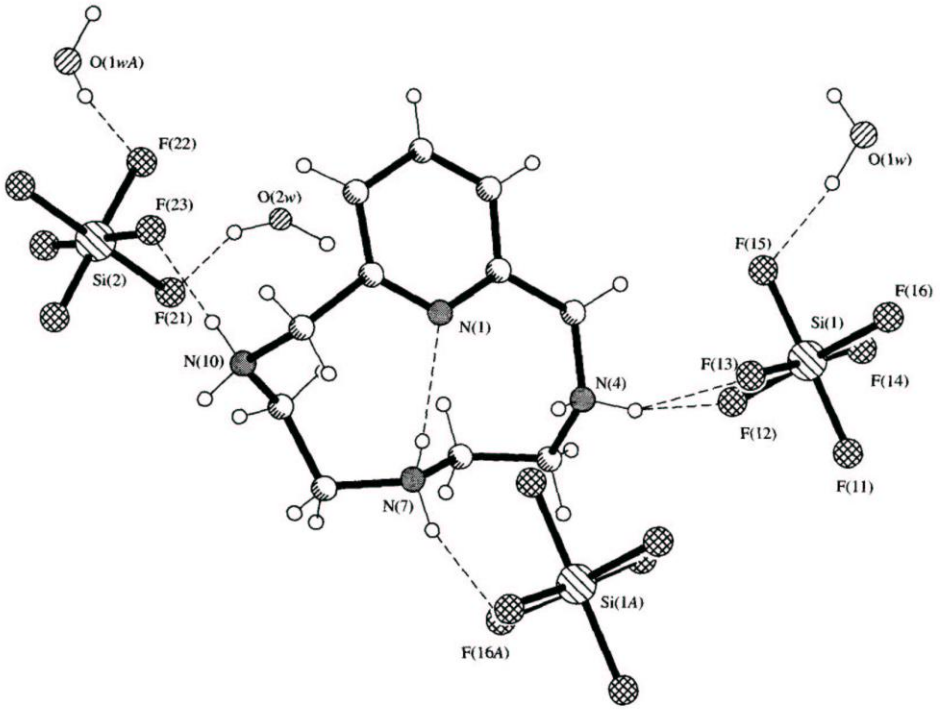


Рис. 6. Окружение катиона 1,4,7,10-тетрааза-2,6-пиридинофана [12] в комплексе VIII.

ется концевой атом азота гидразинового фрагмента, хотя расчеты распределения зарядов на атомах в молекулах гидразидов и тиосемикарбазидов полуэмпирическим методом PM3 указывают на локализацию максимального отрицательного заряда на атомах O и S оснований соответственно [32]. В структуре соединения КФК с гидразидом изоникотиновой кислоты (**L**^{4}) состава $(L^4H_2)SiF_6$ (**X**) [28] протонирован и атом азота пиридинового цикла; все три N-протонодонорных центра катиона участвуют в H-связях с атомами фтора аниона. В то же время в комплексе КФК с гидразидом 5-амино-1-бензил-1,2,3-триазол-4-карбоновой кислоты (**L**^{5}) состава $(L^5H)_2SiF_6 \cdot 3H_2O$ (**XI**), компоненты которого объединены множественными H-связями NH···F, NH···O, OH···F в трехмерный каркас (рис. 7), эндоциклический атом азота пиридинового типа не участвует в протонировании [29].

Особенностью реакции КФК с тиосемикарбазидом (**L**^{6}) является вовлечение части лиганда в процесс циклизации с образованием протонированного по эндоциклическому атому азота 2,5-диамино-1,3,4- тиадиазола (**L**^{7}**H**$^+$), стабилизирующего вместе с L^6H^+ структуру двойного гексафторосиликата $(L^6H^+)_2(L^7H^+)(SiF_6)_{1.5}$ (**XII**) [30]. Компоненты структуры объединены межмолекулярными H-связями NH···F и NH···S. Интересно отметить, что попытка осуществить циклизацию тиосемикарбазида в присутствии хлороводородной кислоты привела к получению продукта его линейной конденсации – гидразодитиоамида. 4-Фенилтиосемикарбазид (**L**^{8}) при контакте с КФК циклизации не подвергается, а образует структурно охарактеризованное соединение $(L^8H)_2SiF_6$ (**XIII**, рис. 8) [31]. В то же время выделить какой-либо кристаллический продукт взаимодействия КФК с менее нуклеофильным 2-фенилтиосемикарбазидом не удалось.

В заключение необходимо сделать ряд общих замечаний. В формировании и стабилизации кристаллических структур соединений II–XIII – продуктов взаимодействия КФК с органическими основаниями различных классов – основная роль принадлежит водородным связям. Для всех структурно изученных комплексов наблюдается диспропорционирование длин связей Si–F фтороанионов в зависимости от того, участвует или нет соответствующий фторолиганд в H-связях и какова прочность последних. Наиболее короткие связи Si–F отмечены для атомов фтора, не вовлеченных в H-связи. В системах H-связей, реализующихся в соединениях N-протонированных органических оснований, превалируют взаимодействия NH···F.

Специфика поведения краун- и азакраун-эфиров при взаимодействии с КФК заключается в формировании систем множественных H-связей

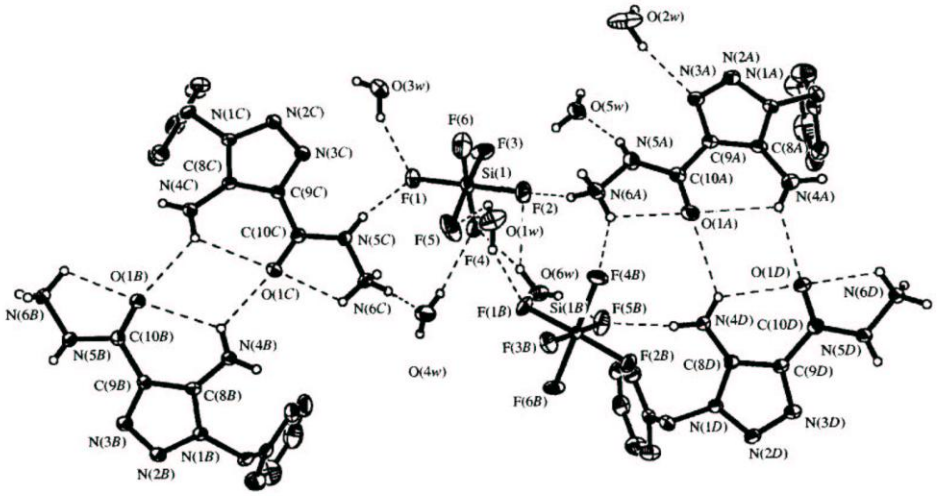


Рис. 7. Независимая часть элементарной ячейки для соединения XI.

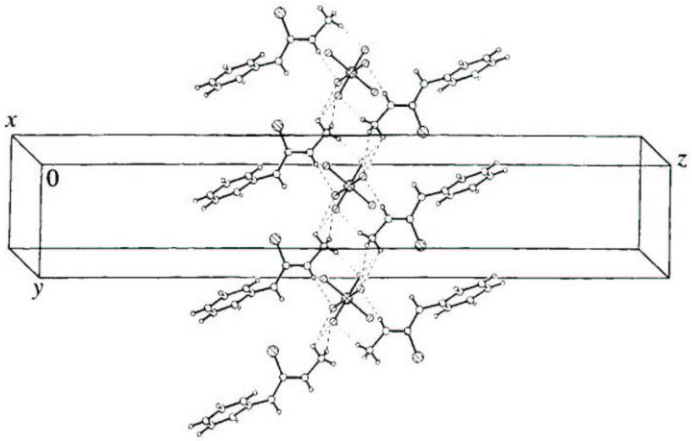


Рис. 8. Ленточная структура комплекса XIII.

между "органической" (X) и "неорганической" (Г) компонентами образующихся комплексов Г–X, позволяющих эффективно стабилизировать в твердой фазе менее симметричные по сравнению с гексафторосиликатным анионом и соответственно более лабильные в поле внешнесферных катионов анионы SiF_5^- и $[SiF_5 \cdot H_2O]^-$ [33], а также неизвестный в индивидуальном состоянии комплекс *транс*-$SiF_4 \cdot 2H_2O$. Приведенные результаты являются структурным аргументом в пользу представлений о растворах КФК как равновесной многокомпонентной системе, включающей анион SiF_6^{2-} и продукты его гидролитических превращений – комплексы $[SiF_5 \cdot H_2O]^-$ и *транс*-$SiF_4 \cdot 2H_2O$ [1, 2, 5, 6], причем комплексы SiF_6^{2-} и $[SiF_5 \cdot H_2O]^-$ присутствуют в КФК в соизмеримых количествах. Существование $[SiF_5 \cdot H_2O]^-$ и *транс*-$SiF_4 \cdot 2H_2O$ в растворах КФК обсуждалось ранее на основании данных спектральных (ЯМР ^{19}F, ИК-), кинетических, потенциометрических и кондуктометрических исследований.

Альтернативная точка зрения [7, 9], основанная преимущественно на данных потенциометрии и предусматривающая безусловное доминирование аниона SiF_6^{2-} в растворах КФК, представляется менее реалистичной. Следует также отметить, что среди продуктов взаимодействия КФК с органическими основаниями не обнаружены соединения полиядерных фторокремниевых анионов, возможность существования которых в растворах КФК обсуждалась в [34, 35]. В частности, авторы

[35] на основании данных гель-хроматографии пришли к выводу о присутствии в растворах технической и реактивной КФК в качестве основной формы соединения состава $H_2Si_2F_{10}$, хотя криоскопические измерения [36] не подтверждают приведенную формулу КФК.

Представленные в [4] результаты ИК-спектроскопического исследования экстрагируемой формы КФК в трибутилфосфате (**ТБФ**) (полосы колебаний ν(SiF) и δ(SiF_2) при 735 и 482 $см^{-1}$ соответственно, аналогичные поглощению в спектрах гексафторосиликатов) послужили одним из аргументов в пользу существования молекулярной формы КФК. Однако подобный характер поглощения наблюдается в ИК-спектрах соединений Г–Х I и II, в которых проявляются колебания ν(SiF) и δ(SiF_2) "гостевого" комплекса *транс*-$SiF_4 \cdot 2H_2O$ [12], а также указанного комплекса в среде сольватирующего ацетона [37]. По мнению авторов [38], именно комплекс $SiF_4 \cdot 2H_2O$ переходит в фазу ТБФ при экстракции кремния из разбавленных растворов КФК. Существование молекулярной формы КФК не нашло подтверждения и в работе [39], авторы которой сравнивали зависимости кажущегося мольного объема и сжимаемости КФК и серной кислоты от концентрации кислоты.

Таким образом, если факт присутствия в растворах КФК гексакоординационных фторокомплексов кремния состава $[SiF_{6-n}(H_2O)_n]^{n-2}$ ($n = 0$–2) можно считать надежно подтвержденным, то возможность существования в таких системах полиядерных фторокомплексов и форм с $n > 2$ [6, 8] продолжает оставаться дискуссионной. Так в частности, в составе продуктов взаимодействия КФК с органическими основаниями не удалось изолировать комплекс предполагаемого состава $[SiF_3(OH) \cdot 2H_2O]$ [6], вклад которого в общий баланс фтора для раствора КФК с $\varphi = \Sigma F/Si \approx 5$, по данным ЯМР ^{19}F, составляет около 3% (для сравнения укажем, что вклад комплекса *транс*-$SiF_4 \cdot 2H_2O$ в это равновесие <5%). Однако нельзя исключить, что расширение ассортимента органических оснований, в частности использование в реакции с КФК функционализированных краун-эфиров с повышенным числом Н-акцепторных и Н-донорных центров, позволит стабилизировать новые малоустойчивые фторидные соединения кремния, реализующиеся в процессе гидролитических превращений гексафторосиликатного аниона.

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Копія статті

“Реакция 1,2,5-тиадиазоло[3,4-d]пиримидин-5,7-дион-2-оксида с водой”

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РЕАКЦИЯ 1,2,5-ТИАДИАЗОЛО[3,4-*d*]ПИРИМИДИН-5,7-ДИОН-2-ОКСИДА С ВОДОЙ

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Выделены и охарактеризованы методом рентгеноструктурного анализа продукты взаимодействия 1,2,5-тиадиазоло[3,4-d]пиримидин-5,7-дион-2-оксида с водой – его дигидрат и 6-амино-2,4-диоксо-1,2,3,4-тетрагидропиримидин-5-сульфамовая кислота.

С момента установления в 1970 г. структуры [1] до настоящего времени N-оксиды 1,2,5-тиадиазолов остаются мало изученным классом соединений. Известно два способа синтеза этих веществ. Первый заключается во взаимодействии монохлорида серы с 1,2-диоксимами, которое приводит к смеси тиадиазолов и их N-оксидов [1, 2]. Второй способ позволяет получить с хорошим выходом 2-оксиды 1,2,5-тиадиазоло[3,4-*d*]пиримидинов по реакции 6-амино-5-нитрозоурацилов с монохлоридом серы в диметилформамиде [3, 4]. В литературе отсутствуют сведения об изучении N-оксидов 1,2,5-тиадиазолов методом рентгеноструктурного анализа. Из химических превращений описан один пример восстановления N-оксида до соответствующего тиадиазола [1], а также два варианта окислительного десульфирования под действием гипохлорита натрия и пероксида водорода [5]. Нами установлено, что 1,2,5-тиадиазол[3,4-*d*]пиримидин-5,7-дион-2-оксид (I) [3] при повышенной температуре вступает во взаимодействие с водой. После непродолжительного нагревания из образовавшегося раствора выделен устойчивый до 140°C кристаллогидрат (II), содержащий две молекулы воды.

Молекула (I) практически плоская (рис. 1). Атомы урацильного цикла копланарны с точностью 0.010 Å, практически в этой же плоскости расположены и карбонильные атомы O^2 [его отклонение от приведенной выше плоскости 0.053(2) Å] и O^3 [–0.045(3) Å]. Атомы тиадиазольного цикла копланарны с точностью 0.005(3) Å, и нитрозильный атом O^1 находится практически в той же плоскости.

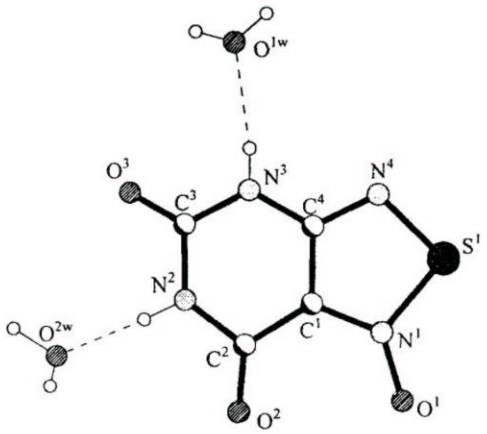

Рис. 1. Вид дигидрата (II) в проекции на плоскость гетероциклического остова молекулы соединения (I).

Диэдральный угол между плоскостями, проведенными через урацильный и тиадиазольный циклы, равен 2.20(1)°. Межатомные расстояния и валентные углы урацильного фрагмента (табл. 1) в целом согласуются с таковыми в 1,2,5-тиадиазоло[3,4-*d*]-пиримидин-5,7-дионе (III) [6]. Значительно более отличаются параметры тиадиазольного цикла. Если связи S–N в молекуле (III) имеют значения 1.633 и 1.612 Å и являются промежуточными между величиной связи S–N (1.74 Å) и связи S=N (1.54 Å), то в N-оксидном цикле (II) связь S^1–N^4 увеличена до 1.647(2) Å, а связь S^1–N^1 очень близка к простой, 1.736(2) Å. Межатомные расстояния N^1–C^1 и N^4–C^4 неодинаковы и составляют 1.347(3) и 1.316(3) Å соответственно. Наблюдаемые величины длин свя-

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Таблица 1

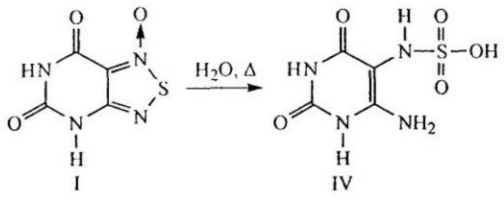
Межатомные расстояния (*d*) и валентные углы (φ) в молекулах (II) и (IV)

Соединение (II)		Соединение (IV)	
Связь	*d*, Å	Связь	*d*, Å
S^1–N^4	1.647(2)	S^{11}–O^{14}	1.443(2)
S^1–N^1	1.736(2)	S^{11}–O^{13}	1.446(2)
O^1–N^1	1.267(2)	S^{11}–O^{15}	1.456(2)
O^2–C^2	1.218(3)	S^{11}–N^{18}	1.662(2)
O^3–C^3	1.220(3)	O^{11}–C^{11}	1.252(2)
N^1–C^1	1.347(3)	O^{12}–C^{13}	1.231(2)
N^2–C^2	1.375(3)	C^{11}–N^{12}	1.392(2)
N^2–C^3	1.393(3)	C^{11}–C^{16}	1.413(2)
N^3–C^3	1.364(3)	N^{12}–C^{13}	1.363(2)
N^3–C^4	1.365(3)	C^{13}–N^{14}	1.365(2)
N^4–C^4	1.316(3)	N^{14}–C^{15}	1.376(2)
C^1–C^4	1.403(3)	C^{15}–N^{17}	1.333(2)
C^1–C^2	1.460(3)	C^{15}–C^{16}	1.392(2)
O^{1w}–H^{1w1}	0.80(3)	C^{16}–N^{18}	1.419(2)
O^{1w}–H^{2w1}	0.84(3)		
O^{2w}–H^{1w2}	0.81(4)		
O^{2w}–H^{2w2}	0.67(3)		
Угол	φ, град	Угол	φ, град
$N^4S^1N^1$	94.9(1)	$O^{14}S^{11}O^{13}$	115.2(1)
$O^1N^1C^1$	128.3(2)	$O^{14}S^{11}O^{15}$	112.3(1)
$O^1N^1S^1$	123.5(2)	$O^{13}S^{11}O^{15}$	110.6(1)
$C^1N^1S^1$	108.2(2)	$O^{14}S^{11}N^{18}$	103.8(1)
$C^2N^2C^3$	128.0(2)	$O^{13}S^{11}N^{18}$	105.6(1)
$C^3N^3C^4$	122.4(2)	$O^{15}S^{11}N^{18}$	108.6(1)
$C^4N^4S^1$	108.4(2)	$O^{11}C^{11}N^{12}$	117.7(1)
$N^1C^1C^4$	110.8(2)	$O^{11}C^{11}C^{16}$	125.8(1)
$N^1C^1C^2$	126.5(2)	$N^{12}C^{11}C^{16}$	116.5(1)
$C^4C^1C^2$	122.6(2)	$C^{13}N^{12}C^{11}$	125.6(1)
$O^2C^2N^2$	122.6(2)	$O^{12}C^{13}N^{12}$	122.3(1)
$O^2C^2C^1$	126.0(2)	$O^{12}C^{13}N^{14}$	122.4(1)
$N^2C^2C^1$	111.4(2)	$N^{12}C^{13}N^{14}$	115.4(1)
$O^3C^3N^3$	122.3(2)	$C^{13}N^{14}C^{15}$	123.7(1)
$O^3C^3N^2$	121.2(2)	$N^{17}C^{15}N^{14}$	117.1(1)
$N^3C^3N^2$	116.5(2)	$N^{17}C^{15}C^{16}$	123.4(1)
$N^4C^4N^3$	123.4(2)	$N^{14}C^{15}C^{16}$	119.5(1)
$N^4C^4C^1$	117.7(2)	$C^{15}C^{16}C^{11}$	119.2(1)
$N3C^4C^1$	118.9(2)	$C^{15}C^{16}N^{18}$	118.9(1)
$H^{1w1}O^{1w}H^{2w1}$	102(3)	$C^{11}C^{16}N^{18}$	121.8(1)
$H^{1w2}O^{2w}H^{2w2}$	111(4)	$C^{16}N^{18}S^{11}$	116.1(1)

зей указывают на отсутствие их делокализации по всему кольцу N-оксида 1,2,5-тиадиазо-ла. Таким образом, можно сделать вывод о неароматическом характере N-оксида (I), что согласуется со способностью атомов N-оксидного фрагмента к повышению валентности (окислению) [5]. По данным работы [7], подобная кратность связей характерна для производных 1,2,5-оксадиазол-2-оксида (фуроксанов). Расстояния между атомами азота и циклическим кислородом близки к величинам простой связи, а связь между атомом азота и экзоциклическим атомом кислородом соответствует значению двойной связи (1.11 Å) [7]. Для дигидрата (II) связь N–O составляет 1.267(2) Å.

Интересна упаковка молекул в кристалле. Две сольватные молекулы воды в качестве акцепторов протонов участвуют в водородных связях N–H···O с аминогруппами урацильного фрагмента на расстояниях $N^3\cdots O^{1w}$ 2.738(3) и $N^2\cdots O^{2w}$ 2.741(3) Å (табл. 2). Молекула воды O^{2w} служит мостиком между двумя связанными центром инверсии молекулами (I), объединяя их в гетеротетрамер за счет водородной связи O–H···O, $O^{2w}\cdots O^3$ ($-x + 2$, $-y + 1$, $-z$) 2.819(3) Å (рис. 2). В результате образуется практически плоский 12-членный синтон [8], объединяющий четыре донора и четыре акцептора, условно обозначаемый $R_4^4(12)$ [9]. Далее эти тетрамеры объединяются в цепочки за счет укороченных центросимметричных контактов S···N, типичных для тиадиазольных производных [10–12]. Эти межмолекулярные взаимодействия реализованы в виде параллелограмма со сторонами, равными межатомному расстоянию S^1–N^4 1.647(2) Å и межмолекулярному взаимодействию $S^1\cdots N^4$ ($-x$, $-y$, $-z$) 2.958(2) Å. Цепочки объединены в трехмерную сетку за счет водородных связей N–H···O с участием молекул воды в качестве доноров протонов и карбонильных и нитрозильного атомов кислорода в качестве акцепторов протонов, а также за счет укороченных контактов S···O, $S^1\cdots O^2$ (1/2 – *x*, 1/2 + *y*, 1/2 – *z*) 3.194(2) Å (рис. 3, табл. 2).

Результатом более длительного нагревания водного раствора (I) является образование 6-амино-2,4-диоксо-1,2,3,4-тетрагидропиримидин-5-сульфамовой кислоты (IV) [схема (1)].



(1)

Таблица 2

Межмолекулярные водородные связи в дигидрате (II)

Связь	D–H, Å	H···A, Å	D···A, Å	∠DHA, град	Преобразование симметрии для H-акцептора
N^2–H^{1N2}···O^{2w}	0.89(2)	1.85(2)	2.741(3)	175(2)	*x*, *y*, *z*
N^3–H^{1N3}···O^{1w}	0.82(2)	1.93(2)	2.738(3)	170(2)	*x*, *y*, *z*
O^{1w}–H^{1w1}···O^1	0.80(3)	2.07(3)	2.845(3)	164(3)	*x* + 1/2, –*y* + 1/2, *z* – 1/2
O^{1w}–H^{2w1}···O^2	0.84(3)	2.00(3)	2.828(3)	173(3)	*x* – 1/2, –*y* + 1/2, *z* – 1/2
O^{2w}–H^{1w2}···O^1	0.81(4)	2.39(4)	2.977(3)	131(3)	–*x* + 3/2, *y* + 1/2, –*z* + 1/2
O^{2w}–H^{1w2}···O^2	0.81(4)	2.32(4)	3.039(3)	148(4)	–*x* + 3/2, *y* + 1/2, –*z* + 1/2
O^{2w}–H^{2w2}···O^3	0.67(3)	2.16(3)	2.819(3)	166(4)	–*x* + 2, –*y* + 1, –*z*

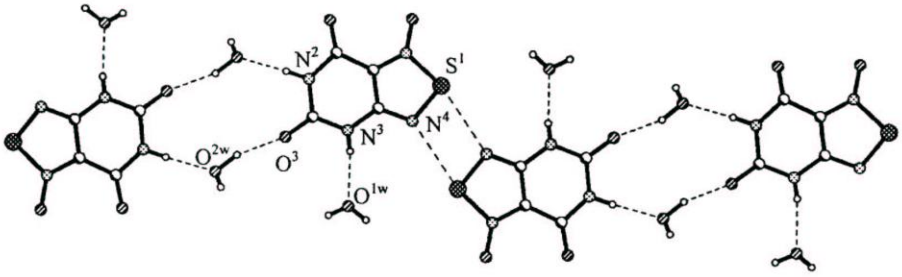


Рис. 2. Цепочки молекул соединения (I), связанных водородными связями и взаимодействиями S···N .

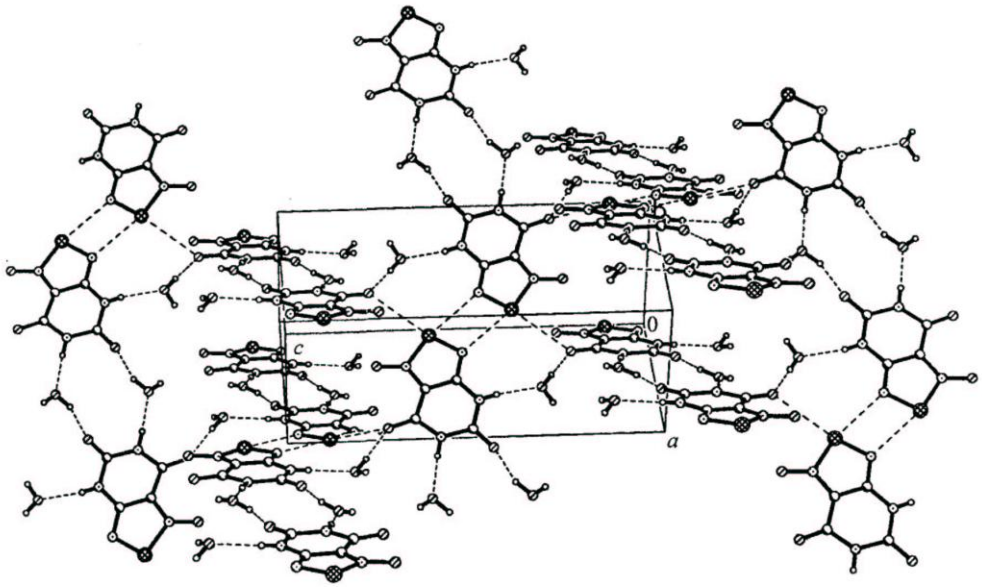
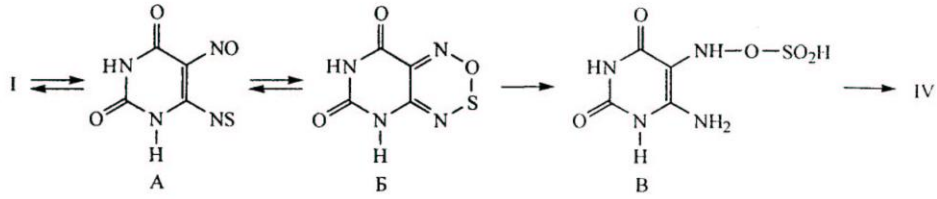


Рис. 3. Упаковка дигидрата (II) в кристалле.

Наиболее вероятно, что начальной стадией этой реакции является образование таутомерных форм, обозначенных на схеме (2) как интермедиаты А и Б, появление которых обусловлено процессом рециклизации исходного N-оксида (I) [схема (2)].



(2)

Дальнейшее присоединение двух молекул воды к производному 1,2,3,6-тиаоксадиазина Б, очевидно, приводит к аминосульфиту В. По имеющимся в литературе данным, аминосульфиты, полученные по реакции гидроксиламинов с SO_2, способны легко перегруппировываться в сульфамовые кислоты [13]. Сульфамовая кислота (IV) представляет собой бесцветное малорастворимое в органических растворителях вещество. Высокая температура плавления (с разложением) и низкая летучесть не позволяют использовать метод масс-спектрометрии для изучения строения кислоты (IV). В связи с этим молекулярная структура (IV) в виде ее комплекса (V) с диаза-18-краун-6 была изучена методом рентгеноструктурного анализа (рис. 4). В данной публикации обсуждается только геометрия аниона сульфамовой кислоты как нового соединения. В табл. 1 приведены геометрические характеристики аниона сульфамовой кислоты.

Пиримидиновый остов аниона практически плоский, атомы цикла, определяющие плоскость, отклоняются от нее в среднем на 0.019(2) Å. Связанные с этим гетероциклом карбонильные атомы O^{11} и O^{12} и атом N^{18} аминогруппы отклоняются от этой плоскости на 0.003(2), –0.028(2) и –0.009(2) Å соответственно. В сульфоксидной группе расстояния S–O находятся в интервале 1.443(1)–1.456(1) Å, что свидетельствует о перераспределении электронной плотности и полуторном характере всех связей S–O. Валентный угол $C^{16}N^{18}S^{11}$ 116.1(1)° близок к тетраэдрическому, что в совокупности с тригональной геометрией сульфоксидной группы способствует развитию структуры комплекса (V) в трех направлениях за счет формируемых с участием аниона RSO_3^- водородных связей.

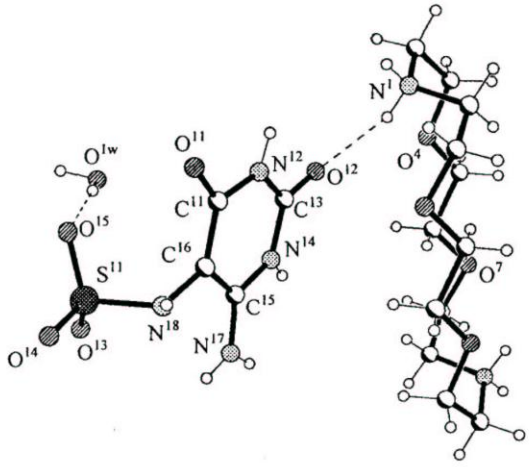


Рис. 4. Строение комплекса (V) (симметрично связанные молекула воды и анион сульфамовой кислоты не указаны).

Экспериментальная часть

Параметры ячейки и интенсивности 2428 независимых отражений кристалла соединения (II) измерены на автоматическом дифрактометре Nonius-CCD с монохроматизированным λMoK_α-излучением, ω-сканирование. Обработка экспериментальных данных выполнена по программе DENZO [14]. Кристаллы моноклинные, a 7.308(2), b 7.003(1), c 16.250(3) Å; β 91.75(3)°, V 831.3(3) Å^3, $d_{выч}$ 1.775 г/см^3, Z 4, пространственная группа $P2_1/n$. В расчетах использовано 1010 отражений с интенсивностью $I \geq 2\sigma(I)$. Структура расшифрована прямым методом и уточнена полноматричным методом наименьших квадратов в анизотропном приближении для неводородных атомов в пакете программ SHELX-97 [15]. Атомы водорода найдены на разностном синтезе электронной плотности и уточнены изотропно. Окончательные факторы расходимости R 0.0386, R_w 0.0592. Основные геометрические характеристики молекул (II) и (IV) приведены в табл. 1, параметры водородных связей для дигидрата (II) – в табл. 2. Кристаллографические данные (cif-файлы) депонированы в Кэмбриджском банке структурных данных (CCDC), номера регистрации CCDC 198420 и CCDC 188812 для соединений (II) и (V) соответственно.

Дигидрат 1,2,5-тиадиазоло[3,4-*d*]пиримидин-5,7-дион-2-оксида (II). 0.01 моля оксида (I) растворяли в минимальном количестве кипящей воды и продолжали нагревание до появления интенсивной малиновой окраски. Горячий раствор фильтровали и выдерживали при комнатной температуре до выпадения кристаллического осадка дигидрата (II), т. пл. 140°C (разл.). Найдено, %: C 21.65; H 2.65; N 25.25. $C_4H_6N_4O_5S$. Вычислено, %: C 21.62; H 2.70; N 25.23.

6-Амино-2,4-диоксо-1,2,3,4-тетрагидропиримидин-5-сульфамовая кислота (IV). 0.01 моля оксида (I) растворяли в минимальном количестве кипящей воды и продолжали нагревание до появления, а затем исчезновения окраски. Раствор отфильтровывали и охлаждали. Выделившийся осадок отделяли фильтрованием, перекристаллизовывали из воды и сушили в вакууме над P_2O_5, выход соединения (IV) 63%, т. пл. >300°C (разл.). Найдено, %: C 21.60; H 2.70; N 25.20. $C_4H_6N_4O_5S$. Вычислено, %: C 21.62; H 2.70; N 25.23.

Комплекс (V) 6-амино-2,4-диоксо-1,2,3,4-тетрагидропиримидин-5-сульфамовой кислоты (IV) с диаза-18-краун-6. 0.001 моля вещества (IV) смешивали с 262 мг диаза-18-краун-6 и добавляли кипящую воду до растворения осадка. Раствор выдерживали при комнатной температуре до выделения кристаллов комплекса (V), т. пл. 227°C. Найдено, %: C 32.31; H 5.76; N 18.93. $C_{20}H_{42}N_{10}O_{16}S_2$. Вычислено, %: C 32.34; H 5.70; N 18.86.

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Додаток 36

Копія статті

“Комплексы «хозяин-гость» краун-эфиров с NH-протонодонорными молекулами”

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КОМПЛЕКСЫ «ХОЗЯИН–ГОСТЬ» КРАУН-ЭФИРОВ С HN-ПРОТОНОДОНОРНЫМИ МОЛЕКУЛАМИ

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Взаимодействием краун-эфиров с HN-протонодонорными молекулами получены кристаллические молекулярные комплексы «хозяин–гость» и установлено, что в зависимости от линейных размеров и способа стерического экранирования активных центров протонодонорных молекул в комплексы связываются краун-эфиры различного строения.

Выяснение особенностей образования комплексов на основе межмолекулярных связывающих взаимодействий краун-эфиров («хозяев») с «гостевыми» молекулами, моделирующих распространенные природные процессы, – одна из приоритетных задач супрамолекулярной химии [1–3]. Согласно работе [4], сформулировавшей требования к «гостевым» молекулам, последние должны обладать заметным дипольным моментом и невысокой молекулярной массой.

Цель работы – определение тенденций, влияющих на результат образования кристаллических молекулярных комплексов кислородсодержащих краун-эфиров (I–IV) – 1,4,7,10-тетраоксациклододекана, 1,4,7,10,13-пентаоксациклопентадекана, 1,4,7,10,13,16-гексаоксациклооктадекана, 2,3,5,6,8,9,11,12-октагидро-1,4,7,10,13-бензопентаоксациклопентадецина, 2,3,5,6,8,9,11,12,14,15-декагидро-1,4,7,10,13,16-бензогексаоксациклооктадецина, *цис-син-цис*-эйкосагидродибензо[*b*,*k*][1,4,7,10,13,16]-гексаоксациклооктадецина и *цис-анти-цис*-эйкосагидродибензо[*b*,*k*][1,4,7,10,13,16]гексаоксациклооктадецина соответственно – с HN-протонодонорными молекулами (V–XIII) и проявляющихся при изменении геометрических размеров «гостевых» молекул и способа пространственного экранирования взаимодействующих центров в «госте» и «хозяине».

Установлено, что при самопроизвольном испарении растворителей из растворов краун-эфиров (I–IV) с тиофен-2-сульфамидом (V), 5-нитро-1,3-тиазол-2-амином (VI), пиридино-3-карботиоамидом (VII), N-1-нафтилтиомочевиной (VIII), 6-нитро-1,3-бензотиазол-2-амином (IX), 2-(тиен-2-илкарбонил)-гидразинокарботиоамидом (X), 5-[(4-нитрофенил)-сульфонил]-1,3-тиазол-2-амином (XI), N-(4-[2-(аминокарбонотиоил)гидразоно]метилфенил)ацетамидом (XII), 1,1,1-трифенилметанамином (XIIIа), тиоцианатом 1,1,1-трифенилметанаммония (XIIIб) и 3-[гидрокси(дифенил)метил]бензолсульфамидом (XIIIв) образуются кристаллические молекулярные комплексы. Приведены состав комплекса и его номер: [(Iв)·(V)] (XIV), [(IIб)·2 (V)] (XV), [(IV)·(V)] (XVI), [(Iв)·(VI)] (XVII), [(IV)·2 (VI)] (XVIII), [(Iв)·(VII)] (XIX), [(IIб)·(VII)] (XX), [(IV)·2 (VII)] (XXI), [(IIа)·2 (VIII)] (XXII), [(Iв)·2 (VIII)] (XXIII), [(IV)·2 (VIII)] (XXIV), [(Iв)·2 (IX)] (XXV), [(Iв)·2 (X)] (XXVI), [(Iв)·2 (XI)] (XXVII), [(IV)·2(XII)] (XXVIII), [(Iа)·2 (XIIIа)] (XXIX), [(Iа)·2 (XIIIб)] (XXX), [(Iв)·2 (XIIIв)] (XXXI) соответственно.

Видно (см. таблицу), что при образовании кристаллических молекулярных комплексов типа «хозяин–гость» с нейтральными ароматическими HN-протонодонорными молекулами (V–VIII) наиболее эффективными являются 18-членные краун-эфиры, имеющие эквивалентно пространственно экранированные стороны полости макроцикла (Iв, IV), что не противоречит данным работ [5–7].

Установлено, что с ростом протяженности «гостевой» HN-протонодонорной молекулы [соединения (IX–XI, XIIIв)] более эффективным лигандом является краун-эфир (Iв). Дальнейшее увеличение протяженности «гостевой» молекулы (XI) (максимальный размер «гостевой» молекулы, со-

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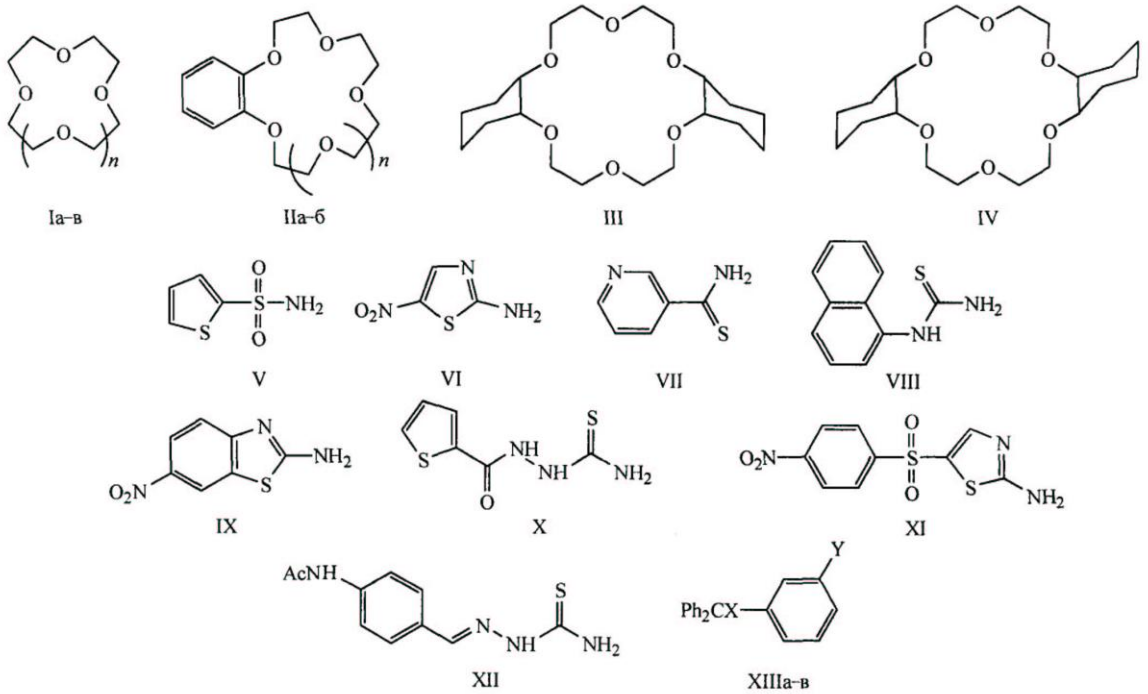
Выходы, температуры плавления, спектры ЯМР ^{1}H и данные элементного анализа комплексов (XIV–XXXI)

№	Выход, %	Т. пл., °С (растворители для кристаллизации)[a]	Спектр ЯМР ^{1}H, δ, м. д.	Найдено, %			Формула	Вычислено, %		
				C	H	N		C	H	N
XIV	79	115–116 (метанол–этилацетат, 1:2)	Ацетон-d_6: 3.57 с (24H, CH_2O), 6.80 с (2H, NH), 7.13 м, 7.59 м, 7.75 м (3H, CH)	44.82	6.80	3.32	$C_{16}H_{29}NO_8S_2$	44.95	6.84	3.28
XV	67	119–121 (ацетон–гексан, 1:1)	Ацетон-d_6: 3.58 с, 3.61 с, 3.68 с, 3.82 м, 4.11 м (20H, CH_2O), 6.82 с (4H, NH), 6.87 м (4H, CH), 7.11 м, 7.59 м, 7.75 м (6H, CH)	45.17	5.33	4.43	$C_{24}H_{34}N_2O_{10}S_4$	45.13	5.36	4.39
XVI	88	103–104 (ацетон–гексан, 1:2)	Ацетон-d_6: 1.25–1.78 м, 3.59 м (36H, CH), 6.81 с (2H, NH), 7.12 м, 7.59 м, 7.75 м (3H, CH)	53.87	7.66	2.64	$C_{24}H_{41}NO_8S_2$	53.81	7.71	2.62
XVII	96	168–170 (метанол–бензол, 1:2)	ДМСО-d_6: 3.50 с, (24H, CH_2O), 8.22 с (1H, CH), 8.74 с (2H, NH)	44.09	6.57	10.34	$C_{15}H_{27}N_3O_8S$	44.00	6.65	10.26
XVIII	93	190–192 (ацетон–гексан, 1:2)	ДМСО-d_6: 1.19–1.46 м, 3.53 м (36H, CH), 8.22 с (2H, CH), 8.74 с (4H, NH)	47.19	6.32	12.75	$C_{26}H_{42}N_6O_{10}S_2$	47.12	6.39	12.68
XIX	91	120–122 (метанол–этилацетат, 1:3)	Метанол-d_4: 3.60 с (24H, CH_2O), 7.45 м, 8.26 м, 8.60 м, 9.00 м (4H, CH)	53.68	7.54	6.93	$C_{18}H_{30}N_2O_6S$	53.71	7.51	6.96
XX	96	140–142 (метанол–этилацетат, 1:2)	ДМСО-d_6: 3.55 м, 3.73 м, 4.05 м (20H, CH_2), 6.90 м (4H, CH), 7.43 м, 8.18 м, 8.64 м, 8.99 м (4H, CH)	58.59	6.83	6.31	$C_{22}H_{30}N_2O_6S$	58.65	6.71	6.22
XXI	71	115–116 (ацетон–гексан, 1:4)	ДМСО-d_6: 1.19–1.71м, 3.55 м (36H, CH), 7.44 м, 8.19 м, 8.65 м, 8.99 м (8H, CH)	57.61	7.59	8.38	$C_{32}H_{50}N_4O_7S_2$	57.63	7.56	8.40
XXII	83	141–143 (метанол–этилацетат, 1:1)	ДМСО-d_6: 3.60 с, 3.75 т, 4.02 т (16H, CH_2), 6.86 м, 6.93 м (4H, CH), 7.53 м, 7.90 м (14H, CH)	64.32	6.06	8.31	$C_{36}H_{40}N_4O_5S_2$	64.26	5.99	8.33
XXIII	83	188–190 (метанол–этилацетат, 1:1)	ДМСО-d_6: 3.50 с (24H, CH_2O), 7.53 с, 7.90 м (14H, CH)	61.14	6.57	8.41	$C_{34}H_{44}N_4O_6S_2$	61.05	6.63	8.38
XXIV	88	186–188 (метанол–этилацетат, 1:1)	ДМСО-d_6: 1.22–1.68 м, 3.52 м (36H, CH), 7.53 м, 7.93 м (14H, CH)	64.94	7.29	7.31	$C_{42}H_{56}N_4O_6S_2$	64.92	7.26	7.21
XXV	80	258–260 (ацетон–гексан, 1:2)	ДМСО-d_6: (24H, CH_2), 7.40 д, 8.09 д, 8.66 с (6H, CH), 8.21 с (4H, NH)	47.74	5.27	12.94	$C_{26}H_{34}N_6O_{10}S_2$	47.70	5.23	12.84
XXVI	80	184–186 (метанол–бензол, 1:3)	ДМСО-d_6: 3.50 с (24H, CH_2O), 7.16 м, 7.63 с, 9.34 с, 10.39 с (4H, NH), 7.80 м (2H, CH)	43.19	5.70	12.63	$C_{24}H_{38}N_6O_8S_4$	43.23	5.74	12.60
XXVII	89	154–156 (ацетон–гексан, 1:2)	ДМСО-d_6: 3.50 м (24H, CH_2O), 7.78 с (2H, CH), 8.21 с (4H, NH), 8.12 д, 8.38 д (8H, CH)	43.19	4.64	10.11	$C_{30}H_{38}N_6O_{14}S_4$	43.16	4.59	10.07
XXVIII	81	240–244 (метанол–этилацетат, 1:4)	ДМСО-d_6: 2.04 с (6H, CH_3), 1.22–1.71 м и 3.55 м (36H, CH), 7.58 д, 7.69 д (8H, CH), 7.97 с, 10.05 с, 11.31 с (8H, HN)	56.85	7.16	13.26	$C_{40}H_{60}N_8O_8S_2$	56.64	7.25	13.07
XXIX	81	94–95 (метанол)	$CDCl_3$: 1.86 с (4H, NH), 3.70 с (16H, CH_2O), 7.20–7.32 м (30H, CH)	79.53	7.24	4.05	$C_{46}H_{50}N_2O_4$	79.51	7.25	4.03
XXX	80	170–172 (пропан-2-ол–пентан-1-ол, 10:1)	$CDCl_3$: 3.70 с (16H, CH_2O), 7.26 м (30H, CH)	70.85	6.48	6.93	$C_{48}H_{52}N_4O_4S_2$	70.91	6.45	6.89
XXXI	98	174–176 (ацетон–гексан, 1:2)	Метанол-d_4: 3.62 с (24H, CH_2O), 7.27 м, 7.44 м (28H, CH)	63.71	6.24	2.99	$C_{50}H_{58}N_2O_{12}S_2$	63.66	6.20	2.97

Примечание. а) Указано объемное соотношение растворителей для кристаллизации.

гласно программе [8], составляет >13.5 Å) приводит к образованию кристаллического молекулярного комплекса с краун-эфиром (IV). Это связано, по видимому, с необходимостью пространственной соразмерности молекул «гостя» и «хозяина». Экранирование HN-протонодонорного центра в «гостевых» молекулах (XIIIa, б) объемным трифенилметильным заместителем позволило при использованиии молекул (XIIIa, б) зафиксировать в кристаллических комплексах «хозяин–гость» (XXIX, XXX) краун-эфир (Ia), для которого известны лишь несколько примеров подобного связывания [9–12].



I, n = 1 (а), 2 (б), 3 (в); II, n = 1 (а), 2 (б); XIII, X = NH_2, Y = H (а); X = $NH_3^+SCN^-$, Y = H (б); X = OH, Y = SO_2NH_2 (в).

Описаные особенности взаимодействия краун-эфиров (I–IV) с различно пространственно экранированными HN-протонодонорными молекулами (V–XIII), приводящие к образованию кристаллических молекулярных комплексов «хозяин–гость» (XIV–XXXI), могут быть учтены как составная часть при моделировании молекулярных взаимодействий сравнительно крупных природных молекул [1–3], а также явиться химической основой разделения смесей краун-эфиров аналогично изложенному в работах [5, 6].

Экспериментальная часть

Спектры ЯМР ^{1}H регистрировали на приборе Varian VXR-300 (300 МГц), внутренний стандарт – ТМС.

Краун-эфиры (III–IV) и соединение (XIIIв) получены соответственно методикам [5, 13], соединения (I–IX, XI–XIIIa) использовали в виде коммерческих образцов (Aldrich) без дополнительной очистки.

2-(Тиен-2-илкарбонил)гидразинокарботиоамид (X). Раствор 1 ммоля тиофен-2-карбогидразида, 10 ммолей тиоцианата калия в смеси 5 мл воды, 10 мл метанола и 0.3 мл 36%-ной соляной кислоты выдерживали при температуре кипения реакционной смеси (~64°C) 12 ч. Метанол отгоняли и к остатку добавляли 10 мл воды. Выпавший при 20°C осадок отфильтровывали и перекристаллизовывали из 40 мл метанола, выход соединения (X) 98%, т. пл. 234–236°C. Спектр ЯМР ^{1}H (ДМСО-d_6), δ, м. д.: 7.20 м, 7.63 с, 9.35 с, 10.40 с (4H, NH), 7.80 с (3H, CH). Найдено, %: C 35.89; H 3.54; N 20.93. $C_6H_7N_3OS_2$. Вычислено, %: C 35.81; H 3.51; N 20.93.

Тиоцианат 1,1,1-трифенилметанаммония (XIIIб). Раствор 5 ммолей 1,1,1-трифенилметанамина, 5 ммолей тиоцианата калия в смеси 5 мл воды, 15 мл метанола и 0.7 мл уксусной кислоты вы-

держивали при температуре кипения реакционной смеси (~64°С) 4 ч. Метанол отгоняли и к остатку добавляли 20 мл воды. Выпавший при 20°С осадок отфильтровывали и перекристаллизовывали из 40 мл бензола, выход соединения (XIIIб) 69%, т. пл. 194–196°С. Спектр ЯМР ^{1}H ($CDCl_3$), δ, м. д.: 7.29 м (30H, CH). Найдено, %: 75.41; H 5.75; N 8.84. $C_{20}H_{18}N_2S$. Вычислено, %: C 75.44; H 5.70; N 8.80.

Молекулярные комплексы (XIV–XXXI). К 1 ммолю краун-эфира (I–IV) добавляли раствор 1 ммоля соединений (V–XIII) в смеси растворителей, указанных в таблице, и растворители испаряли при 20°С. Выделившиеся монокристаллы комплекса (XIV–XXXI) промывали той же смесью растворителей и сушили на воздухе.

Работа финансировалась в рамках проекта NCS 90-2811-M-032.

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Додаток 37

Копія статті

“The 1D and 0D weakly hydrogen-bonded adducts 18-crown-6/4-phenylthiosemicarbazide (1/2) and cis–anti–cis-dicyclohexyl-18-crown-6/N,N'-diphenylthiourea (1/2)”

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The 1D and 0D weakly hydrogen-bonded adducts 18-crown-6/4-phenylthiosemicarbazide (1/2) and *cis–anti–cis*-dicyclohexyl-18-crown-6/*N,N′*-diphenylthiourea (1/2)

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Abstract

Two title compounds, 18-crown-6/4-phenylthiosemicarbazide, **1**, and *cis anti cis*-dicyclohexyl-18-crown-6/*N,N′*-diphenylthiourea, **2**, both of 1:2 ratio, exhibit one-dimensional (chain) and zero-dimensional (molecular complex) structures correspondingly. The crystals of **1** are monoclinic, space group $P2_1/c$, $a-13.142(2)$, $b-20.367(5)$, $c-12.090(3)$ Å, $\beta-92.32(1)°$, $V-3233.4(1)$ Å^3, $Z-4$. The crystals of **2** are triclinic, space group *P-1*, $a-9.958(2)$, $b-13.223(3)$, $c-17.293(4)$ Å, $\alpha-87.96(3)$, $\beta-86.93(3)$, $\gamma-86.55(3)°$, $V-2268.5(8)$ Å^3, $Z-2$. The adducts are sustained by N H···O hydrogen bonds. Weak C(aryl) H···S interactions are responsible for the corrugated chain formation in **1**.
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Keywords: 1D and 0D H-bonded adducts; 18-Membered crown ethers; Synthesis and crystal structure

1. Introduction

Host–guest chemistry is primarily based on the complementarity of the sites of the host with those of the guest [1]. A small change in each of the components can alter this complementarity and thus the binding properties of the guest. Classic crown ethers are very suitable modules to imitate substrate-receptor functions and are successfully used to study binding properties of small biologically active molecules [2–4]. 4-Phenylthiosemicarbazide and *N,N′*-diphenylthiourea as well as their derivatives are very important biologically active molecules that possess both H-donor (NH, NH_2) and H-acceptor (S=C) binding functions and thus exhibit different types of coordination in the solid state.

A search of the Cambridge Structural Database (April 2002 release) [5] produced a list of seven entries that covers 4-phenylthiosemicarbazide [6–7] and its derivatives, 4-(4-methoxyphenyl)thiosemicarbazide [8], 4-(4-chlorophenyl)-thiosemicarbazide [9], 4-(3-chlorophenyl)thiosemicarbazide [10], and 4-(4-bromophenyl)thiosemicarbazide [11]. The molecules are combined into 3D network via hydrogen bonds and short intermolecular contacts, mainly via two N–H···S hydrogen bonds that formulate the planar or twisted $R_2^2(8)$ supramolecular synthon [12,13].

N,N′-Diphenylthiourea itself exists in the form of two polymorphs differing by the hydrogen bonding system, the dimer polymorph [14] that is stabilized via N–H···S $R_2^2(8)$ planar synthon and is favored by the *trans–cis* configuration of aromatic rings, the similar dimer association is fixed for 1,3-bis(*o*-chlorophenyl)thiourea [15] and chain polymorph, where the molecules have a butterfly shape with the *cis–cis* configuration of aromatic rings [16] and are joined into chain via $R_2^1(6)$ ring closed by two N–H···S hydrogen

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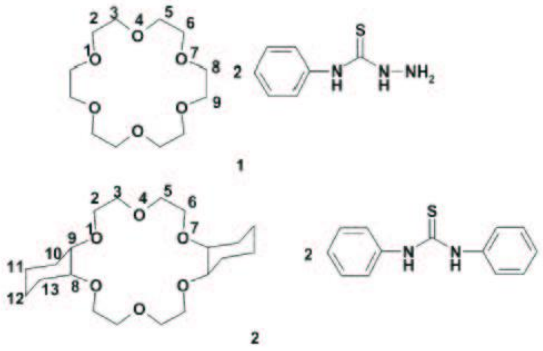

Scheme 1. Schematic presentation of the molecular complexes **1** and **2** with the atomic numbering scheme in the crown molecules.

bonds. A very similar chain architecture is also found in *N,N′*-bis(*p*-chlorophenyl)thiourea structure and in the twisted *N*-*o*-tolyl-*N′*-*p*-tolylthiourea [17–18]. The authors are unaware of the examples of 4-phenylthiosemicarbazide and *N,N′*-diphenylthiourea crystalline complexes with crown ethers.

We report here two novel structures, complexes of 18-crown-6 with 4-phenylthiosemicarbazide, **1** and *cis–anti–cis* isomer of dicyclohexano-18-crown-6 with N,N′-diphenylthiourea, **2**, both of 1:2 composition (Scheme 1).

2. Experimental

Commercially available reagents were used as received. **1** and **2** were analyzed for C, H, N and S in a Perkin Elmer 240 C. The thin layer chromatographic control of the substances purity was performed on Silufol UV-254 plates.

2.1. Synthesis

1. 4 N,N′-phenylthiosemicarbazide (167 mg, 1 mmol) and 18-crown-6 (264, 1 mmol) were dissolved in methanol (5 ml) at 64 °C, following the addition of ethyl acetate (10 ml). The resulting clear solution was slowly reduced in volume by evaporating the solvents at room temperature. Colorless transparent crystals suitable for X-ray analysis were selected in a yield of 82% (245 mg), m.p. 128–130 °C. Analysis: found C 52.12, H 7.11, N 14.12, S 10.79%; $C_{26}H_{42}N_6O_6S_2$ requires C 52.15, H 7.07, N 14.04, S 10.71%.
2. N,N′-diphenylthiourea (228 mg, 1 mmol) and *cis–anti–cis* dicyclohexyl-18-crown-6 (372 mg, 1 mmol) were dissolved in acetone (5 ml) at 56 °C, following the addition of hexane (10 ml). The resulting clear solution was slowly reduced in volume by evaporating the solvents at room temperature. Colorless transparent crystals suitable for X-ray analysis were selected in a yield of 77% (320 mg), m.p. 138–140 °C. Analysis: found C 66.57, H 7.28, N 6.82, S 7.76%; $C_{46}H_{60}N_4O_6S_2$ requires C 66.63, H 7.30, N 6.78, S 7.74%.

2.2. X-ray crystallography

The X-ray intensity data for **1** were collected on a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo Kα radiation using ϕ–ω scans. Unit cell parameters were obtained and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO [19]. The scaling and the global refinement of crystal parameters were performed by SCALEPACK [19]. The X-ray intensity data for **2** were collected on a Phillips PW1100 diffractometer with a local program [20]. Unit cell parameters were obtained and refined from angular values of 24 reflections (θ range = 5.6–16.2°) accurately well centered on the diffractometer. The intensity of one standard reflection, recorded for every 100

Table 1
Crystal data summary for complexes **1** and **2**

Complex	1	2
CCDC number	227432	227433
Empirical formula	$C_{26}H_{42}N_6O_6S_2$	$C_{46}H_{60}N_4O_6S_2$
Formula weight	598.78	829.10
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\text{-}1$
Unit cell dimensions		
a (Å)	13.142(2)	9.958(2)
b (Å)	20.367(5)	13.223(3)
c (Å)	12.090(3)	17.293(4)
α (deg.)	–	87.96(3)
β (deg.)	92.32(1)	86.93(3)
γ (deg.)	–	86.55(3)
Cell volume (Å ^{3})	3233.4(1)	2268.5(8)
Formula units/unit cell	4	2
D_{calc} (g cm $^{-3}$)	1.230	1.214
μ (mm $^{-1}$)	0.211	0.168
$F(000)$	1280	888
Crystal dimensions (mm)	0.36×0.27×0.15	0.33×0.26×0.23
θ Range for data collection (deg.)	3.01 to 25.34	3.05 to 26.00
Limiting indices	$-15\le h\le 15$, $-21\le k\le 24$, $-14\le l\le 14$	$0\le h\le 11$, $-16\le k\le 16$, $-21\le l\le 21$
Reflections collected/unique	24682/5788	8632/8632
Reflections with $I>2\sigma(I)$	3502	2210
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5788/0/405	8632/0/535
Goodness-of-fit on F^2	1.015	0.714
Final R indices $[I>2\sigma(I)]$ %	$R_1=0.0443$, $wR_2=0.0908$	$R_1=0.0584$, $wR_2=0.0590$
R indices (all data) %	$R_1=0.0925$, $wR_2=0.1022$	$R_1=0.2933$, $wR_2=0.0838$
Largest diff. peak and hole (eÅ $^{-3}$)	0.134/−0.169	0.236/−0.207

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Table 2
Selected torsion angles (deg°) in the crown ethers in the complexes **1** and **2**

Complex **1**	Crown a[1]	Crown b[2]
C(9)–O(1)$^{\#1,2}$–C(2)$^{\#1,2}$–C(3)$^{\#1,2}$	171.9(2)	178.7(2)
O(1)–C(2)–C(3)–O(4)	66.5(2)	−65.6(3)
C(2)–C(3)–O(4)–C(5)	177.2(2)	−178.7(2)
C(3)–O(4)–C(5)–C(6)	−177.4(2)	−177.7(2)
O(4)–C(5)–C(6)–O(7)	−63.5(3)	73.3(2)
C(5)–C(6)–O(7)–C(8)	−169.7(2)	179.9(2)
C(6)–O(7)–C(8)–C(9)	178.0(2)	174.1(2)
O(7)–C(8)–C(9)–O(1)$^{\#1,2}$	68.4(3)	−68.0(2)
C(8)–C(9)–O(1)$^{\#1,2}$–C(2)$^{\#1,2}$	−179.6(2)	−174.5(2)
Complex 2	**Crown a[1]**	**Crown b[3]**
C(9)–O(1)–C(2)–C(3)	−172.0(4)	−159.5(3)
O(1)–C(2)–C(3)–O(4)	71.2(5)	−75.4(4)
C(2)–C(3)–O(4)–C(5)	177.8(4)	−178.3(4)
C(3)–O(4)–C(5)–C(6)	174.1(3)	176.3(5)
O(4)–C(5)–C(6)–O(7)	75.9(4)	−67.1(6)
C(5)–C(6)–O(7)–C(8)$^{\#1,3}$	162.6(3)	163.0(5)
C(6)–O(7)–C(8)$^{\#1,3}$–C(9)$^{\#1,3}$	57.6(5)	−151.4(4)
O(7)–C(8)$^{\#1,3}$–C(9)$^{\#1,3}$–O(1)$^{\#1,3}$	54.9(4)	55.9(5)
C(8)–C(9)–O(1)–C(2)	158.6(3)	−60.4(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$; #2 $-x$, $-y+1$, $-z+2$; #3 $-x$, $-y$, $-z+2$.

reflections, showed no significant changes. The recorded data were corrected for polarization and Lorentz effects. The structure solution and refinement proceeded similarly for both structures using SHELX-97 program package [21]. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were treated anisotropically (full-matrix least squares method on F^2). In **1** the sulfur atoms S11 and S21 were assumed to be disordered over two orientations. The occupancy factors refined to 0.648(1) for the major component (S11) and 0.352(1) for the minor component (S11A), and to 0.674(1) for the major component (S21) and 0.326(1) for the minor component (S21A), both positions were treated anisotropically. C-bound hydrogen atoms were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while the N-bound H-atoms were found from differential Fourier maps at an intermediate stage of the refinement and were treated isotropically.

The X-ray data and the details of the refinement for **1** and **2** are given in Table 1, the selected geometric parameters are summarized in Table 2, and H-bonding data are given in Table 3.

3. Results and discussion

3.1. Complex *1*

18-Crown-6 and 4-phenylthiosemicarbazide form a molecular complex, $C_{12}H_{24}O_6 \cdot 2C_7H_9N_3S$, **1**. Fig. 1 shows two crystallographically independent complexes (the crown molecules are denoted as **a** and **b**) of the title compound **1**.

Both macrocyclic molecules lie across the centers of inversion and adopt D_{3d} conformation (the torsion angles for the independent part of the molecules are given in Table 2). They are arranged in a T-shape mode with the dihedral angle between the least-square planes formed by six oxygen atoms equal to 82.12(3)°. The 4-phenylthiosemicarbazide and 18-crown-6 molecules in the individual complexes are also arranged in a T-shape mode with the dihedral angle between the least squares planes of the phenyl ring and the six O atoms of the crown ether equal to 83.52(5)° for crown molecule **a** and to 83.93(5)° for crown molecule **b** [further data for the **b** molecule are given in brackets]. The 1:2 adducts are sustained by six N–H···O hydrogen bonds with the participation of the hydrazine functionality of 4-phenylthiosemicarbazide (Table 3). The similar mode of interaction between the crown molecule and N–H-containing substrate is found in the 18-crown-6 complexes with the hydrazides of 1,2,5-oxadiazole-3-carbonic, 2-aminobenzoic and 1,2,3-triazole-4carbonic acids [2,22,23].

Table 3
Hydrogen bonding in complexes **1** and **2**

D-H···A	r(H···A) (Å)	r(D···A) (Å)	∠(DH···A) (deg)	Symmetry transformation for H-acceptor.
1				
N(11)-H(11)···N(13)	2.15(2)	2.620(2)	114(2)	x, y, z
N(12)-H(12)···O(4A)	2.09(2)	2.947(2)	175(2)	$-x+1, -y+1, -z+1$
N(13)-H(13)···O(7A)	2.29(2)	3.148(3)	179(3)	x, y, z
N(13)-H(13B)···O(1A)	2.42(2)	3.168(3)	156(3)	x, y, z
N(21)-H(21)···N(23)	2.14(2)	2.618(2)	115(2)	x, y, z
N(22)-H(22)···O(4B)	2.13(2)	2.983(2)	165(2)	$-x, -y+1, -z+2$
N(23)-H(23)···O(7B)	2.28(2)	3.110(3)	174(2)	x, y, z
N(23)-H(23B)···O(1B)	2.36(2)	3.223(2)	160(2)	x, y, z
2				
N(1)-H(1N)···O(1B)	2.56(2)	3.317(5)	154(4)	x, y, z
N(2)-H(2N)···O(1B)	2.06(4)	2.924(4)	168(4)	x, y, z
N(3)-H(3N)···O(7A)	2.01(4)	2.880(4)	168(4)	x, y, z
N(4)-H(4N)···O(7A)	2.52(4)	3.337(5)	146(3)	x, y, z

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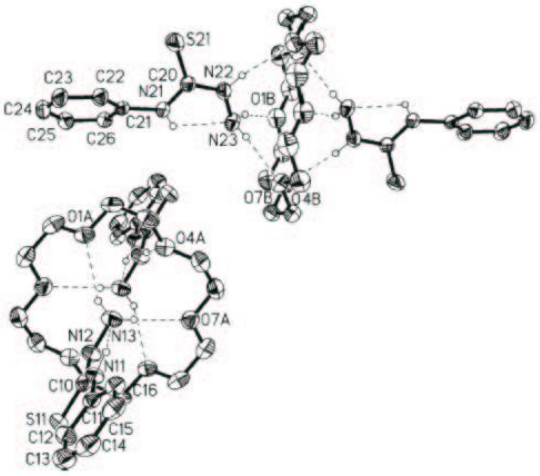

Fig. 1. ORTEP view of **1**. Displacement ellipsoids are drawn at the 30% probability level. C-bound H-atoms are omitted for clarity. Only the asymmetric unit is numbered. The minor positions of sulfur are not shown.

The conformation of 4-phenylthiosemicarbazide molecules is fixed by the intramolecular N–H···N hydrogen bond, the N···N separation is 2.620(2) Å in unit **a** [2.618(2) Å in unit **b**], which closes the 5-membered ring, the dihedral angle between this ring and the phenyl unit in the molecule is equal 12.7(4)° in unit **a** [35.7(4)° in unit **b**]. In the 1:2 units there are no any important N–H···S contacts for 4-phenylthiosemicarbazide itself.

The interesting feature of supramolecular architecture is a weak single C(aryl)-H···S interaction between crystallographically independent adducts **a** and **b**, C16···S21 3.685(3), H16···S21 2.77(2) Å. These contacts combine the N–H···O hydrogen-bonded units into alternate corrugated chain, the fragment of which is denoted in Fig. 2. A search of the CSD [5] produced a list of 150 entries where the short C(aryl)–H···S=C contacts fall in the range 2.674–3.000 Å and contribute into structure organization.

3.2. Complex 2

Cis–anti–cis-dicyclohexyl-18-crown-6 and *N,N′*-diphenylthiourea form the molecular complex, $C_{20}H_{36}O_6 2C_{13}H_{12}N_2S$, **2**. Fig. 3 shows two crystallographically independent complexes (**a** and **b**) of the title compound **2**.

Similar to **1**, both macrocyclic molecules lie across centers of inversion and adopt a C_i-conformation (the torsion angles for the independent part of the molecules are given in Table 2). The dihedral angle between the least square planes through their 6 O atoms equals 33.55(7)°. Each of the 1:2 units is sustained by four N–H···O hydrogen bonds which involve two related by the inversion crown oxygens, O7A and its counterpart in cycle **a**, and O1B and its counterpart in cycle **b** (Table 3). It is noteworthy that the intermolecular hydrogen bonding mode in **2** is very similar to that found in a pure diphenylthiourea [15] with the substitution of sulfur by crown oxygen.

The N,N′-diphenylthiourea molecules in **2** supramolecular and have a butterfly shape, the angle between the two phenyl rings is 28.2(2)° in unit **a** [31.9(2)° in unit **b**] and is close to that in pure N,N′-diphenylthiourea, 37.0° [16].

4. Conclusion

The complexes (18-crown-6)/2(4-phenylthiosemicarbazide), **1**, and (*cis–anti–cis*-dicyclohexyl-18-crown-6)/2(*N,N′*-diphenylthiourea), **2** were synthesized in approximately the same conditions and characterized by X-ray diffraction analysis. Both complexes represent 1:2 molecular units sustained by moderate (2.880 – 2.983 Å) and weak (3.110–3.337 Å) N–H···O hydrogen bonds, which include all the crown oxygens in **1** and only 2 of 6 crown oxygens in

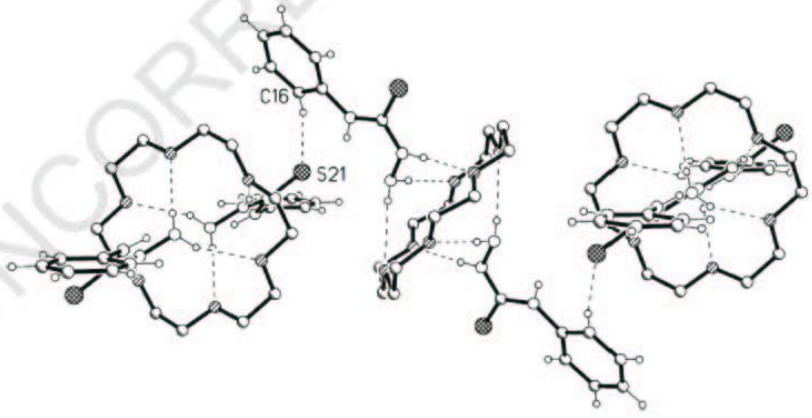

Fig. 2. C–H···S bonded chain in **1**. C-bound hydrogens of crown molecules are omitted for clarity.

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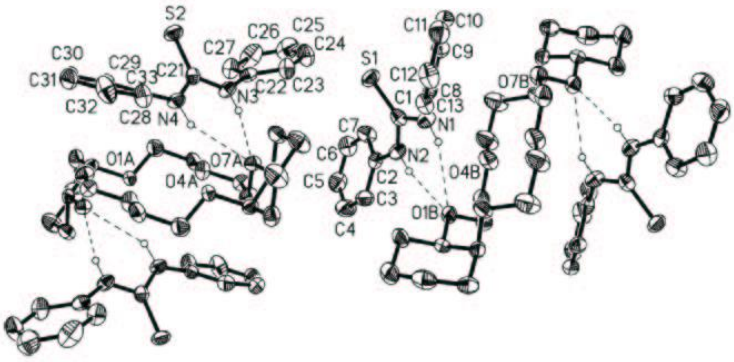

Fig. 3. ORTEP view of **2**. Displacement ellipsoids are drawn at the 50% probability level. C-bound H-atoms are omitted for clarity. Only the asymmetric unit is numbered.

2. **1** displays 1D chain sustained by weak C(aryl)–H···S interactions, while **2** exhibits 0D.

5. Supplementary material

Crystallographic data for the structural analysis of complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 227432 and 227433. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1233 336 033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Додаток 38

Копія статті

“Получение и кристаллическая структура стабильной формы "дигидрата" кремнефтороводородной кислоты - гексафторосиликата оксония”

ЖУРНАЛ НЕОРГАНИЧЕСКОЙ ХИМИИ, 2005, том 50, № 2, с. 1–6

СИНТЕЗ И СВОЙСТВА НЕОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

УДК 546.284'161–32:548.736.5

ПОЛУЧЕНИЕ И КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА СТАБИЛЬНОЙ ФОРМЫ "ДИГИДРАТА" КРЕМНЕФТОРОВОДОРОДНОЙ КИСЛОТЫ – ГЕКСАФТОРОСИЛИКАТА ОКСОНИЯ

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При попытке осуществить взаимодействие 45%-ной кремнефтороводородной кислоты (КФК) с гидразидом нитрилуксусной кислоты (L) в мольном соотношении КФК : L = 3 : 1 выделены кристаллы соединения состава $H_2SiF_6 \cdot 2H_2O$ (I). По данным РСА, соединение I представляет собой гексафторосиликат оксония. Кристаллы $(H_3O)_2SiF_6$ ромбические: a = 5.928(1), b = 17.790(4), c = 25.152(2) Å, V = 2652.6(9) Å^3, Z = 18, пр.гр. *Immm*, R = 0.0846 по 1344 отражениям с $I > 2\sigma(I)$. В высокосимметричной структуре катионы оксония и анионы SiF_6^{2-} объединены разветвленной сетью слабых (преимущественно вилочных) Н-связей OH···F типа в трехмерный каркас (расстояния O···F 2.95–3.05 Å).

Кремнефтороводородная кислота (**КФК**) – крупнотоннажный побочный продукт производства фосфорных удобрений – представляет интерес в качестве перспективного источника фтора для химической промышленности [1, 2]. Как и другие комплексные фторокислоты, КФК не существует в индивидуальном виде [3, 4], а образует ряд гидратных форм. Результаты ранних работ, посвященных получению кристаллогидратов КФК состава $H_2SiF_6 \cdot 2H_2O$ ($t_{пл}$ = 19°C) [5] и $H_2SiF_6 \cdot nH_2O$ (n = 1, 4; $t_{пл}$ = 20 и 0°C соответственно) [6] были пересмотрены в [7]. При изучении системы H_2SiF_6–H_2O в области высоких концентраций H_2O методом низкотемпературного дифференциального термического анализа авторы [7] установили существование кристаллических гидратов состава $H_2SiF_6 \cdot nH_2O$ (n = 4, 6, 9.5; $t_{пл}$ = 20, –12, –54°C соответственно), являющихся, по данным РСА, солями оксония $(H_5O_2)_2SiF_6$, $(H_5O_2)_2SiF_6 \cdot 2H_2O$ и $(H_5O_2)(H_7O_3)SiF_6 \cdot 4.5H_2O$. При этом подтвердились данные [8] о выделении гидрата КФК с высоким содержанием воды, плавящегося при –13°C. Получен также нестойкий дигидрат $H_2SiF_6 \cdot 2H_2O$ неустановленного строения, легко разлагающийся при температуре "несколько ниже комнатной" [7].

В настоящей работе представлены результаты изучения кристаллической структуры относительно стабильного соединения состава $H_2SiF_6 \cdot 2H_2O$ – гексафторосиликата оксония, выделенного при попытке осуществить реакцию КФК с гидразидом нитрилуксусной кислоты.

ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

Синтез. Бесцветные монокристаллы соединения $(H_3O)_2SiF_6$ (**I**), плавящиеся с разложением при $t \geq 60$°C, выделены с низким выходом в процессе изотермического испарения при комнатной температуре реакционной смеси 45%-ной КФК ("ч. д. а.", фторное число $\varphi = \Sigma F/\Sigma Si = 5.84$) и метанольного раствора гидразида нитрилуксусной кислоты (L) (мольное соотношение КФК : L = 3 : 1).

ИК-спектр I (спектрофотометр Specord 75IR, область 4000–400 см$^{-1}$, образец в виде суспензии в вазелиновом масле, стекла KRS-5): 3290 ср.ш. ($\nu(H_3O)^+$, $\nu_1 + \nu_3$), 1698 ср. ($\delta(H_3O)^+$, ν_4), 767 пл., 717 с. ($\nu(SiF)$, ν_3), 473 ср. ($\delta(SiF_2)$, ν_4).

РСА. Кристаллы I ($H_6F_6O_2Si$, M = 180.14) ромбические: a = 5.928(1), b = 17.790(4), c = 25.152(2) Å, V = 2652.6(9) Å^3, $\rho_{выч.}$ = 2.030 г/см^3, $\mu(MoK_\alpha)$ = = 0.467 мм$^{-1}$, $F(000)$ =1620, Z = 18, пр.гр. *Immm*.

Экспериментальный материал получен с бесцветного монокристалла размером 0.39 × 0.28 × × 0.56 мм при комнатной температуре на автоматическом четырехкружном дифрактометре Enraf-Nonius CAD-4 (λMoK_α, λ = 0.71073 Å, графитовый монохроматор, ω-сканирование, $2\theta_{max}$ = 49.9°). Всего снято 2545 отражений ($-6 \leq h \leq 7$, $0 \leq k \leq 21$, $-7 \leq l \leq 29$), из них 1344 независимых рефлекса (R_{int} = = 0.0303). Поглощение не учитывалось.

Структура определена прямыми методами (SHELXS-86 [9]) и уточнена методом наименьших

Таблица 1. Координаты атомов и их тепловые параметры $U_{экв}/U_{изо}$ в структуре I

Атом	x	y	z	$U_{экв}/U_{изо}$, Å^2
Si(1)	0	0	0	0.012(3)
Si(2)	0	0.3331(4)	0	0.019(2)
Si(3)	0.5	−0.5	−0.1671(3)	0.020(2)
Si(4)	0.5	−0.1666(3)	−0.1664(2)	0.015(2)
F(1)	0	0	0.0667(6)	0.030(4)
F(2)	0.199(2)	0.0673(5)	0	0.027(3)
F(3)	0.203(2)	0.2658(4)	0	0.024(3)
F(4)	0	0.3342(5)	0.0676(4)	0.021(3)
F(5)	0.205(2)	0.4008(5)	0	0.024(3)
F(6)	0.5	−0.5	−0.0993(4)	0.020(4)
F(7)	0.5	−0.5	−0.2341(5)	0.022(4)
F(8)	0.704(2)	−0.4324(4)	−0.1660(2)	0.024(2)
F(9)	0.5	−0.1670(5)	−0.0991(4)	0.025(3)
F(10)	0.699(2)	−0.0996(4)	−0.1676(2)	0.028(3)
F(11)	0.5	−0.1670(5)	−0.2330(4)	0.024(3)
F(12)	0.702(2)	−0.2341(3)	−0.1663(2)	0.025(2)
O(1w)	0	0.5	0.2500(7)	0.043(6)
O(2w)	1	−0.1646(7)	−0.2497(5)	0.045(4)
O(3w)	0	0.5	0.0829(7)	0.026(5)
O(4w)	0	0.1687(5)	0.4163(5)	0.024(4)
O(5w)	0	0.1656(7)	0.0833(5)	0.044(5)
O(6w)	0.5	0	−0.081(1)	0.065(7)
H(1)	0.171	0.5	0.263	0.05
H(2)	1	−0.212	−0.228	0.05
H(3)	0.835	−0.158	−0.267	0.05
H(4)	1	−0.124	−0.220	0.05
H(5)	0.0	0.454	0.112	0.05
H(6)	0.183	0.5	0.076	0.05
H(7)	0	0.209	0.449	0.05
H(8)	0.178	0.174	0.406	0.05
H(9)	0.163	0.168	0.069	0.05
H(10)	0	0.127	0.113	0.05
H(11)	0.5	−0.038	−0.053	0.05
H(12)	0.657	0	−0.102	0.05

квадратов по F^2 (SHELXL-97 [10]) в полноматричном анизотропном приближении. Анализ распределения пиков на разностных синтезах электронной плотности однозначно свидетельствует о том, что гидратные единицы в кристалле I присутствуют в виде катионов оксония H_3O^+. Большинство атомов водорода катионов оксония определено из разностных синтезов Фурье и включено в уточнение в фиксированных позициях (U_H = 0.05 Å^2). Шесть из двенадцати локализованных независимых атомов водорода (H(1), H(3), H(6), H(8), H(9) и H(11)) статистически неупорядочены в двух равновероятных позициях каждый (подробнее см. ниже).

Окончательные результаты уточнения: $R1$ = = 0.0846, $wR2$ = 0.4660, $GOOF$ = 2.418 по 252 отражениям с $I > 2\sigma(I)$; $R1$ = 0.2171, $wR2$ = 0.5395 по всем отражениям; 124 уточняемых параметра. Коэффициент экстинкции равен 0.0000(4), значения $\Delta\rho_{max}$ и $\Delta\rho_{min}$ составляют соответственно 0.773 и –0.751 e Å^{-3}.

Координаты и температурные факторы атомов структуры I приведены в табл. 1, межатомные расстояния и валентные углы – в табл. 2.

РЕЗУЛЬТАТЫ И ИХ ОБСУЖДЕНИЕ

В ходе РСА установлено, что структурными единицами кристалла I – формально дигидрата КФК $H_2SiF_6 \cdot 2H_2O$ – являются октаэдрические анионы SiF_6^{2-} и катионы оксония H_3O^+ (рис. 1), объединенные разветвленной сетью Н-связей. Упомянутые выше высокогидратные кристаллические фазы $(H_5O_2)_2SiF_6$ (**II**), $(H_5O_2)_2SiF_6 \cdot 2H_2O$ (**III**) и $(H_5O_2)(H_7O_3)SiF_6 \cdot 4.5H_2O$ (**IV**) [7] содержат, как и I, анионы SiF_6^{2-} и ди- или триоксониевые катионы.

Структура I высокосимметрична: 19 из 22 неводородных атомов и девять из 12 локализованных атомов водорода занимают позиции *m*, *mm* и *mmm*. Симметрия четырех кристаллографически неэквивалентных атомов кремния: Si(1) – *mmm*, Si(2) и Si(3) – *mm*, Si(4) – *m*. Октаэдры SiF_6 достаточно регулярны: интервал длин связей Si–F составляет 1.67–1.71°, углов FSiF – 89.1°–91.1°. Среднее расстояние Si–F в I (1.69(1) ± 0.02 Å) согласуется с аналогичными величинами в центросимметричных октаэдрах SiF_6 структур II, III и IV: 1.682(1) ± 0.016, 1.691(1) ± 0.014 и 1.692(1) ± 0.014 Å соответственно (в структуре IV один из двух независимых анионов SiF_6^{2-} имеет кристаллографическую симметрию C_2).

Все шесть независимых гидратных атомов кислорода занимают частные положения mm (O(1w), O(3w), O(6w)) и m (O(2w), O(4w), O(5w)). Все шесть катионов оксония в той или иной степени неупорядочены: часть атомов водорода, попарно связанных плоскостями m, занимает по две статистически равновероятные позиции (факторы заселенности 0.5). В соответствии с неупорядоченностью

Таблица 2. Основные длины связей (*d*) и валентные углы (ω) в структуре I

Связь	*d*, Å	Связь	*d*, Å
Si(1)–F(1)	1.68(2)	Si(1)–F(2)	1.68(1)
Si(2)–F(3)	1.70(1)	Si(2)–F(4)	1.700(9)
Si(2)–F(5)	1.71(1)	Si(3)–F(6)	1.70(1)
Si(3)–F(7)	1.69(1)	Si(3)–F(8)	1.705(9)
Si(4)–F(9)	1.69(1)	Si(4)–F(10)	1.68(1)
Si(4)–F(11)	1.67(1)	Si(4)–F(12)	1.694(8)
Угол	ω, град	Угол	ω, град
F(1)Si(1)F(2)	90.0(4)	F(3)Si(2)F(4)	90.4(4)
F(3)Si(2)F(5)	89.6(4)	F(4)Si(2)F(5)	89.6(4)
F(6)Si(3)F(7)	180.0(4)	F(6)Si(3)F(8)	89.1(4)
F(7)Si(3)F(8)	90.9(4)	F(9)Si(4)F(10)	91.1(4)
F(9)Si(4)F(11)	179.5(5)	F(9)Si(4)F(12)	89.7(4)
F(10)Si(4)F(11)	89.2(4)	F(10)Si(4)F(12)	90.4(4)
F(11)Si(4)F(12)	89.9(4)	H(2)O(2w)H(3)	108
H(2)O(2w)H(4)	102	H(3)O(2w)H(4)	103
H(5)O(3w)H(6)	96	H(7)O(4w)H(8)	96
H(5)O(3w)H(5A)	96	H(11)O(6w)H(12)	111
H(9)O(5w)H(10)	107		

Операция симметрии A: $-x, 1-y, z$.

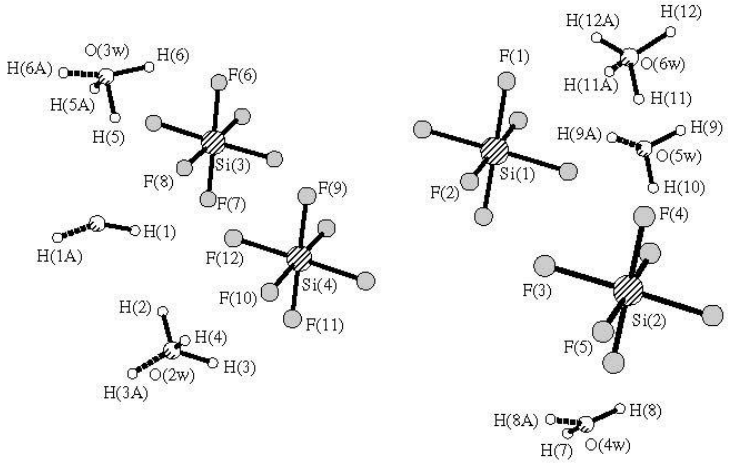

Рис. 1. Структурные единицы кристалла I – анионы SiF_6^{2-} и катионы H_3O^+.

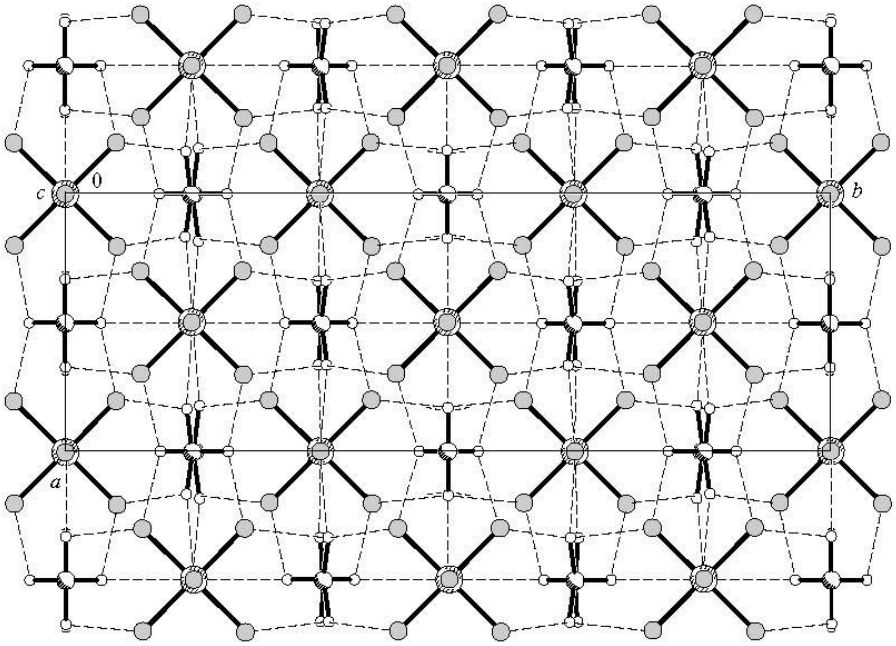

Рис. 2. Упаковка структурных единиц в кристалле I (проекция вдоль оси *c*).

ряда атомов водорода (и локализацией не всех, а части оксониевых атомов H) вокруг атомов O(2w), O(3w), O(6w); O(4w), O(5w) и O(1w) имеются соответственно по четыре; три и две позиции атомов H на расстояниях O(w)–H 0.97–1.11 Å. В качестве критерия для выбора каждого иона оксония из нескольких возможных приняты пирамидальность иона H_3O^+; интервал углов HOH 96°–121° и интервал невалентных внутрикатионных контактов H···H 1.59–1.87 Å. Предпочтительность пирамидальной геометрии иона оксония (симметрия C_{3v}) перед плоской (D_{3h}) подтверждена расчетом ab initio [11], согласно которому оптимальное значение угла HOH составляет 111.6°.

В трех катионах H_3O^+ имеют место по две равновероятные ориентации трех атомов H: H(2), H(3), H(4) и H(2), H(3A), H(4A) для O(2w) (отклонение атома O от плоскости трех атомов H (Δ) составляет 0.43 Å, сумма углов HOH (Σ) равна 313°); H(5), H(5A), H(6) и H(5), H(5A), H(6A) при O(3w) (Δ = 0.57 Å, Σ = 288°); H(11), H(12), H(12A) и H(11A), H(12), H(12A) при O(6w) (Δ = 0.26 Å, Σ = = 343°). В двух катионах оксония (с атомами O(4w), O(5w)) "недостает" одного, а в катионе H_3O^+ с атомом O(1w) – двух атомов водорода. Эти три гидратные единицы также имеют по две равновероятные ориентации относительно локализованных атомов H: H(7), H(8) и H(7), H(8A) для O(4w) (угол H(7)O(4w)H(8) равен 96°); H(9), H(10) и H(9A), H(10A) для O(6w) (угол H(9)O(6w)H(10) равен 107°); H(1) и H(1A) для O(1w). Нереалистичны остальные шесть вариантов расположения пар атомов водорода, связанных плоскостями m, при каждом из шести атомов O(1w)–O(6w): углы H(1)O(1w)H(1A), H(3)O(2w)H(3A), H(6)O(3w)H(6A), H(8)O(4w)H(8A), H(9)O(5w)H(9A), как и соответствующие контакты H···H, слишком велики (131°–162° и 1.93–2.17 Å), а H(11)O(6w)H(11A) и H(11)···H(11A), наоборот, очень малы (88° и 1.36 Å).

Пирамидальное строение оксониевого иона установлено и для кристаллов трех соединений с 18-краун-6 (L): комплексов $(H_3O)[M^VOCl_4(H_2O)] \cdot L$, M = Mo (**V**), Re (**VI**) [12] и $(H_3O)\{L \cdot (COOH)_4\}Cl$ (**VII**) [13]. Атом кислорода "приподнят" над плоскостью трех атомов водорода на 0.21, 0.38 и 0.33 Å в V, VI и VII соответственно.

Упаковка структурных единиц в кристалле I показана на рис. 2. Гексафторосиликатные анионы и катионы оксония объединены разветвленной сетью слабых (преимущественно вилочных) водородных связей (табл. 3). Каждый катион H_3O^+ с учетом контактов O···F ≤ 3.05 Å, взаимодействует с несколькими (от двух до шести) анионами SiF_6^{2-}.

В заключение отметим, что "дигидрат" $H_2SiF_6 \cdot 2H_2O$ (гексафторосиликат гидроксония) может,

Таблица 3. Короткие межионные контакты O–H···F (O···F ≤ 3.05 Å) в структуре I

Контакт O–H···F	Расстояния, Å			Угол OHF, град	Координаты атома F
	O···F*	O–H	H···F		
O(1w)–H(1)···F(7)	2.99	1.06	2.08	142	$1-x, 1-y, z$
O(1w)–H(1)···F(10)	2.97	1.06	2.50	106	$-0.5+x, 0.5+y, 0.5+z$
O(1w)···F(8)	3.00				$1-x, 1+y, -z$
O(1w)···F(11)	3.00				$-1-x, -y, -z$
O(2w)–H(2)···F(11)	3.03	1.00	2.37	123	$-x, -1+y, -1+z$
O(2w)–H(2)···F(12)	3.01	1.00	2.39	119	x, y, z
O(2w)–H(3)···F(8)	2.99	1.08	2.34	117	$0.5-x, -0.5-y, -0.5-z$
O(2w)–H(3)···F(11)	2.99	1.08	2.17	132	x, y, z
O(2w)–H(3)···F(12)	3.02	1.08	2.56	105	$1.5-x, -0.5-y, -0.5-z$
O(2w)–H(4)···F(7)	2.96	1.05	2.48	106	$1+x, -y, -1-z$
O(2w)–H(4)···F(10)	2.96	1.05	2.25	123	x, y, z
O(3w)–H(5)···F(4)	2.98	1.11	2.41	110	x, y, z
O(3w)–H(5)···F(8)	2.98	1.11	2.25	122	$-1+x, -y, -z$
O(3w)–H(6)···F(6)	2.99	1.10	1.97	154	$1-x, 1-y, z$
O(3w)···F(5)	2.99				x, y, z
O(4w)–H(7)···F(3)	2.98	1.08	2.23	125	$x, y, -z$
O(4w)–H(7)···F(9)	2.95	1.08	2.52	103	$-1-x, -y, -z$
O(4w)–H(8)···F(4)	2.99	1.09	2.02	146	$-x, y, z$
O(4w)–H(8)···F(12)	2.96	1.09	2.46	107	$-0.5+x, 0.5+y, 0.5+z$
O(4w)···F(5)	3.00				$x, y, -z$
O(4w)···F(6)	3.03				$-1-x, y, -z$
O(5w)–H(9)···F(2)	2.97	1.04	2.50	107	x, y, z
O(5w)–H(9)···F(3)	3.00	1.04	2.46	112	x, y, z
O(5w)–H(9)···F(9)	2.99	1.04	2.14	138	$x, -y, -z$
O(5w)–H(10)···F(1)	2.98	1.02	2.53	105	x, y, z
O(5w)–H(10)···F(10)	3.01	1.02	2.30	125	$-1+x, -y, -z$
O(5w)···F(4)	3.03				x, y, z
O(5w)···F(12)	3.00				$-1+x, -y, -z$
O(6w)–H(11)···F(2)	2.99	0.97	2.29	125	$1-x, -y, z$
O(6w)–H(11)···F(9)	3.01	0.97	2.57	108	x, y, z
O(6w)–H(12)···F(1)	2.99	1.07	2.22	127	$1-x, -y, z$
O(6w)–H(12)···F(10)	3.05	1.07	2.44	115	x, y, z

* σ(O···F) = 0.01 Å.

по-видимому, существовать в различных кристаллических модификациях, и нам удалось получить и охарактеризовать более стабильную по сравнению с описанной в [5, 7] форму соединения. Обнаруженная возможность выделения соединения I из системы КФК–L–H_2O представляется достаточно неожиданной. Не исключено, что фиксируемая на поверхности монокристаллов I окрашенная аморфная пленка – очевидно, продукт гидролитических превращений гидразида L в кислом реакционном растворе – благоприятствует изоляции комплекса I. При этом не наблюдается образования ожидаемого продукта кислотно-основного взаимодействия типа ранее описанных гексафторосиликатов, протонированных по концевому атому азота гидразидных лигандов [14, 15].

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Додаток 39

Копія статті

“A new phase of 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane,and 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(tetrafluoroborate) monohydrate, both determined at 123 K”

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A new phase of 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, and 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(tetrafluoroborate) monohydrate, both determined at 123 K

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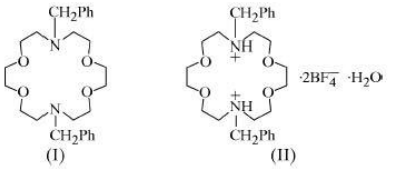
7,16-Dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, $C_{26}H_{38}N_2O_4$, (I), crystallizes in space group $P2_1/c$, with two independent molecules adopting different conformations. The 'free' crowns adopt a typical 'parallelogram' shape, in which two methylene groups are turned inward toward the center of the ring and the benzyl groups splay out from the ring. In 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(tetrafluoroborate) monohydrate, $C_{26}H_{40}N_2O_4^{2+}\cdot 2BF_4^-\cdot H_2O$, (II), the macrocycle is centrosymmetric, and the protonated N atoms adopt an *endo–endo* orientation that is stabilized by a bifurcated N—H···O hydrogen bond, where the O atoms of the macrocycle act as hydrogen-bond acceptors. The phenyl groups of the benzyl side arms are turned above and below the macrocycle; C—H···π interactions between the phenyl substituents and two macrocyclic methylene H atoms govern the overall conformation of the macrocycle. Bridging tetrafluoroborate anions link the macrocyclic cations *via* weak C—H···F hydrogen bonds into channels running along [100], which are filled by the weakly hydrogen-bonded water molecules.

Comment

The ability of crown ethers to form host–guest complexes with normally unstable or volatile species is well known (Bott *et al.*, 1991; Chuit *et al.*, 1993; Feinberg *et al.*, 1993). We have previously reported that the classic crown ethers (18-crown-6 and isomers of dicyclohexyl-18-crown-6) provide the opportunity to hold harmful gaseous (SiF_4; Simonov *et al.*, 1994) or low-melting substances ($BF_3\cdot H_2O$; Fonari *et al.*, 1997) in the form of hydrogen-bonded molecular or ionic complexes.

A general method of synthesis of host–guest-type complexes of boron–fluoro complexes with crown ethers, based on the interaction of boron trifluoride etherate, $BF_3\cdot OEt_2$, with the corresponding ligand in the atmosphere not protected from moisture, has been developed (Gelmboldt *et al.*, 1995; Simonov *et al.*, 1995). This method was further elaborated for the preparation of complexes based on nitrogen-containing macrocycles (Fonari *et al.*, 1999; Lipkowski *et al.*, 2001). On the basis of these studies, it was shown that the composition of the 'guest', the product of hydrolytic transformations of $BF_3\cdot OEt_2$, is dictated by the nature of the macrocycle. Crown ethers offering different extents of shielding of the macrocyclic cavity stabilize either molecular ($BF_3\cdot H_2O$) or ionic ($H_3O^+\cdot BF_4^-$) complexes, while nitrogen-containing macrocycles, which are easily protonated in the acidic medium, form complexes exclusively with the tetrafluoroborate anions. The components are linked in the crystal structure *via* a diverse system of O—H···O and N—H···F hydrogen bonds.

As part of our investigation of the coordination abilities of boron trifluoride with crown ethers and their derivatives, we focus here on *N*,*N*′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, (I). Compound (I) contains a mixed N,O-atom donor function that could provide diverse possibilities for the realization of hydrogen bonds with neutral boron trifluoride molecules or with the tetrafluoroborate anion. C—H···π interactions may also contribute to the conformational stability of the macrocycle.



The Cambridge Structural Database (CSD; Allen, 2002) contains data for two single-crystal X-ray determinations of (I), carried out under ambient conditions [T = 295 K; CSD refcodes XESSUJ (Arnold *et al.*, 1988) and XESSUJ01 (Fewings & Junk, 1999)]. Both determinations are in space group $C2/c$, with similar unit-cell dimensions but with high R factors. The unit-cell parameters for the two compounds [a = 19.487 (6) Å, b = 11.259 (2) Å, c = 13.656 (5) Å and β = 121.10 (3)° for XESSUJ, and a = 19.479 (2) Å, b = 11.235 (3) Å, c = 17.038 (3) Å and β = 136.68 (0)° for XESSUJ01] can be easily transformed to the same unit cell [with dimensions a = 13.656 Å, b = 11.259 Å, c = 17.068 Å and β = 102.14° for XESSUJ, and a = 13.668 Å, b = 11.235 Å, c = 17.038 Å and β = 102.11° for XESSUJ01] using the transformation matrices (001/010/101) and ($\bar{1}0\bar{1}/0\bar{1}0/001$), respectively. In the new setting, both structures again belong to space group

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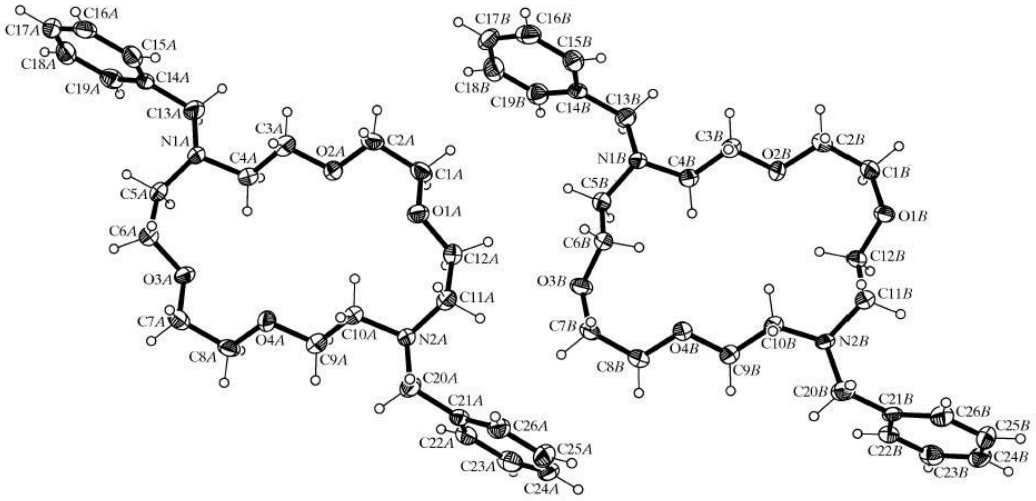

Figure 1
The structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

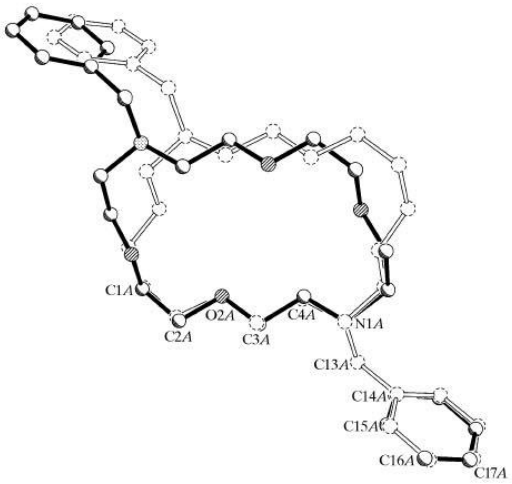

Figure 2
Superimposition of molecules *A* and *B* in (I), in projection on the labeled atoms.

*C*2/*c*, so XESSUJ and XESSUJ01 report the same structure, as confirmed by the practically ideal superposition of these molecules.

In our experiment, carried out at 123 K, the unit-cell dimensions [a = 16.993 (3) Å and c = 13.391 (3) Å] are close to the calculated c and a parameters of the new setting, although in an inverted order and with a reduction explained by the low-temperature conditions of the experiment, while the b parameter [b = 22.455 (5) Å] is about two times longer. We found a structure solution in space group $P2_1/c$. The phase transition and the structure of (I) are assumed to correspond to a low-temperature phase with lower symmetry. Fig. 1 shows the asymmetric unit, containing two independent crown molecules (molecules *A* and *B*), which differ essentially in their conformations. This difference is clearly evident from Fig. 2, which depicts the superposition of molecules *A* and *B*. The lack of inversion centers in the two molecules is evidenced by the values of the dihedral angles between the planes of the aromatic rings C14–C19 and C21–C26 [3.6 (2) and 4.4 (2)° in molecules *A* and *B*, respectively], which deviate from 0° as expected in a molecule imposed on an inversion center. The 'free' crowns adopt a typical 'parallelogram' shape, in which two methylene moieties turn inward toward the center of the ring. The shortest intramolecular distances across the cavity are C4···O4 and C10···O2, being 4.157 (3) and 4.151 (3) Å in molecule *A*, and 4.299 (3) and 4.306 (3) Å in molecule *B*; the longest distances are C1···C7 and C5···C11, being 7.384 (4) and 8.611 (4) Å in molecule *A*, and 8.518 (4) and 7.387 (4) Å in molecule *B*.

Each conformer in (I) is very close to being centrosymmetric, as shown by the torsion angles in Table 1. The torsion angles run in the sequences *gḡaagaaaaāḡgaaḡaaaa* and *gaaḡgaaaāḡaagḡaaaa* in molecules *A* and *B*, respectively [in the anticlockwise direction, beginning from the C4—N1—C5—C6 angle, where *g* denotes *gauche* (+60 to +120°), *ḡ* denotes *gauche* (−60 to −120°) and *a* denotes antiperiplanar (±120 to ±180°)]. The differences in the values of the angles that are situated in the macrocycles in the same positions relative to the centers of the rings (the point of the intersection of three transannular O···O distances) range from 0° for the C5—C6—O3—C7 and C11—C12—O1—C1 angles, up to 2.1° for the C6—O3—C7—C8 and C12—O1—C1—C2 angles in molecule *A*, and range from 0.2° for the C2—O2—C3—C4 and C8—O4—C9—C10 angles, up to 3.1° for the C6—O3—C7—C8 and C12—O1—C1—C2 angles in molecule *B*.

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Our calculations of the torsion angles in the independent part of the centrosymmetric molecule of XESSUJ revealed the following sequence (anticlockwise, running from the C4—N1—C5—C6 angle to the C9—C10—N2—C11 angle): −73.1, 107.7, −179.1, 139.2, −69.4, 171.8, 173.2, 177.1 and −159.2°. These values are close to the inverse of the torsion-angle pattern given in Table 1. The common point is a sequence of four *anti* torsion angles that is typical for the pure phases of oxygen-containing crown ethers, for example 18-crown-6 (Maverick *et al.*, 1980) and *cis-trans-cis*-dicyclohexano-18-crown-6 (Kravtsov *et al.*, 2002). The benzyl side arms splay out from the crown rather than lying below and above the macrocyclic plane. Surprisingly, there does not appear to be any intermolecular π stacking in (I).

The centrosymmetric formula unit of compound 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(tetrafluoroborate) monohydrate, (II), is shown in Fig. 3. The slight distortion of the BF_4^- tetrahedron is indicated by the B—F distances being in the range 1.384 (2)–1.399 (2) Å and the F—B—F angles being in the range 108.05 (15)–110.94 (14)°.

The twofold protonated macrocyclic cation exhibits crystallographically imposed C_i symmetry. The protonated N atoms adopt an *endo–endo* orientation that is stabilized by three-center N—H···O hydrogen bonds of 2.709 (2) and 2.901 (2) Å, where the O atoms of the macrocycle act as hydrogen-bond acceptors (Table 3). The 18-membered macrocyclic cavity exhibits a degree of rigidity and adopts a chair conformation, with the O atoms lying exactly in one plane and the N atoms deviating 1.609 (2) Å above and below this plane. This rigidity probably stems from the intramolecular N—H···O hydrogen bonds, and from the presence of C—H···π interactions between two methylene H atoms and the aromatic subunits, as well as a C—H···O intramolecular hydrogen bond of 3.395 (2) Å (Table 3 and Fig. 3). These interactions effectively anchor the ring into its present conformation, and turn the phenyl groups of the benzyl side arms above and below the macrocycle in such a way that the dihedral angle between the plane of the aromatic ring and the plane of the crown O atoms is 42.70 (5)°. The C···*Cg*1 and H···*Cg*1 (*Cg*1 is the centroid of the C11–C16 ring) distances of 3.758 (2) and 2.82 Å, and the C—H···*Cg*1 angle of 164°, suggest the presence of strong π···H interactions at the center of the aromatic ring (Braga *et al.*, 1998). Both of these types of intramolecular interaction in this dication have been noted for a series of lanthanoid complexes (Evans *et al.*, 2002) and seem to be reasonable in $[(I)H_2]I_8$ (Gaballa *et al.*, 2004). The involvement of methylene H atoms in these interactions is unusual in the light of possible competition with, for example, water H atoms.

The conformation of the macrocyclic cavity strongly deviates from that of the 'free' macrocycle; the corresponding torsion angles are listed in Table 2. Inspection of the torsion angles (absolute values 50–87 and 152–176°) reveals that the macrocycle is characterized by partial conformations [(*anti*, *gauche*, *anti*), (*anti*, *gauche*, *anti*) and (*gauche*, *gauche*, *gauche*)] of the N1—C2—C3—O4, O4—C5—C6—O7 and O7—C8—C9—N1′ subunits. The shape and conformation of the macrocyclic cation in (II) is close to that found in its complex with octaiodide (Gaballa *et al.*, 2004) and in the neodymium complex $[(I)H_2][Nd(NO_3)_5(H_2O)]$ (Saleh *et al.*, 1998). Protonation of the aza-crown ether and the above-mentioned intramolecular interactions close the cavity against the inclusion of neutral (water) or charged (BF_4^-) species that appear to occupy the outer space of the crowns.

BF_4^- anions fulfill bridging functions, and in the *bc* plane they bind the macrocyclic cations *via* multiple weak C—H···F hydrogen bonds, forming channels propagated along the *a* direction. The shortest C—H···F contacts range from 3.278 (2) to 3.395 (2) Å and are summarized in Table 2, both aromatic and aliphatic H atoms being involved in these interactions. Water molecules are held in the center of the channel, as seen in Fig. 4, and because of the weak O—H···F

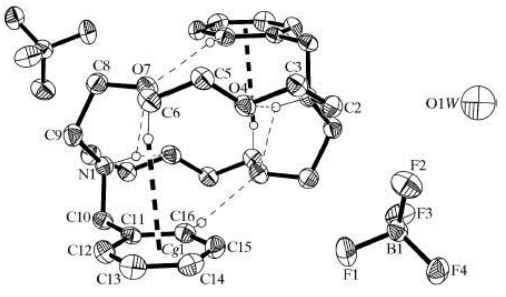

Figure 3
The structure of (II), showing the C—H···π interactions. *Cg*1 is the centroid of the C11–C16 ring. Displacement ellipsoids are drawn at the 50% probability level and only H atoms involved in specific contacts are shown.

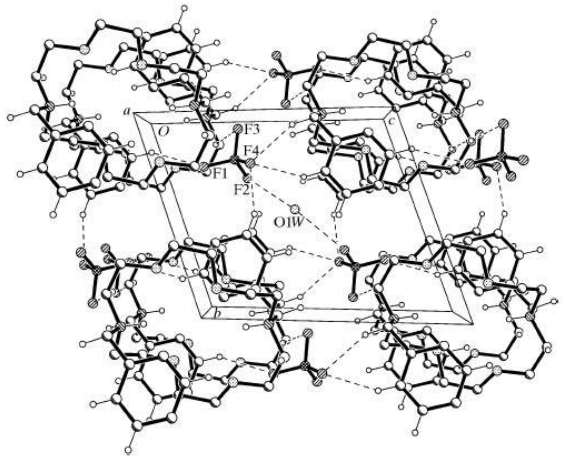

Figure 4
Part of the crystal structure of (II), showing the channels formed by hydrogen-bonded macrocyclic cations and BF_4^- anions, and the water molecules that occupy these channels. Only H atoms involved in specific contacts are shown.

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hydrogen bond (O···F = 2.83 Å) they are disordered around the inversion center. As shown above, the idealized stoichiometry of the $[(I)H_2](BF_4)_2{\cdot}H_2O$ complex is 1:2:1, whilst really only about 20% of the water content of each complex appears to be retained in the crystal lattice.

Experimental

Compound (I) was prepared according to the procedure of Gustowski *et al.* (1987). To obtain complex (II), compound (I) (244 mg, 0.1 mmol) was dissolved in methanol (5 ml). The reaction mixture was allowed to stand until crystals were deposited. These were filtered off and recrystallized from a 1:1 mixture of methanol and ethyl acetate to yield colorless transparent crystals (m.p. 441 443 K). Analysis calculated for $C_{26}H_{42}B_2F_8N_2O_5$: C 49.1, H 6.65, F 23.9, N 4.4%; found: C 49.0, H 6.7, F 23.9, N 4.4%.

Compound (I)

Crystal data

$C_{26}H_{38}N_2O_4$
M_r = 442.58
Monoclinic, $P2_1/c$
a = 16.993 (3) Å
b = 22.455 (5) Å
c = 13.391 (3) Å
β = 103.48 (3)°
V = 4968.9 (18) Å^3
Z = 8
D_x = 1.183 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 860 reflections
θ = 1–27.5°
μ = 0.08 mm^{-1}
T = 123 (2) K
Prism, colorless
0.20 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
25 950 measured reflections
8591 independent reflections
5565 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 25.0°
h = 20 → 19
k = 26 → 20
l = 15 → 15

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.141
S = 1.10
8591 reflections
577 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 2.1759P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

O1*A*—C1*A*—C2*A*—O2*A*	−70.7 (3)	O1*B*—C1*B*—C2*B*—O2*B*	−74.7 (3)
C1*A*—C2*A*—O2*A*—C3*A*	174.2 (2)	C1*B*—C2*B*—O2*B*—C3*B*	178.7 (2)
C2*A*—O2*A*—C3*A*—C4*A*	174.4 (2)	C2*B*—O2*B*—C3*B*—C4*B*	171.7 (2)
O2*A*—C3*A*—C4*A*—N1*A*	178.1 (2)	O2*B*—C3*B*—C4*B*—N1*B*	178.0 (2)
C3*A*—C4*A*—N1*A*—C5*A*	−162.6 (2)	C3*B*—C4*B*—N1*B*—C5*B*	−156.1 (2)
C4*A*—N1*A*—C5*A*—C6*A*	68.6 (3)	C4*B*—N1B—C5*B*—C6B	76.6 (3)
N1*A*—C5*A*—C6*A*—O3*A*	−87.2 (3)	N1*B*—C5*B*—C6*B*—O3*B*	−161.3 (2)
C5*A*—C6*A*—O3*A*—C7*A*	178.1 (2)	C5*B*—C6*B*—O3*B*—C7*B*	167.3 (2)
C6*A*—O3*A*—C7*A*—C8*A*	−157.6 (2)	C6*B*—O3*B*—C7*B*—C8*B*	−88.1 (3)
O3*A*—C7*A*—C8*A*—O4*A*	72.4 (3)	O3*B*—C7*B*—C8*B*—O4*B*	72.1 (3)
C7*A*—C8*A*—O4*A*—C9*A*	−174.7 (2)	C7*B*—C8*B*—O4*B*—C9*B*	−177.4 (2)
C8*A*—O4*A*—C9*A*—C10*A*	−173.6 (2)	C8*B*—O4*B*—C9*B*—C10*B*	−171.9 (2)
O4*A*—C9*A*—C10*A*—N2*A*	177.9 (2)	O4*B*—C9*B*—C10*B*—N2*B*	−173.7 (2)
C9*A*—C10*A*—N2*A*—C11*A*	159.7 (2)	C9*B*—C10*B*—N2*B*—C11*B*	158.2 (2)
C10*A*—N2*A*—C11*A*—C12*A*	−68.9 (3)	C10*B*—N2*B*—C11*B*—C12*B*	−78.4 (3)
N2*A*—C11*A*—C12*A*—O1*A*	87.8 (3)	N2*B*—C11*B*—C12*B*—O1*B*	164.1 (2)
C11*A*—C12*A*—O1*A*—C1*A*	−178.1 (2)	C11*B*—C12*B*—O1*B*—C1*B*	−164.7 (2)
C12*A*—O1*A*—C1*A*—C2*A*	159.1 (2)	C12*B*—O1*B*—C1*B*—C2*B*	85.0 (3)

Compound (II)

Crystal data

$C_{26}H_{40}N_2O_4^{2+}{\cdot}2BF_4^-{\cdot}H_2O$
M_r = 621.48
Triclinic, $P\overline{1}$
a = 7.9290 (6) Å
b = 9.3870 (6) Å
c = 11.6070 (7) Å
α = 69.342 (4)°
β = 72.226 (4)°
γ = 81.480 (4)°
V = 768.98 (9) Å^3
Z = 1
D_x = 1.342 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3035 reflections
θ = 1–27.5°
μ = 0.12 mm^{-1}
T = 123 (2) K
Prism, colorless
0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
4974 measured reflections
2660 independent reflections
2159 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°
h = 9 → 9
k = 11 → 11
l = 13 → 13

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.102
S = 1.04
2660 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.1724P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 2
Selected torsion angles (°) for (II).

N1^i—C2—C3—O4	−50.1 (2)	C6—O7—C8—C9	74.0 (2)
C2—C3—O4—C5	165.4 (1)	O7—C8—C9—N1	60.3 (2)
C3—O4—C5—C6	−176.2 (1)	C8—C9—N1—C2^i	86.8 (2)
O4—C5—C6—O7	64.6 (2)	C9—N1—C2^i—C3^i	−164.0 (1)
C5—C6—O7—C8	152.6 (1)		

Symmetry code: (i) $1-x, -y, -z$.

Table 3
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O4^i	0.91 (2)	2.25 (2)	2.709 (2)	110.2 (14)
N1—H1N···O7	0.91 (2)	2.43 (2)	2.901 (2)	112.6 (14)
C2—H2*B*···F3	0.99	2.43	3.278 (2)	143
C10—H10*B*···F4^{ii}	0.99	2.43	3.345 (2)	154
C12—H12*A*···F4^{ii}	0.95	2.53	3.383 (2)	150
C13—H13*A*···F4^{iii}	0.95	2.41	3.279 (2)	152
C15—H15*A*···F1	0.95	2.51	3.368 (2)	151
C16—H16*A*···O7^i	0.95	2.52	3.395 (2)	154

Symmetry codes: (i) $1-x, -y, -z$; (ii) $x, y, z-1$; (iii) $2-x, 1-y, -z$.

All non-H atoms, except O1*W*, were refined with anisotropic displacement parameters. C-bound H atoms in (I) and in the $[(I)H_2]^{2+}$ ion in (II) were placed in calculated positions and treated using a riding model. The N-bound H atom in (II) was located in a difference Fourier map and refined [U_{iso}(H) = 1.5U_{eq}(N)]. After the refinement, the difference Fourier map revealed a peak of 0.8 e Å^3. The reasonable O···F distances permit the conclusion that this is caused by a water molecule partially occupying a disordered position around an inversion center. The refined site occupancy is 0.102 (6). Because

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this value is so low, atom O1*W* was refined with an isotropic displacement parameter and its H atoms were not localized.

For both compounds, data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1362). Services for accessing these data are described at the back of the journal.

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Додаток 40

Копія статті

“1,4,7,10-Tetraoxacyclododecane–triphenylmethanethiol (1/2)”

Acta Crystallographica Section C
Crystal Structure Communications
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1,4,7,10-Tetraoxacyclododecane–triphenylmethanethiol (1/2)

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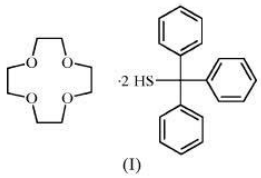
In the centrosymmetric formula unit of the title complex, $C_8H_{16}O_4{\cdot}2C_{18}H_{16}S$, the 1,4,7,10-tetraoxacyclododecane molecule adopts the biangular [66] conformation, and the triphenylmethanethiol molecules are linked to the macrocycle *via* a long S—H···O hydrogen bond [S···O = 3.460 (2) Å and S—H···O = 161 (2)°]. Attractive interactions of phenyl groups in edge-to-face conformations combine inversion-related formula units into chains running along the [111] direction in the crystal structure. Association of the chains into sheets is achieved *via* C—H···π interactions.

Comment

Thiols fulfill numerous functions in biological systems, including a central role in coordinating antioxidant defences (Sen & Packer, 2000). A search of the Cambridge Structural Database (CSD; Version 5.26, plus one 2005 update; Allen, 2002) revealed only a few examples of thiol-containing adducts with neutral organic molecules, predominantly with organic solvents or water. In 2-mercapto-6-methylpurine monohydrate (Srinivasan & Chandrasekaran, 1968) and D-*N*-γ-L-glutamyl-L-cysteine ethyl ester monohydrate (Takimoto-Kamimura *et al.*, 1990), the thiol functional group is involved in an S—H···O(water) hydrogen bond, while in the case of adducts with organic solvents, the thiol molecules exhibit a tendency to be self-assembling and the thiol functional group contributes to the overall system of hydrogen bonding *via* S—H···O(=C), C—H···S(SH) (Evans *et al.*, 1993; Pyrka *et al.*, 1992), S—H···S (Ung *et al.*, 1994; Hardy *et al.*, 1979) or S—H···π interactions (Walsdorff *et al.*, 1997). Only one compound, namely bis(4-aminophenyl) disulfide 4-aminothiophenol (Vangala *et al.*, 2002), exhibits assembly of different molecules *via* C—H···S hydrogen bonds.

For more than two decades, crown ethers have been a very useful tool for following interaction pathways between neutral molecules, including biologically important pathways. As a continuation of our contribution to this topic (Simonov *et al.*, 2003), we report here the crystal structure of the title binary adduct, (I), of triphenylmethanethiol with 1,4,7,10-tetraoxacyclododecane (12-crown-4, 12C4). Compound (I) is the first example of an adduct between a thiol and a crown ether to be structurally described. The main points of this report concern the mode of mutual interaction in this binary system, and the similarities and differences in the crystal packing of triphenylmethanethiol itself and its binary adduct.



(I)

The published metal-free crystal structures of 12C4 with neutral molecules include a ternary clathrate with γ-cyclodextrin and water (Kamitori *et al.*, 1986), binary adducts of the general formula 12C4·2*D*, where *D* is the zwitterion $^+H_3NSO_3^-$ (Simonov *et al.*, 1993), Ph_3SiOH (Babaian *et al.*, 1990), $(PhSO_2)_2NH$ (Wijaya *et al.*, 1998), $(EtSO_2)_2CH_2$ (Michalides *et al.*, 1995) or $Me_2CNNHC(=S)NH_2$ (Moers *et al.*, 1999), and the binary adduct with dithiobisurea, $(NH_2CSNH)_2$, in a 1:1 ratio (Simonov *et al.*, 2003). The structures of these adducts are held together by O—H···O, N—H···O or C—H···O hydrogen bonds between the respective substrate and 12C4. No examples of crown ether complexes held together by S—H···O hydrogen bonds are known to date.

The centrosymmetric formula unit of (I) is shown in Fig. 1 and selected intramolecular geometric data are listed in Table 1. The geometries of both molecules are in reasonable agreement with the precise data obtained for crown ethers and triphenylmethanethiol itself (Bernardinelli *et al.*, 1991). The macrocycle in (I) adopts the C_i symmetric and biangular [66] conformation, which also occurs in pure 12C4 (Groth, 1978) in the aforementioned 1:2 complexes and in several structures containing metal cations. The torsion angles of the 12C4 ring are given in Table 1.

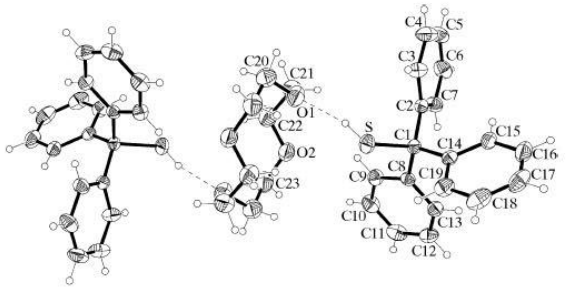


Figure 1
The structure of (I) in the crystal, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the asymmetric unit is numbered; unlabelled atoms are related by the symmetry code $(1-x, -y, 1-z)$. Hydrogen bonds are shown as dashed lines.

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Within the centrosymmetric formula unit, a long S—H···O hydrogen bond (and its symmetry equivalent) links the thiol molecules to the crown ether. Inversion-related formula units are then associated into chains (Fig. 2) *via* attractive interactions of the phenyl groups in an edge-to-face (ef) conformation. This concerted intermolecular attraction uses six phenyl ef interactions from two inversion-related triphenylmethanethiol moieties. As shown in Fig. 2, the two Ph_3C groups approach each other such that each phenyl ring is interleaved between two rings on the other molecule, with two H atoms on each ring directed towards C atoms of a phenyl ring on the other molecule. This concerted motif, known as a sextuple phenyl embrace (SPE; Dance & Scudder, 1995), was primarily explored for structures containing PPh_4^+ cations or terminating XPh_3 ligands and covering P···P separations in the range 5.5–8.0 Å (Scudder & Dance, 2002). The SPE in (I) is characterized by a C1···C1($-x$, $1-y$, $-z$) distance of 6.393 (3) Å. Finally, interchain crosslinking is achieved *via* C—H···π interactions [C5—H5···*Cg*2: C···*Cg* = 3.679 (3) Å, H···*Cg* = 2.99 Å and C—H···*Cg* = 132°, where *Cg*2 is the centroid of phenyl ring C8–C13 at ($x-1$, y, z)], resulting in the association of the chains into sheets.

Some similarities between the supramolecular architecture of (I) and the triphenylmethanethiol molecules in the pure form (CSD refcode SIZBAE, space group $P\overline{1}$; Bernardinelli *et al.*, 1991) are noteworthy. There are two independent molecules in the SIZBAE structure. For the molecule containing atom S1, there is one significant S—H···π interaction [S1—H1···*Cg*: H···*Cg* = 2.62 Å, S···*Cg* = 3.73 Å and S—H···*Cg* = 141°, where *Cg* is the centroid of ring C14–C19 at ($1-x$, $2-y$, $1-z$)], which combines these molecules into centrosymmetric dimers. These dimers are further combined into chains *via* the SPE; the distance between the tetrahedral C atoms [C1···C1($1-x$, $1-y$, $1-z$)] is 6.058 Å. For the molecule containing atom S2, the SPE is characterized by the distance between the tetrahedral C atoms [C20···C20($1-x$, $-y$, $2-z$)] of 6.312 Å. Only the SPE interaction remains in (I), while the S—H···π contact is replaced by the S—H···O(crown) hydrogen bonds.

Comparison of (I) with the complex 12C4·2Ph_3SiOH (CSD refcode SELFIY; Babaian *et al.*, 1990) reveals that these two structures are isomorphous. Similar to (I), the structure of SELFIY is sustained by two inversion-related O—H···O hydrogen bonds (H···O = 1.91 Å and O···O = 2.756 Å) and the SPE; there is an Si1···Si1($-x$, $1-y$, $-z$) separation of 6.538 Å.

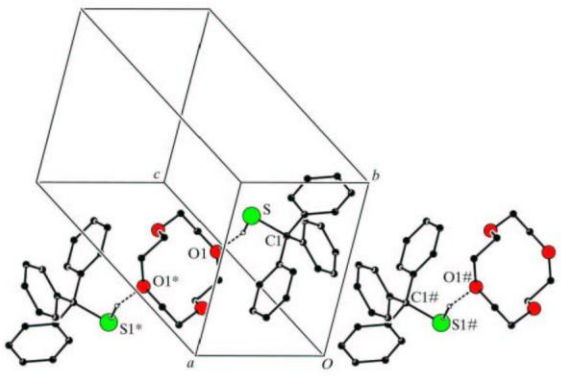

Figure 2
The chain organization in (I) sustained by S—H···O hydrogen bonds and SPE interactions. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($1-x$, $-y$, $1-z$) and ($-x$, $1-y$, $-z$), respectively. Only S-bound H atoms are shown.

Experimental

A solution of 12C4 (0.176 g, 1 mmol) and Ph_3CSH (276 mg, 1 mmol) in a benzene–ethyl ether mixture (1:2 *v*/*v*, 4.5 ml) was stored for 1 d at 293 K in an open flask. Colourless transparent crystals of (I) suitable for X-ray analysis separated in a yield of 83% (0.303 g; m.p. 341–343 K). The crystals were soluble in methanol, ethanol, acetone and chloroform. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62 (*s*, 2H, SH), 3.71 (*s*, 16H, 12C4), 7.22–7.30 (*m*, 30H, aromatic H). Analysis calculated for $C_{46}H_{48}O_4S_2$: C 75.79, H 6.64, S 8.80%; found: C 75.81, H 6.69, S 8.77%.

Crystal data

$C_8H_{16}O_4·2C_{19}H_{16}S$
M_r = 728.96
Triclinic, $P\overline{1}$
a = 8.596 (1) Å
b = 9.803 (1) Å
c = 12.353 (1) Å
α = 84.35 (1)°
β = 89.18 (1)°
γ = 73.61 (1)°
V = 993.7 (2) Å^3
Z = 1
D_x = 1.218 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 4.8–12.5°
μ = 0.18 mm^{-1}
T = 293 (2) K
Prism, yellow
0.40 × 0.36 × 0.21 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical (using intensity measurements) (*SHELXTL-Plus*; Sheldrick, 1995)
T_{min} = 0.877, T_{max} = 0.964
4190 measured reflections
3914 independent reflections
2730 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 26.0°
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: 13.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.121
S = 1.03
3914 reflections
239 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.0975P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—C1	1.8632 (17)		
C2—C1—S	109.48 (12)	C8—C1—S	108.70 (12)
C14—C1—S	104.82 (11)		
C20—O1—C21—C22	−89.1 (3)	C22—O2—C23—C20^i	−106.5 (3)
O1—C21—C22—O2	−69.4 (3)	O2—C23—C20^i—O1^i	72.2 (3)
C21—C22—O2—C23	171.6 (2)	C23—C20^i—O1^i—C21^i	−141.6 (2)

Symmetry code: (i) $-x+1$, $-y$, $-z+1$.

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Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
S—H1···O1	1.33 (3)	2.17 (3)	3.460 (2)	161 (2)

The S-bound H atom was located in a difference Fourier map and refined isotropically. C-bound H atoms were placed in calculated positions, with C H distances of 0.93 or 0.97 Å, and were treated using a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1238). Services for accessing these data are described at the back of the journal.

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Додаток 41

Копія статті

“2,4-Dithiouracil: the reproducible H-bonded structural motifs in the complexes with 18-membered crown ethers”

ARTICLE

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2,4-Dithiouracil: the reproducible H-bonded structural motifs in the complexes with 18-membered crown ethers

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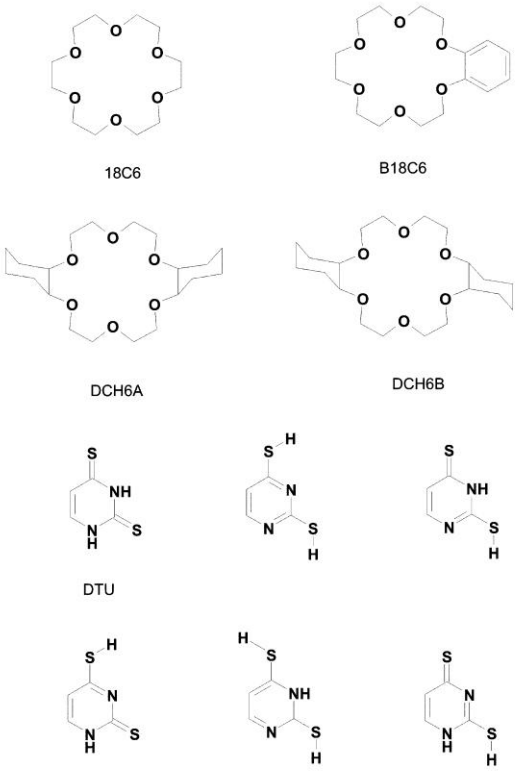
2,4-Dithiouracil (DTU) forms in the crystals the H-bonded monohydrates of a 1 : 1 : 1 ratio with 18-crown-6 (18C6) **1**, *cis*,*syn*,*cis*-isomer of dicyclohexano-18-crown-6 (DCH6A) **2**, and benzo-18-crown-6 (B18C6) **3**, while the anhydrous adduct with *cis*,*anti*,*cis*-isomer of dicyclohexano-18-crown-6 (DCH6B) **4** is of a 2 : 1 ratio. In **1**–**3** the components reproducibly alternate in the chains, while in **4** the chains are built of the alternative centrosymmetric dimers of 2,4-dithiouracil and the molecules of the *cis*,*anti*,*cis*-isomer of dicyclohexano-18-crown-6.

The mimicry of natural recognition processes is one of the challenging research topics of supramolecular chemistry. In biological receptors, the recognition sites offer a precise stereochemistry and exhibit very efficient recognition processes. However, this is achieved at the expense of a high molecular weight. The development of artificial receptors for neutral molecules is an important challenge in modern bioorganic chemistry. A possible strategy for the development of synthetic receptors comprises the combination of medium-sized organic building blocks to which functional groups for molecular recognition can be attached. In addition to compatibility of shape and size, effective molecular recognition requires a precise alignment of binding groups on the receptor with complementary regions on the substrate.[1,2] On the other hand, the traditional widely explored receptors, *e.g.*, macrocyclic crown ether molecules, could give a new insight into the binding of biologically important small molecules.[3,4]

The 1*H*-pyrimidine-2,4-dione ring system plays a significant role in traditional duplex formation, associated with complementary base pairing through hydrogen bonding involving NH and CO functionalities which have been studied in detail.[5,6] Essentially, fewer efforts have been made to examine the interactions involving the divalent sulfur atom with its partners.[7] Cambridge Structural Database studies of the divalent sulfur as acceptor for the system C=S, carried out by Allen *et al.*,[8] described the geometry based on van der Waals cut-off definition $d < 2.9$ Å for O–H and N–H donors.

The sulfur derivatives of pyrimidines and purines are widely used as antitumor agents in clinical treatment.[9] The tautomerism of purine and pyrimidine bases naturally occurring in nucleic acids, nucleotides, and enzymes may play a role in mutagenesis.[10] In recent years, much effort, both experimental and theoretical, has been devoted to the study of their structural properties and stabilities. The *ab initio* and spectroscopic studies for 2-thiouracil, 4-thiouracil, and 2,4-dithiouracil[11–16] revealed that oxothione and dithione tautomers are the most stable forms in crystal, solution and in the gas phase. In the crystalline state the agreement between theory and experiment is fairly good because of the crystal forces and hydrogen-bonding interactions. So far available are the crystallographic data for the pure 2-thiouracil,[17] 2,4-dithiouracil,[16] and the complex of 2-thiouracil with DCH6B.[18]

The present study was undertaken to follow the binding mode of 2,4-dithiouracil with the 18-membered crown ethers shown in Scheme 1 with the aim of finding any reproducible similarities



Scheme 1 Structural formulas of the crown ethers used and possible tautomers of 2,4-dithiouracil.

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Table 1 Bond lengths and angles for the DTU molecule in **1**–**4**

	1	2	3	4
Bond distances/Å				
S1–C1U	1.665(2)	1.642(4)	1.664(4)	1.665(3)
S2–C2U	1.662(2)	1.649(4)	1.654(4)	1.652(3)
N1U–C1U	1.370(2)	1.370(4)	1.352(5)	1.365(4)
N1U–C2U	1.382(2)	1.379(4)	1.383(5)	1.379(4)
N2U–C1U	1.355(2)	1.356(4)	1.368(5)	1.363(4)
N2U–C4U	1.354(3)	1.354(4)	1.361(5)	1.349(4)
C2U–C3U	1.420(3)	1.414(4)	1.409(5)	1.421(4)
C3U–C4U	1.337(3)	1.343(4)	1.319(6)	1.334(4)
Bond angles/deg				
C1U–N1U–C2U	126.1(1)	127.7(3)	127.1(3)	127.8(3)
C1U–N2U–C4U	123.2(2)	123.6(4)	122.4(4)	123.6(3)
N2U–C1U–N1U	114.6(2)	113.1(4)	114.2(4)	113.3(3)
N2U–C1U–S1	122.5(1)	122.9(3)	122.5(3)	123.8(2)
N1U–C1U–S1	123.0(1)	124.1(3)	123.3(3)	123.0(2)
N1U–C2U–C3U	115.0(2)	114.3(3)	114.1(4)	113.6(3)
N1U–C2U–S2	121.0(1)	121.7(3)	121.2(3)	120.6(2)
C3U–C2U–S2	124.0(1)	124.0(3)	124.7(3)	125.8(3)
C4U–C3U–C2U	119.6(2)	119.7(4)	120.8(4)	120.5(3)
C3U–C4U–N2U	121.6(2)	121.5(4)	121.3(4)	121.1(3)

in the organization of the structural units of the macrocyclic receptor, 2,4-dithiouracil, and in the supramolecular architecture.

2,4-Dithiouracil,[16] forms monohydrates in a 1 : 1 : 1 ratio with 18C6, DCH6A and B18C6 (complexes **1**, **2** and **3**), whereas its anhydrous adduct with DCH6B (complex **4**) is in a 2 : 1 ratio. For 2,4-dithiouracil,[16] six possible tautomers are known, which differ by the positions of two hydrogens in the vicinity of either the ring nitrogens or the exocyclic sulfur atoms. From six tautomeric forms only one form, the 2,4-dithione, denoted as DTU[11,12] is registered in complexes **1**–**4** (Scheme 1). It is confirmed by the equal (within the cut-off of 2σ) C=S distances that correspond to the double bond and by the location of the hydrogen atoms on the ring nitrogens. The bond distances and angles in the DTU molecule in **1**–**4** are given in Table 1. Fig. 1 shows the ORTEP diagrams for **1**–**4** with the atomic numbering schemes.

In **1**–**3** the ternary complexes are organized in a similar way, so that DTU mediates crown ether and water molecules *via* N–H···O and C–H···O hydrogen bonds with participation of its acidic H-donor centers. The hydrogen bonding data of **1**–**4** are summarized in Table 2. In **1** the DTU and 18C6 molecules are held together by one N–H···O hydrogen bond, between N2U and O16 atoms with an N···O distance of 2.810(2) Å and N2U–H1···O16 angle of 170(2)°, and one CH···O hydrogen bond, between C3U and O7 atoms with C···O distance of 3.260(2) Å and C3U–H1···O4 angle of 129°. In **2** the DTU and DCH6A molecules are held together only by one NH···O hydrogen bond, between atoms N2U and O16 with the N···O distance of 2.862(4) Å and N2U–H2U···O16 angle of 171°. Similar to **1**, the H4U hydrogen atom of the neighboring CH group is directed just in the center of the macrocyclic ring with H4U···O(crown) distances that all exceed the cut-off limit of the hydrogen bonding (<2.6 Å). Similar to **1**, in **3** the DTU and B18C6 are held together also by one NH···O and one CH···O hydrogen bonds, although different CH groups of uracil ring are involved in these interactions, The N–H···O hydrogen bond involves N2U and O13 atoms, with N···O distance of 2.970(4) Å and N2U–H2U···O13 angle of 153(4)°, and CH···O hydrogen bond involves C4U and O7 atoms with C···O separation of 3.550(5) Å and C4U–H4U···O7 angle of 168°. The difference is that the neighboring NH and CH groups of DTU molecule are involved in these contacts. The mutual arrangement of the crown ether and DTU molecules approaches to the orthogonal one and is characterized by the dihedral angle between the pyrimidine and crown ether rings (least-squares-planes were calculated through atoms O1/O4/O7/O10/O13/O16 and

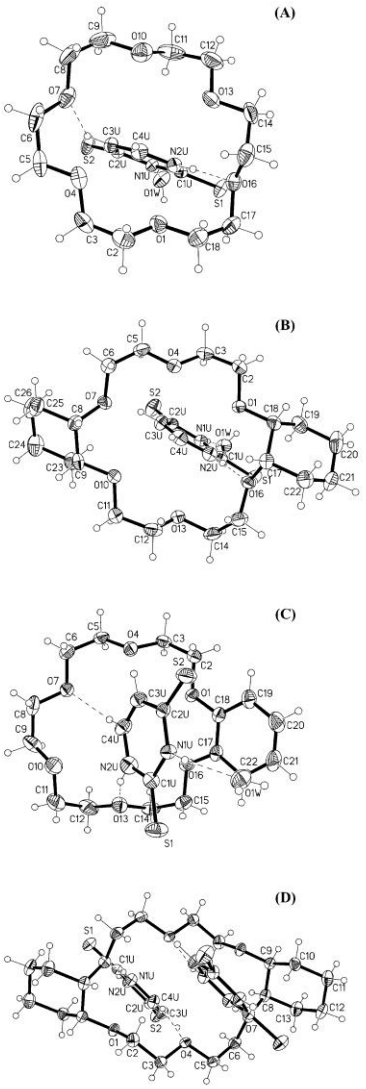


Fig. 1 (A)–(D) ORTEP view for **1**–**4** in projection on the plane of crown ether oxygen atoms. Ellipsoids for non-hydrogen atoms are drawn at the 30% probability level.

C1U/C2U/C3U/C4U/N1U/N2U) equal to 84.4(1)° in **1**, 86.8(1)° in **2**, whereas in **3** this angle is decreased to 53.8(1)°. The pronounced deviation from orthogonality in **3** is defined by the aromatic ring in the B18C6 molecule that is responsible for the π–π stacking interactions between the off-set overlapping phenyl and uracil rings with the dihedral angle between these aromatic systems equal to 15.9(2)° and the deviations of the atoms of uracil ring from the plane of the phenyl ring (C17/C18/C19/C20/C21/C22) being in the range 3.04–3.73 Å. The water molecule acts in a reproducible way in **1**–**3**. It blocks the second aminogroup of the DTU ring, thus precluding the typical nucleic bases pairing[17–19] *via* $R_2^2(8)$ NH···S synthon.[20] Strong intermolecular H-bonding, N1U–H1U···O1w is described by the N1U···O1w separation of 2.826(2) Å and N1U–H1U···O1w angle of 175(2)° in complex **1**, by N1U···O1w separation of 2.911(4) Å and N1U–H1U···O1w angle of 175° in **2**, and by N1U···O1w separation of 2.974(2) Å and N1U–H1U···O1w angle of 166(4)° in **3**. Our search of the Cambridge

Table 2 Hydrogen bonding geometry in **1**–**4**

D–H···A	*r*(D–H)/Å	*r*(H···A)/Å	*r*(D···A)/Å	∠D–H···A/deg	Symmetry transformation for H-acceptor
1					
N2U–H2U···O16	0.84(2)	1.98(2)	2.810(2)	170(2)	*x*, *y*, *z*
N1U–H1U···O1W	0.80(2)	2.03(2)	2.826(2)	175(2)	*x*, *y*, *z*
C3U–H3U···O7	0.93	2.60	3.260(2)	129	*x*, *y*, *z*
O1W–H1W···O10	0.84(2)	2.37(2)	3.124(3)	150(2)	$x + 1/2, -y + 1/2, z - 1/2$
O1W–H1W···O13	0.84(2)	2.47(2)	3.158(2)	139(2)	$x + 1/2, -y + 1/2, z - 1/2$
O1W–H2W···O4	0.84(2)	2.12(2)	2.955(2)	174(3)	$x + 1/2, -y + 1/2, z - 1/2$
2					
N2U–H2U···O16	0.86	2.01	2.862(4)	171	*x*, *y*, *z*
N1U–H1U···O1W	0.86	2.05	2.911(4)	175	*x*, *y*, *z*
O1W–H1W···O10	0.83(2)	2.21(2)	2.990(4)	159(4)	$x + 1/2, -y + 3/2, z - 1/2$
O1W–H2W···O1	0.83(2)	2.60(3)	3.267(4)	138(4)	$x + 1/2, -y + 3/2, z - 1/2$
O1W–H2W···O4	0.83(2)	2.44(3)	3.145(4)	143(3)	$x + 1/2, -y + 3/2, z - 1/2$
3					
N1U–H1U···O1W	0.85(2)	2.14(2)	2.974(4)	166(4)	*x*, *y*, *z*
N2U–H2U···O13	0.86(2)	2.18(3)	2.970(4)	153(4)	*x*, *y*, *z*
C4U–H4U···O7	0.93	2.63	3.550(5)	168	*x*, *y*, *z*
O1W–H1W···O7	0.86(1)	2.34(2)	3.171(4)	164(4)	$-x - 3/2, -y - 1, z + 1/2$
O1W–H2W···O1	0.86(2)	2.40(3)	3.191(4)	155(5)	$-x - 3/2, -y - 1, z + 1/2$
O1W–H2W···O16	0.86(2)	2.47(4)	3.179(4)	141(5)	$-x - 3/2, -y - 1, z + 1/2$
4					
N1U–H1N···S1	0.85(2)	2.61(2)	3.430(3)	163(3)	$-x - 1, -y - 1, -z$
N2U–H2N···O7	0.85(3)	2.10(3)	2.939(3)	167(3)	$-x, -y - 1, -z - 1$
C4U–H4U···O4	0.93	2.37	3.273(4)	163	*x*, *y*, *z*

Structural Database[21] revealed the similar type of water binding in 2,4-dithio-5-fluoro-2′-deoxyuridine monohydrate, 6-amino-2-thiouracil monohydrate (two independent determinations), tris(5-carboxymethylaminomethyl-2-thiouridine) tetrahydrate, and in 2-thioxo-5,6-dimethyl-1*H*,3*H*-thieno(2,3-d)pyrimidin-4-one monohydrate with N···O separations of 2.917, 2.848(2.850), 2.838 and 2.729 Å, correspondingly.[22]

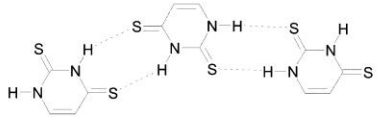
The anhydrous complex **4** differs in composition from **1–3**. The DCH6B molecule imposes on the inversion center, thus providing the 1 : 2 ratio of the components (Fig. 1d). The mode of interaction of DTU with DCH6B molecule absolutely coincides with that found in **3**; the neighboring N2U and C4U atoms of DTU molecule are involved in these interactions. The DTU and DCH6B molecules are held together by one NH···O and one CH···O hydrogen bonds, between atoms N2U and O7($-x$, $-y$ + 1, $-z$ + 1) with an N···O distance of 2.939(3) Å and an N2U–H2U···O16 angle of 167(3)°, and the CH···O hydrogen bond, C4U–H4U···O4 with a C···O distance of 3.273(4) Å and a C4U–H4U···O4 angle of 163°. The angle between the pyrimidine and crown ether rings is 88.0(1)°.

The packing diagrams (Fig. 2a–c) for **1–3** reveal the very similar organization of the complexes in the chains *via* an intermolecular O(water)···O(crown) hydrogen bonding, where the water molecule donates both of its hydrogen atoms to the symmetry-related macrocycle with the formation of one single and one bifurcated O1w–H···O(crown) hydrogen bonds, the O···O separations for the single hydrogen bond neatly increasing from 2.955(2) to 3.171(4) Å, and for the bifurcated hydrogen bond from 2.990(4) Å up to 3.267(4) Å. A water molecule is displayed at 1.864(2), 1.904(3), and 1.983(3) Å from the mean plane defined by the six crown ether's oxygen atoms in **1**,**2**,**3** correspondingly.

Only in **4** is the intermolecular H-bonding of the type N–H···S (typical for nucleic bases between the N1U and S1($-x$ – 1, $-y$ + 1, $-z$) atoms) with an N···S separation of 3.430(3) Å and an N1U–H1U···S1 angle of 163(3)° pairing two DTU molecules into a centrosymmetric dimer. The DCH6B molecules and DTU dimers alternate in the chains running along *c* direction in the unit cell (Fig. 2d).

In the four complexes described above, the hydrogen-bonded DTU : CE unit is supported by three different types of mutual interactions. Only in **1** due to high flexibility of 18C6 molecule the cross-cavity coordination occurs that results in the participation of N2U and C3U atoms of uracil ring, separated by CH_2–methylene group, in hydrogen bonding. In **2** the space obstacles, arising from the dicyclohexyl rings oriented in the DCH6A molecule in the same direction, provide the participation of only one NH group of DTU molecule in the hydrogen bonding with the CE. In **3** and **4** the neighboring NH and CH groups of uracil ring are involved in two hydrogen bonds with the crown oxygens separated by the –CH_2–O–CH_2– fragment, the similar type of hydrogen bonding was previously found in the complex of DCH6B with 2-thiouracil.[18] **1–4** reveal two supramolecular motifs: **1–3** represent the 1 : 1 : 1 alternative chains, where crown molecules behave as different-faced ligands, and coordinate on their two faces two different molecules, DTU and water, and only **4** represents the chain of 1 : 2 composition due to the equal-face symmetry of DCH6B.

Only in **4** do we observe the preservation of the centrosymmetric dimer of DTU as the fragment of the supramolecular architecture typical for its pure form. In the crystalline DTU itself[5] the molecules are associated in the chains sustained by two similar alternating $R_2^2(8)$ synthons[19] (Scheme 2) built on the NH···S hydrogen bonds.



Scheme 2 Association of the DTU molecules in the crystal *via* NH···S hydrogen bonds.

These chains are further aggregated into ladder-like layers due to ability of sulfur to participate in the multiple short contacts (in this case weak CH···S).

The interaction with DCH6B results in the breakage of the weakest CH···S interactions and their substitution by the interactions with the crown oxygens as H-acceptors. These contacts occur in the plane of the planar skeleton of DTU and are decisive for chain organization. This chain motif was previously found in the crystal structure of DCH6B·2(2-thiouracil),[18] where the centrosymmetric dimer of 2-thiouracil is sustained by the $R_2^2(8)$ NH···O base-pairing supramolecular

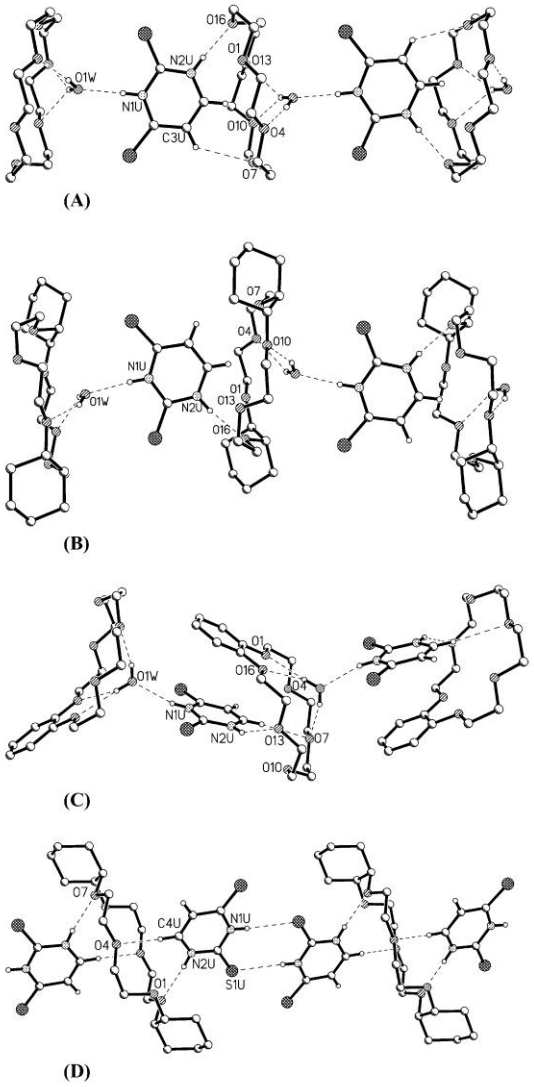


Fig. 2 (A)–(D). Fragment of chain in **1**–**4**. C-bound hydrogen atoms of crown molecules are omitted for clarity.

synthon instead of $R_2^2(8)$ NH···S supramolecular synthon in **4**.

Conclusion

Four complexes of 2,4-dithiouracil (DTU) with 18-membered crown ethers (CE) were synthesized in approximately the same conditions and characterized by X-ray diffraction analysis. From six possible tautomeric forms of DTU, only 2,4-dithione form was registered in all crystalline products. The crystal structures revealed two 1D structural motifs, ···CE···water···DTU···CE··· and ···CE···$(DTU)_2$···CE···, both sustained by diverse hydrogen bonding. In the first motif all the hydrogen bonding interactions typical for pure DTU itself were substituted by the interactions with the oxygen atoms of water and crown ether, as the stronger hydrogen acceptors. In the second motif the only $R_2^2(8)$ NH···S base-pairing supramolecular synthon responsible for the centrosymmetric dimer of DTU remains, as the part of self-assembling DTU molecules in its pure form.

Experimental

All the chemicals used (crown ethers, and 2,4-dithiouracil) were purchased from Aldrich Chemical Co .and were not purified prior to use. In all the experiments a 1 : 1 mixture of DTU (0.144 g, 1 mmol) and 0.1 mmol of the corresponding crown ether was dissolved in a mixture of methanol (20 ml) and ethyl acetate (40 ml), and the solution was stored for 3–4 d at 20–25 °C in an open flask. Crystals suitable for the X-ray diffraction experiments were isolated from the mass of crystals obtained.‡ Suitable microanalyses were obtained for all compounds. ^{1}H spectra were obtained in DMSO-d_6 on a 300−MHz Bruker instrument. Unit cell dimension and intensity data collection for **1**–**4** were performed at room temperature on a Philips PW1100 diffractometer equipped with graphite monochromated Mo Kα radiation. The lattice parameters were obtained by least-square fit to 25 reflections ($13.22° < \theta < 17.90°$) for complex **1**, 39 reflections ($4.69° < \theta < 12.61°$) for complex **2**, 39 reflections ($5.37° < \theta < 15.30°$) for complex **3**, 24 reflections ($7.04° < \theta < 16.39°$) for complex **4**, respectively. All the data sets were collected by ω-2θ scan mode. There was no significant intensity decay. Structure solutions were performed by direct methods (SHELXS-97) and refinements by full-matrix least-squares methods on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically. In all the structures H atoms attached to carbons were included in idealized positions in a riding model with isotropic temperature factors (1.2 times the carbon temperature factor), whereas those on N and O(water) atoms were found from difference Fourier maps at an intermediate stage of the refinement and were constrained by distance only (N–H and O–H = 0.86 Å) and were refined with isotropic temperature factors (1.5 times the parent N(O) temperature factor).

Transparent yellow crystals of **1**, soluble in methanol, ethanol, acetone, mp 265 °C (decomp). Found, %C, 45.02, H, 7.13, N, 6.65, S, 15.09 required for $C_{16}H_{30}N_2O_7S_2$: C, 45.05, H, 7.09, N, 6.57, S, 15.03%. ^{1}NMR: δ = 3.50 s (24H, 18C6), 6.49 d, 7.25 d (2H, CH–DTU).

Crystal data for **1**, monoclinic, $P2_1/n$, a = 7.707(2), b = 17.374(4), c = 16.622(3)Å, β = 92.17(3)°, V = 2224.1(8) Å^3, Z = 4, D_x = 1.274 g cm^{-3}, λ(Mo Kα) 0.71073 Å, μ = 2.76 cm^{-1}, $F(000)$ = 912, GooF = 1.088, R indices (all data) $R1$ = 0.0667, $wR2$ = 0.1320 for 4380 reflections and 256 parameters and R indices $R1$ = 0.0452, $wR2$ = 0.1237 for 3152 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Transparent yellow crystals of **2**, soluble in methanol, ethanol, acetone, mp 260 °C (decomp). Found, %C, 53.82, H, 7.88, N, 5.28, S, 12.04 required for $C_{24}H_{42}N_2O_7S_2$: C, 53.90, H, 7.92, N, 5.24, S, 12. ^{1}NMR: δ = 1.19–1.71 m and 3.49 m (36H, DCH6A), 6.50 d, 7.23 d (2H, CH–DTU).

Crystal data for **2**, monoclinic, $P2_1/n$, a = 7.988(2), b = 21.627(4), c = 16.439(3)Å, β = 93.17(3)°, V = 2835.6(10) Å^3, Z = 4, D_x = 1.253 g cm^{-3}, λ(Mo Kα) 0.71073 Å, μ = 2.30 cm^{-1}, $F(000)$ = 1152, GooF = 0.709, R indices (all data) $R1$ = 0.2645, $wR2$ = 0.0929 for 5555 reflections and 322 parameters and R indices $R1$ = 0.0556, $wR2$ = 0.0668 for 1556 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Transparent yellow crystals of **3**, soluble in methanol, ethanol, acetone, mp 250 °C (decomp.). Found, %C, 50.68, H, 6.41, N, 5.99, S, 13.48% required for $C_{20}H_{30}N_2O_7S_2$: C, 50.61, H, 6.37, N, 5.90, S, 13.51. ^{1}NMR: δ = 3.59 m, 3.73 m, 4.05 m (20H, CH_2) and 6.89 m (4H, CH–B18C6), 6.49 d, 7.25 d (2H, CH–DTU).

Crystal data for **3**, orthorhombic, $P2_12_12_1$, a = 7.973(2), b = 16.918(3), c = 17.566(4)Å, V = 2369.4(8) Å^3, Z = 4, D_x = 1.330 g cm^{-3}, λ(Mo Kα) 0.71073 Å, μ = 2.67 cm^{-1}, $F(000)$ = 1008, GooF = 0.881, R indices (all data) $R1$ = 0.1051,

‡ CCDC reference numbers 268384–268387. See http://dx.doi.org/10.1039/b505807d for crystallographic data in CIF or other electronic format.

$wR2 = 0.0922$ for 2644 reflections and 292 parameters and R indices $R1 = 0.0446$, $wR2 = 0.0805$ for 1493 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Transparent yellow crystals of **4**, soluble in methanol, ethanol, acetone, mp > 250 °C (decomp). Found, %C, 50.90, H, 6.74, N, 8.54, S, 19.43 required for $C_{28}H_{44}N_4O_6S_4$ C, 50.87, H, 6.71, N, 8.48, S, 19.41. ^{1}NMR: δ = 1.19–1.70 m and 3.53 m (36H, DCH6B), 6.49 d, 7.25 d (4H, CH–DTU).

Crystal data for **4**, monoclinic, $P2_1/n$, $a = 11.624(2)$, $b = 12.698(3)$, $c = 12.093(2)$Å, $\beta = 109.69(3)°$, $V = 1680.6(6)$ Å^3, $Z = 2$, $D_x = 1.306$ g cm^{-3}, λ(Mo Kα) 0.71073 Å, $\mu = 3.27$ cm^{-1}, $F(000) = 704$, GooF = 0.853, R indices (all data) $R1 = 0.1279$, $wR2 = 0.1316$ for 3302 reflections and 196 parameters and R indices $R1 = 0.0536$, $wR2 = 0.1129$ for 1669 reflections obeying $I > 2\sigma(I)$ criterion of observability.

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Додаток 42

Копія статті

“1D and 3D supramolecular architectures in the salts of meso-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane with (2e)-2-cyano-2-(hydroxyimino)acetamide and 2-(2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)hydrazinecarboxamide sustained by charge-assisted and conventional hydrogen bonds”

ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

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1D AND 3D SUPRAMOLECULAR ARCHITECTURES IN THE SALTS OF *MESO*-5,7,7,12,12,14-HEXAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECANE WITH (2*E*)-2-CYANO-2-(HYDROXYIMINO)ACETAMIDE AND 2-(2,6-DIOXO-1,2,3,6-TETRAHYDROPYRIMIDIN-4-YL)HYDRAZINECARBOXAMIDE SUSTAINED BY CHARGE-ASSISTED AND CONVENTIONAL HYDROGEN BONDS

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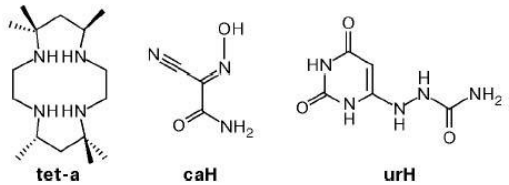
Meso-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-a) — (2*E*)-2-cyano-2-(hydroxyimino)acetamide (caH) (1:4) (**1**) is a salt $[tet\text{-}aH_2]^{2+}\cdot 2[caH]\cdot 2[ca]^-$ containing both neutral and deprotonated acetamide units. The acetamide units of the two types are linked by NH···O and OH···O hydrogen bonds into negatively charged chains; the chains are connected by the macrocyclic cations to form H-bonded ribbons. Tet-a, 2-(2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)hydrazinecarboxamide, (urH) forms a salt of 1:2:2 stoichiometry, $[tet\text{-}aH2]^{2+}\cdot 2[ur]^-\cdot 2H_2O$ (**2**). In (**2**), the deprotonated ur^- units form a negatively charged 2D network substructure, and the layers are linked by the cations and water molecules to form a 3D framework. The tetraazamacrocycle shows different modes of the protonation of amine functionalities that depend on a substrate.

Keywords: tetraazamacrocycle, carboxamide derivative, salt-like adduct, hydrogen bonding, supramolecular synthon.

LIST OF ABBREVIATIONS USED

Tet-a —	*Meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
cyclen —	1,4,7,10-tetraazacyclododecane
cyclam —	1,4,8,11-tetraazacyclotetradecane
azacyclam —	1,4,6,8,11-pentaazacyclotetradecane
caH —	(2*E*)-2-cyano-2-(hydroxyimino)acetamide
urH —	2-(2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)hydrazinecarboxamide
18C6 —	18-crown-6



tet-a **caH** **urH**

Scheme 1. Schematic representation of tet-a, caH, and urH in their neutral forms

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INTRODUCTION

The assembly of small molecular units is of continuous interest because of its potential use to mimic interactions in biologically important systems [1]. The development of new molecules predisposed to self-assembly in aqueous solutions is highly required. The aqueous medium causes the dissociation of soluble substrates and their transformation into charged species. The fact that 70—75 % of all enzyme substrates and cofactors are negatively charged clearly illustrates the importance of anion recognition.

The usage of mixed N, O- and N-containing macrocycles easily protonated by acidic organic molecules results in various supramolecular architectures sustained by charge-assisted and conventional hydrogen bonds. These macrocycles act as unique hydrogen-bond-expanded templates for novel nanosized assemblies which comprise biologically active heterocycles (barbiturates, nucleic bases) and their derivatives. Kimura and coauthors [2—3] discovered that Zn^{II}-cyclen complex is a highly selective host for thymidine, uridine, and cyanuric acid in aqueous solution. The same group reported [4] a nucleobase receptor comprising a Zn^{II}-cyclen complex attached to a redox active anthraquinone moiety. Hayes et al. [5] reported azacyclam-CuII complexes comprising melamine and ammeline triazine rings that have the well-documented H-bonding properties. Tetraazamacrocycles such as cyclam and its *meso* and *racemic* hexamethylated analogs are strong bases and they readily add two protons to form doubly charged cations. In these cations, two H atoms are held in the interior of the N4 ring by intramolecular N—H···N hydrogen bonds, while four external N—H bonds can act as hydrogen bond donors situated in certain geometry with respect to one another. This is why the tetraazamacrocycles currently are widely exploited as versatile building blocks in crystal engineering for the recognition of organic anions.

In this work the single crystal XRD study of two adducts formed between tet-a and acidic organic molecules, caH and urH, is reported; the study demonstrates the versatility of tet-a as a useful building element for the organization of components of the solution into 1D (**1**) and 3D (**2**) supramolecular architectures.

EXPERIMENTAL

Preparations. **urH** was prepared according to [6]. The complexes were obtained by dissolving the equal amounts (1 mmol) of the corresponding components in a boiling mixture of 10 ml of methanol and 10 ml of water. Yellow transparent plate-like crystals of (**1**) and colorless transparent plate-

Table 1

Crystal Data and Structure Refinement for Compounds (**1**) *and* (**2**)

Compound	**1**	**2**
Empirical formula	$C_{28}H_{48}N_{16}O_8$	$C_{26}H_{54}N_{14}O_8$
Formula weight	736.82	690.83
Crystal system, space group	Triclinic, $P\,{-}1$	Triclinic, $P\,{-}1$
Unit cell dimensions		
a, Å / α, deg	7.716(1) / 78.84(1)	8.918(2) / 78.74(2)
b, Å / β, deg	11.182(2) / 80.31(1)	9.952(2) / 78.45(2)
c, Å / γ, deg	11.212(1) / 86.70(1)	10.327(2) / 70.12(2)
V, Å^3	935.2(2)	836.4(3)
Z, Calculated density, g cm^{-3}	1, 1.308	1, 1.372
Reflections collected / unique	7206 / 4863 [R(int) = 0.021]	10145 / 3845 [R(int) = 0.056]
Data / parameters	4863 / 270	3845 / 261
Observed data [$I \geq 2\sigma(I)$]	3006	2546
Final R indices [$I \geq 2\sigma(I)$]	R_1 = 0.0494, wR_2 = 0.1319	R_1 = 0.0385, wR_2 = 0.0911
GOOF on F^2	0.932	0.927
Largest peak / hole, e Å^{-3}	0.20 / –0.17	0.35 / –0.19

CCDC deposition number	223137	223136

Table 2

Distances (Å) *and Angles* (deg) *Defining Hydrogen Bonding in* (**1**) *and* (**2**)

Compound	D—H···A	H···A	D···A	DHA	Symmetry code for A
1	N4—H41N···N1	2.04(2)	2.836(2)	147(2)	–*x*, –*y*+1, –*z*+1
	N1—H1N···N21	2.31(2)	3.059(2)	144(2)	–*x*, –*y*+1, –*z*+1
	N4—H42N···O22	2.13(2)	3.004(2)	157(2)	*x*, *y*, *z*
	O12—H12O···O22	1.53(3)	2.557(2)	177(2)	*x*–1, *y*, *z*+1
	N13—H132···O21	2.05(2)	2.878(2)	172(2)	*x*, *y*, *z*
	N13—H131···N12	2.31(2)	2.686(2)	107(2)	*x*, *y*, *z*
	N23—H231···O11	1.99(3)	2.960(2)	175(2)	*x*, *y*, *z*
	N23—H232···N22	2.35(3)	2.738(2)	112(2)	*x*, *y*, *z*
2	N1—H1N···N4	1.97(2)	2.778 (2)	148(2)	–*x*, –*y*+1, –*z*+1
	N1—H2N···N22	1.92(2)	2.879 (2)	172(2)	–*x*, –*y*+1, –*z*+1
	N4—H4N···O22	2.46(2)	3.234 (2)	153(2)	*x*, *y*, *z*
	N21—H21N···O21	1.99(2)	2.863 (2)	165(2)	–*x*, –*y*+2, –*z*
	N23—H23N···O1W	2.18(2)	2.902 (2)	142(2)	–*x*–1, –*y*+2, –*z*+1
	N24—H24N···O21	1.98(2)	2.847 (2)	161(2)	–*x*–1, –*y*+2,-*z*
	N25—H125···O23	2.07(2)	2.953 (2)	178(2)	–*x*–1, –*y*+1
	N25—H225···O21	2.39(2)	3.092 (2)	147(2)	–*x*–1, –*y*+2,-*z*
	O1w—H1w···O22	2.05(2)	2.871 (2)	177(2)	*x*, *y*, *z*
	O1w—H2w···O22	2.01(3)	2.869 (2)	152(2)	–*x*, –*y*+2, –*z*+1

like crystals of (**2**) were obtained in quantitative yield by slow evaporation of the solutions at room temperature for several days. The complexes are soluble in water and low alcohols, and insoluble in benzene and hexane.

(**1**) M. p. 187 °C. Anal. (%): calcd for $C_{28}H_{48}N_{16}O_8$: C 45.64, H 6.57, N 30.42; found: C 45.91, H 6.48, N 30.42.

(**2**). M.p. ~ 230 °C. Anal. (%): calcd for $C_{26}H_{54}N_{14}O_8$: C 45.21, H 7.88, N 28.39; found: C 45.36, H 7.80, N 29.12.

X-ray diffraction analysis. Intensity data for (**1**) were collected on a Bruker P4 single crystal diffractometer [7] with CCD area detector at 153(2) K and for (**2**) on a Nonius KappaCCD diffractometer [8] at 293(2) K (graphite-monochromated MoK_α radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 using SHELX-97 package [9]. All non-hydrogen atoms were refined anisotropically. The H atoms attached to O and N were found from difference Fourier synthesis; they were refined isotropically. The H atoms attached to C were added geometrically and refined using a riding model. Details of crystallographic data for (**1**) and (**2**) are summarized in Table 1. Hydrogen bonds are listed in Table 2. Full crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC) and are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving. html; CCDC deposition numbers are given in Table 1.

RESULTS AND DISCUSSION

Ferguson et al. [10] emphasized that the preferable molar ratio of tet-a to hydrogen bond donors is 1:2 due to the formation of $[tet\text{-}aH2]^{2+}$ cation through the addition of two protons from two donor molecules. Both (**1**) and (**2**) complexes exhibit this 1:2 cation:anion ratio with a doubly protonated tet-a molecule. In (**1**) (Fig. 1), the two additional hydrogen atoms were located on two nitrogen atoms, related by centrosymmetry, adjacent to the gem-dimethyl unit. Two intramolecular N4—H···N1

hydrogen bonds generate three cyclic motifs, two R11(6) and one R22(10) rings (notation by Etter [11]). The $[tet\text{-}aH2]^{2+}$ cation links, in a chelate mode, to two anions; one charge-assisted N—$H^{+}\cdots O^{-}$

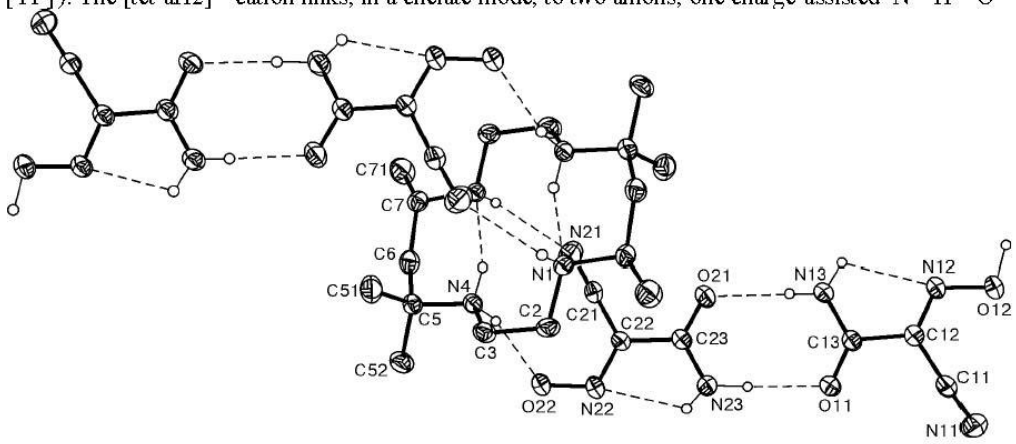

Fig. 1. ORTEP view of (**1**) with thermal ellipsoids drawn at the 30 % probability level. Hydrogen bonding is shown as dashed lines. C-bound hydrogens are omitted for clarity

and one conventional N—H···N hydrogen bonds are to the oximate and adjacent nitrile functionalities of each anion, respectively.

In (**2**), the N-binding sites adjacent to the singular gem-methyl group of the tet-a molecule are protonated by the amide functionalities of two urH molecules (Fig. 2). Similar to (1), the two $R_1^1(6)$ and one $R_2^2(10)$ H-bonded intramolecular motifs are generated. The $[tet\text{-}aH2]^{2+}$ cation links, in a chelate mode, to two ur^{-} anions; one charge-assisted N—$H^{+}\cdots N^{-}$ and one conventional N—H···O(=C) hydrogen bonds are formed to the monodeprotonated amide and the adjacent carbonyl functionality of the cation, respectively. The protonated N-binding sites of the tet-a molecule in (**2**) are less sterically shielded, resulting in decreased dimensions of the chelate rings as compared to the corresponding

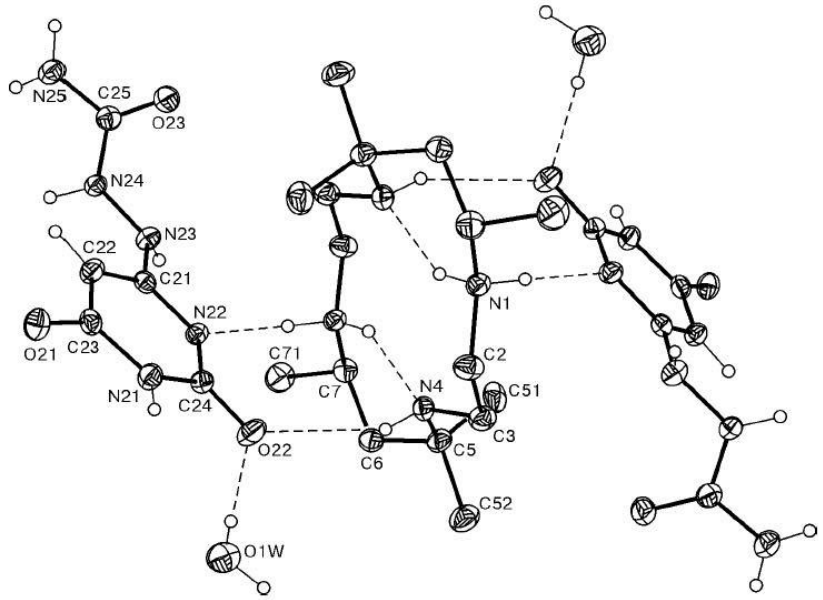

Fig. 2. ORTEP view of (**2**) with thermal ellipsoids drawn at the 30 % probability level. Hydrogen bonding is shown as dashed lines. C-bound hydrogens in $[tet\text{-}aH_2]^{2+}$ are omitted for clarity

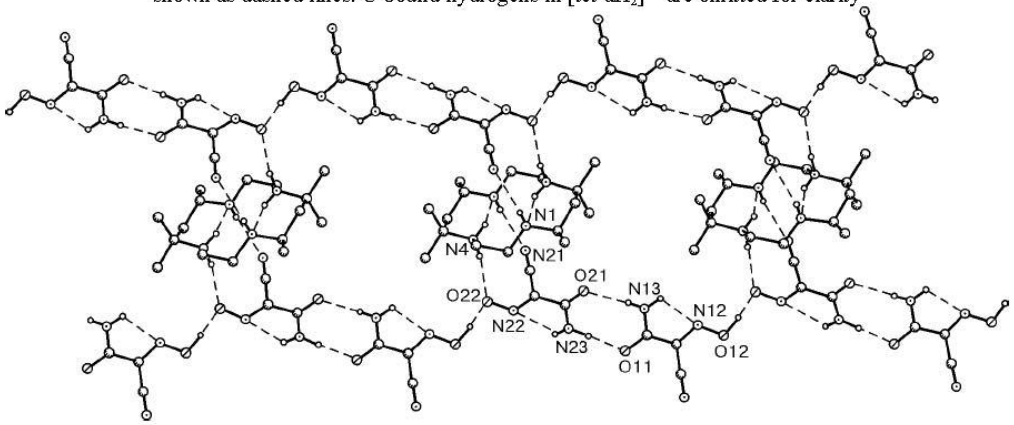

Fig. 3. Fragment of the ribbon in (**1**). The atoms that participate in H-bonding are labeled

rings in (**1**). The same site of the uracil ring is deprotonated by diaza-18C6 in a pyrimidine derivative described in [12].

In (**1**) and (**2**) all of the H-donor opportunities of $[tet\text{-}aH2]^{2+}$ are used within the neutral associate comprising one doubly charged cation and two anions.

The $C(=O)NH_2$ carboxamide functionality participates in the assembly and self-assembly of the caH, ca^-, and ur^- units in (**1**) and (**2**). Both the neutral caH and the negatively charged ca^- adopt planar conformations sustained by the intramolecular N—H···N hydrogen bonds (Fig. 1, Table 2). The ur^- anion consists of two planar parts, the uracil ring with two carbonyl oxygens and one nitrogen of the hydrazine group, and the carboxamide group, with the dihedral angle between these parts being equal to 89.24(5)°. The planar shape of caH and ca^- and the angular shape of ur^- dictate the mode of self-organization of these units in (**1**) and (**2**). In (**1**) the caH and ca^- units alternate in a flat negatively charged chain; these units link to each other through alternating $R_2^2(8)$ rings and singular O—H···O^- hydrogen bonds (Fig. 3). Two negatively charged chains link to each other through the $[tet\text{-}aH2]^{2+}$ cations giving rise to ribbons consisting of cyclic fragments, each fragment formed by two $[tet\text{-}aH2]^{2+}$ cations, four ca^- anions, and two caH neutral molecules and sustained by 14 hydrogen bonds, including four N—H^+···O^-, four N—H···O, four N—H···N, and two O—H···O^- bonds.

In (**2**) (Fig. 4), two adjacent ur^- anions related by centrosymmetry are combined into a dimer fastened with two $R_2^2(8)$ hydrogen bonding patterns typical of patterns observed for nucleic-acid bases association. These dimers are combined into a 1D wave-shaped negatively charged chain through the $R_2^2(8)$ pattern built upon two H_2N—C(=O) carboxamide groups. The chains are combined, by means of N—H···O hydrogen bonds that form a $R_2^1(6)$ ring and involve carbonyl oxygen as a double acceptor, into negatively charged sheets in the (110) plane of the crystal, with the uracil rings arranged approximately perpendicularly to the plane (Fig. 4a). In this sheet, the cages of two types alternate along the [010] direction. The small cages are formed by two ur^- anions related by centrosymmetry and assembled by four N—H···O hydrogen bonds. The big cages are formed by three pairs of anions related by centrosymmetry and assembled by 12 N—H···O hydrogen bonds; four of these six anions also take part in the creation of adjacent small cages. The sheets stack along the [100] direction and are H-bonded to the water molecules and $[tet\text{-}aH2]^{2+}$ cations to form a 3D grid. The water molecules function as double H-donors and single H-acceptors. The resulting $R_4^2(8)$ synthon, formed by two water molecules and two carbonyl oxygens, is centrosymmetric and flat, presenting a practically ideal rhomb with dimensions of 2.869(2) and 2.871(2) Å (Fig. 4b).

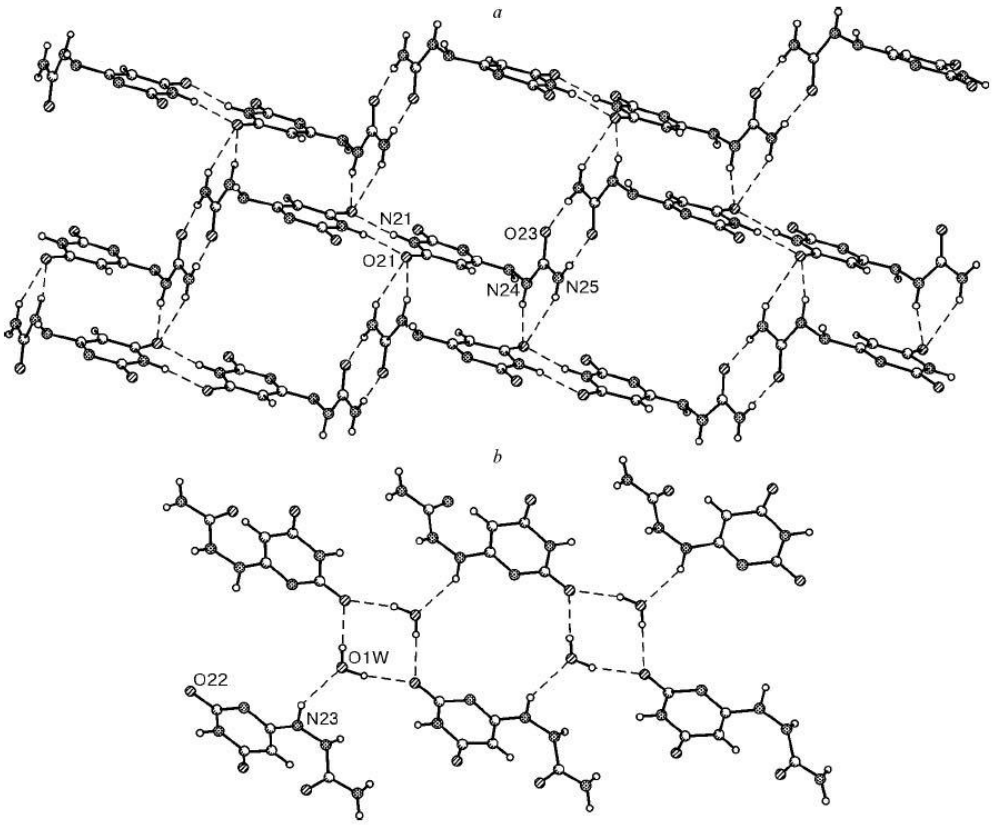

Fig. 4. (*a*) Fragment of an H-bonded negatively charged sheet in (**2**) composed of ur$^-$ anions. (*b*) Another fragment, showing the association of the neighboring sheets with the help of water molecules, generating $R_4^2(8)$ and $R_4^4(16)$ alternating rings

In summary, the 3D grid in (**2**) is built of the negatively charged corrugated layers combined by the water molecules. The $[tet\text{-}aH2]^{2+}$ cations are incorporated as guests in the cavities of this grid interacting with the host lattice by N—H$^+$···N$^-$ and N—H$^+$···O charge-assisted hydrogen bonds.

The search in the Cambridge Structural Database [13] for structures with $[tet\text{-}aH2]^{2+}$ cations protonated by organic molecules revealed an equal number of hits for cations with protonated N atoms adjacent to one gem- and two gem-methyl groups (10 hits each). The majority of these complexes were discussed by Ferguson and coauthors [10, 14]. At this moment it is difficult to rationalize the reasons that define the preferences for the protonation of the N-atoms in the tet-a molecule.

There are 276 hits of organic molecules that exhibit an $R_2^2(8)$ ring built on the carboxamide groups (Figs. 2, 4a), with (N)H…O distances ranging from 1.81 to 2.34 Å and N···O distances ranging from 2.8 to 3.0 Å. This synthon is also responsible for the self-association of caH in its pure form [15]. The $R_2^1(6)$ ring typical for the urea derivatives (Fig. 4a) was found in 97 compounds with the same range of H···O and N···O distances, while 12 pyrimidine derivatives exhibit an $R_2^2(8)$ association mode found for the ur$^-$ anion in (**2**) (Fig. 4a).

The association of the neutral oxime molecule and the oximate anion similar to that found in (**1**) was previously found in the diaqua-(18C6)-(ca)-(Rb^+)-caH monohydrate [16], in (18C6—Cs^+)-(cyano-hydroxyimino-acetophenone)-(dehydro-cyano-hydroxyimino-acetophenone) [17], and in the complexes of (4Z, 5E)-pyrimidine-2,4,5,6-(1H,3H)-tetraone dioxime with (NH_4^+-*cis-syn-cis*-dicyclohexano-18C6) and with diaza-18C6 [18].

The results of the X-ray structural analysis of (**1**) and (**2**) confirmed the tendencies previously observed for the studied molecules. These tendencies include deprotonation of caH and urH molecules by the tet–a molecule with the formation of charge-assisted hydrogen bonds between the generated charged units and the self-organization of the ca^- and ur^- anions by means of robust supramolecular synthons built upon N—H···O hydrogen bonds. However, the preferences for the protonation of certain N-atoms of the tet-a molecule, as well as the final supramolecular structure the studied molecules form, remain difficult to predict.

ACKNOWLEDGMENT

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Додаток 43

Копія статті

“Nitrosation of hydrochlorothiazide and the modes of binding of the N-nitroso derivative with two macrocycles possessing an 18-membered crown ether cavity”

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Nitrosation of hydrochlorothiazide and the modes of binding of the *N*-nitroso derivative with two macrocycles possessing an 18-membered crown ether cavity

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Abstract The hydrochlorothiazide, 6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide, (**HCTZ**), widely used as a diuretic and anti-hypertensive drug, was transformed into its *N*-nitroso-derivative, 6-chloro-4-nitroso-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide (**O—N HCTZ**) by sodium nitrite in an acidic medium. The crystalline complexes of **O—N HCTZ** with 18-crown-6 (18C6) and *cis-anti-cis*-dicyclohexyl-18C6 (DCH6B) demonstrated different H-bonding modes from those present in the co-crystals of **HCTZ** with the same crown ethers. The influence of the nitroso-group on the binding mode and crystal packing is discussed.
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1. Introduction

The application of macrocycles, mainly crown ethers, as low molecular weight receptors used in assessing non-covalent bondings important in chemistry and biology attracts relentless attention.[1] These model systems have distinct advantages over biological macromolecules due to their relative simplicity, which allows for specific interactions to be isolated and studied in the absence of the many others that are present in biological macromolecules. Verification of unusual properties in synthetic receptor systems can give an insight into the biological implications for such chemical interactions. Classic O-containing crown ethers act as hydrogen acceptors, forming exclusively C–H···Ocrown, N–H···Ocrown, or O–H···Ocrown hydrogen bonds. It is interesting to estimate the contribution of these interactions to the binding of biologically important molecules.

Previously we revealed the decisive role of NH···O hydrogen bonds in the interactions of some diuretic drugs, hydrochlorothiazide,[2,3] acetazolamide[4] with 18-membered crown ethers. As far as the chemistry of *N*-nitrosamines is a subject of considerable interest with regard to their strong carcinogenic and mutagenic properties,[5] we are currently interested in the mutagenic transformations of the secondary amino-group-containing drugs upon nitrite treatment under acidic conditions and in the differences in molecular recognition of the initial drug and the product of its metabolism with crown ethers, as simple model compounds.

In the present study, the drug hydrochlorothiazide, 6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide, **HCTZ**[6] has been chosen. **HCTZ** is a popular diuretic drug that belongs to the thiazide class of diuretics and acts by inhibiting the kidney's ability to retain water. It is often used to treat hypertension, congestive heart failure and symptomatic edema, and is effectiveness in diabetes insipidus and in hypercalciuria, acting on the kidney to reduce sodium re-absorption in the distal convoluted tubule. As artificial receptors the 18-membered crown ethers have been chosen, 18-crown-6 (18C6) and *cis-anti-cis* dicyclohexyl-18C6 (DCH6B), which are powerful collective H-acceptors, very effective in forming interactions with the amino-group.[7]

Keywords: *N*-nitrosohydrochlorothiazide; Crown ethers; H-binding.
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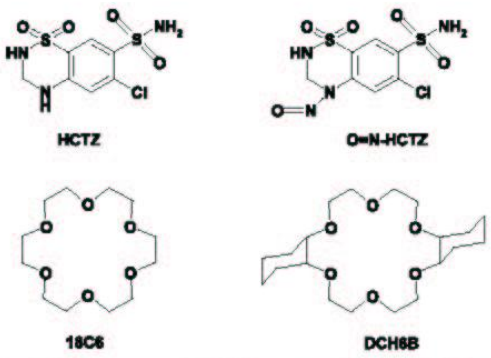
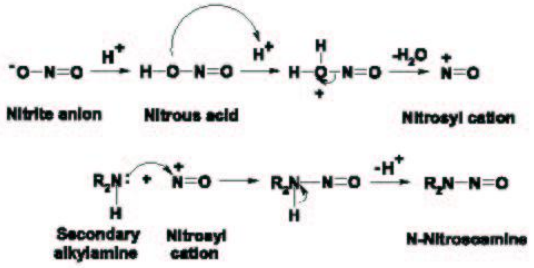


Scheme 1. The components of the binary co-crystals discussed herein.

Herein we describe the synthesis of *N*-nitroso derivative of **HCTZ**, **O=N–HCTZ** and the crystal structures of its two complexes with 18C6 (complex **1**) and DCH6B (complex **2**) with 1:2 and 1:1 ratios, correspondingly (Scheme 1), and make the comparisons with the H-bonded complexes of **HCTZ** with the same crown ethers.

2. Results and discussion

It has previously been reported that micro-organisms commonly present in human saliva, which can be isolated from the human gastro-intestinal tract, have the capacity in vitro to catalyse *N*-nitrosation of a series of medicinal drugs and other compounds.[3] On the other hand, the nitrosation of amines is possible in two ways, namely, by endogenous



Scheme 2. Mechanism of nitrosation of secondary alkylamine.

nitrogen oxide (NO) in the conditions of the oxidation reaction and by exogenous nitrites in the acidic medium. The typical reagents for this reaction are sodium nitrite and aqueous solutions of hydrochloric HCl or sulfuric H_2SO_4 acids (this mixture yields nitrous acid, HNO_2). The actual nitrosation reagent is the NO^+ nitrosyl cation which is formed in situ. The nature of the product depends on the nature of the initial amine. Primary alkyl or aryl amines yield diazonium salts. Secondary alkyl or aryl amines yield *N*-nitrosoamines. Tertiary alkyl amines do not react in a useful fashion. Tertiary aryl amines undergo nitrosation of the ring.[5] Scheme 2 shows the route by which secondary amines are transformed to the dangerous *N*-nitroso compounds.

In our case, the nitrosation of **HCTZ** occurs by sodium nitrite in acetic acid and results in the formation of *N*-nitroso-**HCTZ** (**O=N–HCTZ**). The attack of the electrophilic nitrosyl cation occurs on the cyclic secondary amino-group, which is a more powerful nucleophile in comparison with secondary and primary sulfamido-groups. Thus, only one of the two NH-groups of **HCTZ** is nitrosated.

2.1. Complexes of 18C6 and DCH6B with O=N–HCTZ

Due to the poor crystal quality of **2** and the low accuracy of the final data obtained, the geometric parameters of **O=N–HCTZ** will be discussed only with reference to the complex formed with 18C6, while the hydrogen bonding system will be compared between **1**, **2** and the complexes of **HCTZ** with the same crown ethers. Hydrogen bonds in both complexes are listed in Table 1. The geometry of the cyclic skeleton of **O=N–HCTZ** is very close to **HCTZ** in its pure form[9] and in its complexes with 18C6[2] and DCH6B.[3] It is characterized by a dihedral angle of 10.7 (1)° between the planes through the two fused six-membered rings, aromatic, C1G>C6G and heterocyclic, C3G/C4G/S2G/N3G/C7G/N2G ones. The atoms of the aromatic ring are co-planar with the four heteroatoms attached to it within a mean-square deviation of 0.051 Å. The neighboring six-membered heterocycle has the shape of a distorted half-chair, with a maximal deviation of 0.698 (2) Å for the N3G atom from the C3G/C4G/N2G/N3G/S2G mean plane, where the atoms are coplanar within 0.020 Å. The nitroso-group geometry with an N=O distance of 1.228 (2) Å and

Table 1. Hydrogen bonding geometry in 1 and 2

D–H···A	d(H···A)/Å	d(D···A)/Å	∠(DHA)/°	Symmetry code for acceptor
1				
N1G–H11G···O4	2.09 (2)	2.932 (2)	174 (2)	*x*, *y*, *z*
N1G–H12G···O1	2.13 (2)	2.928 (2)	162 (3)	$-x+2, -y+2, -z$
N3G–H31G···O7	2.20 (2)	3.062 (2)	170 (2)	$-x+1, -y+2, -z$
C7G–H71G···O2G	2.24	3.096 (3)	150	$-1+x, y, z$
2				
N1G–H11G···O10	2.06 (2)	2.976 (10)	178 (11)	*x*, *y*, *z*
N1G–H12G···O4	2.06 (2)	2.982 (11)	174 (10)	*x*, *y*, *z*
N3G–H3GB···O1A	2.22 (2)	2.972 (12)	143 (4)	*x*, *y*, *z*
C7G–H7J···O4A	2.48	3.444 (14)	172	$1-x, 3-y, -z-1$
N11G–H11A···O16	2.22 (4)	3.028 (11)	159 (10)	*x*, *y*, *z*
N11G–H11B···O4	2.13 (4)	2.936 (11)	156 (8)	*x*, *y*, *z*
N13G–H13B···O7B	2.12 (3)	2.975 (11)	174 (10)	*x*, *y*, *z*
C17G–H17J···O4B	2.37	3.343 (13)	179	*x*, *y*, *z*

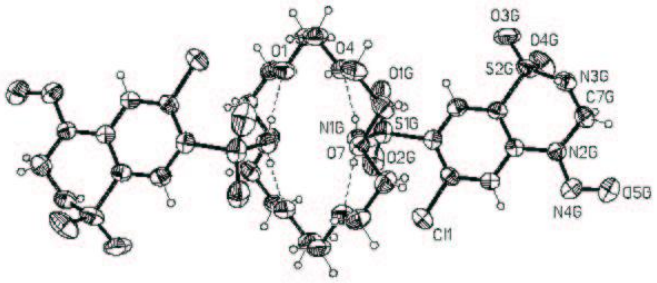


Figure 1. ORTEP view of complex **1**.

N–N═O bond angle of 112.8 (2)° does not exhibit any new features compared with the earlier structure determinations.[10]

Complex **1** has a trivial 1:2 ratio, with the crown ether imposed on the inversion center.[7] The aromatic ring of **O═N–HCTZ** is inclined at an angle of 42.2(1)° to the mean plane of the crown ether oxygen atoms, the N1G-S1G bond deviates at an angle of 21.1° from the normal to the same plane of 18C6. Two molecules of **O═N–HCTZ**, arranged in a head to head fashion, are linked via two NH···O hydrogen bonds of the sulfamide group with the oxygens of two equal faces of 18C6 (Fig. 1, Table 1).

The secondary sulfamido-group is linked via a single NH···O hydrogen bond with the next crown molecule translated along the *a* direction (Fig. 2). Thus, each molecule of 18C6 is bound with four molecules of **O═N–HCTZ** via six NH···O hydrogen bonds. In their turn, the **O═N–HCTZ** translated molecules are combined into chains via weak CH···O hydrogen bonds between the methylene hydrogen and the oxygen atom of the sulfamide group. Through these interactions, the components are organized into a ribbon where the crown spacers occupy the mean positions between two rows of **O═N–HCTZ** molecules.

Previously we described the mode of interaction of **HCTZ** with 18C6[2] (refcode VITWIE in CSD[11]) and DCH6B[3] (refcode REZXEZ in the CSD). In the 1:1 complex with 18C6, **HCTZ** coordinates in different modes on two non-equivalent faces of the crown ether. The lack of steric impediments in the molecule of **HCTZ** facilitates the participation of all its H-donor centers in coordination of two **HCTZ** molecules to one molecule of 18C6 in a head to face mode via two NH···O hydrogen bonds of amino-group on one face and two NH···O and one CH···O hydrogen bonds on the other one, and the association of the components into 1:1 alternative chain (Fig. 3), where each **HCTZ** molecule bridges two neighbouring 18C6 molecules. The introduction of the nitroso-group in the molecule of **HCTZ** obliterates one of the NH···O interactions and induces the rearrangement of the CH···O contact from **HCTZ**···18C6 (Fig. 3) to **O═N–HTCZ**···**O═N–HTCZ** in **1** (Fig. 2).

Complex **2** crystallizes in the triclinic crystal system with two crystallographically independent **O═N–HTCZ**

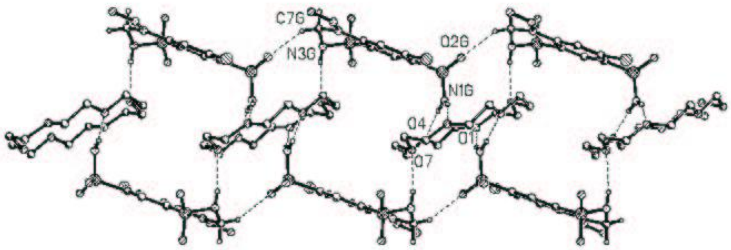


Figure 2. Organization of ribbon in **1**.

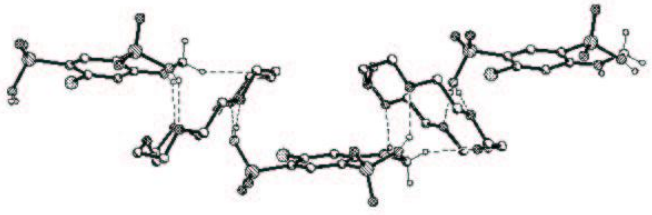


Figure 3. Mode of interaction of **HCTZ** with 18C6 in the alternative chain.

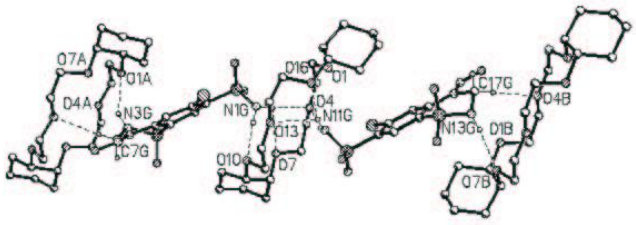


Figure 4. View of complex **2**. Symmetry-related **O═N–HCTZ** molecules are not shown.

molecules and one DCH6B molecule occupying the general positions and two DCH6B molecules occupying the partial positions, on the inversion centers. The overall complex stoichiometry is 1:1, and as is evident from Figure 4, the components alternate in the chains where each molecule of **O═N–HCTZ** bridges two DCH6B molecules.

The unique fragment of this chain includes three different three-membered H-bonded nodes. In the central node (Figs. 4 and 5a) two crystallographically independent **O═N–HCTZ** molecules are linked with the crown molecule via one single and one bifurcated NH···O hydrogen bond of the sulfamido-group. In two other, very similarly organized nodes (Fig. 5b), the crown molecules (A or B) are imposed on the inversion centers, and the NH-group and the neighboring methylene group are linked with the crown molecule via one NH···O and one CH···O hydrogen bonds. Thus, all H-donor groups are involved in interactions within the alternative chain: ···DCH6B··· **O═N–HCTZ**···DCH6B···**O═N–HCTZ**···.

Now an intriguing question arises, whether the striking differences similar to those found in the system including 18C6 as a receptor appear in the complexes of **HCTZ** and **O═N–HCTZ** with DCH6B? The answer should be: no. The crystal structure of the 1:2 complex of **HCTZ** with DCH6B reveals two types of the alternative chains, where **HCTZ** molecules coordinate to the crown ether in a head to head and tail to tail modes, via two amino-groups, or two CH and two NH groups (Fig. 6). The chains differ only by

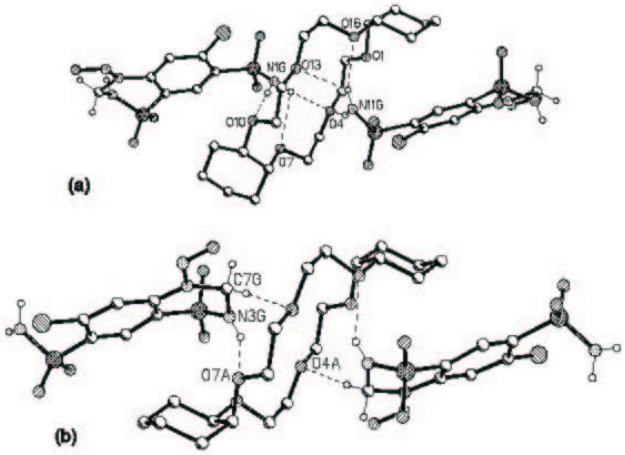


Figure 5. Modes of interaction of **O═N–HCTZ** with DCH6B in **2**.

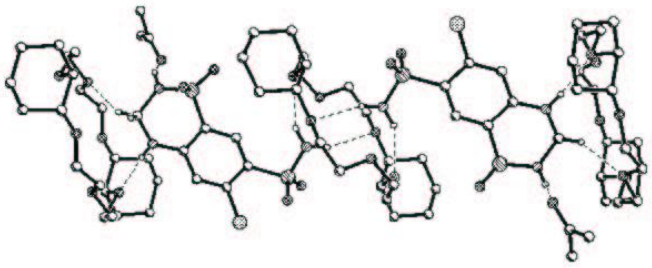


Figure 6. Fragment of infinite chain including acetone molecules in the complex of **HCTZ** with DCH6B.

the acetone molecule which via NH···O hydrogen bond blocks up the NH-group of **HCTZ** molecule, that is nitrosylated in **O=N–HCTZ**.

Thus, the contribution of the cyclohexyl substituents of DCH6B in the organization of supramolecular architectures is decisive here. In the case of **HCTZ** they shield the secondary sulfamide-group from the interaction with the crown ether cavity in such a way that this NH-group does not influence the overall system of hydrogen bonding and its nitrosation does not change the overall system of interactions in **2**.

3. Conclusion

The widely used diuretic, 6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide, hydrochlorothiazide (**HCTZ**), was treated with sodium nitrite under acidic conditions (the presence of acetic acid) simulating the conditions of gastric juice. The potentially carcinogenic derivative, 6-chloro-4-nitroso-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide, **O=N–HCTZ**, was obtained and its binding mode with two artificial macrocyclic receptors, 18-crown-6 and *cis-anti-cis* dicyclohexyl-18-crown-6 was compared with the initial **HCTZ**. In the case of the flexible and responsive 18C6, the change in the substrate-receptor interaction was dictated by the prohibition of the secondary amino-group of **O=N–HCTZ** in NH···O (crown) interactions, whilst in the case of its substituted analogue, DCH6B, the steric impediments of cyclohexyl units appeared to be decisive and exclude the participation of the secondary amino group of **HCTZ** in interactions with crown ether, thus nitrosation of this group does not influence the overall mode of the **HCTZ/O=N–HCTZ** DCH6B interaction.

4. Experimental

4.1. General

The initial chemicals were used as received without further purification. IR spectra were recorded on a Specord-80 spectrophotometer as KBr disks. The ^{1}H NMR spectra were recorded with a Bruker DPX-250 instrument at 250 MHz using tetramethylsilane as internal reference. Crystallographic measurements were carried out on a KUMA KM4CCD κ-axis diffractometer with a graphite-monochromatised Mo Kα radiation (λ=0.71073 Å) at 293 K for **1** and 130 K for **2**. Cell parameters were obtained by the global refinement of the positions of all collected reflections. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-97 package. All non-hydrogen atoms were refined anisotropically. Locations of H atoms attached to N were justified by difference Fourier synthesis and refined isotropically. H atoms attached to C were added geometrically and refined using the riding model.

4.1.1. Compound O=N–HCTZ. To a suspension of **HCTZ** (297 mg, 1 mmol) in hot acetic acid (15 ml) sodium nitrite (483 mg, 7 mmol) was added with intensive stirring. The reaction mixture was diluted by water (50 ml) and filtered off. The yield of **O=N–HCTZ** was 150 mg, (46%), mp> 180 °C (decomp.), found, %: C 25.78, H 2.08, Cl 10.83, N 17.02, S 19.58, required for $C_7H_7ClN_4O_5S_2$: C 25.73, H 2.16, Cl 10.85, N 17.15, S 19.63. IR (cm^{-1}, peaks of strong absorption only): 3410, 3070, 3000, 1580, 1430, 1290. ^{1}H NMR ($CDCl_3$) δ ppm: 4.93 (s, 2H, CH_2), 7.0 (s, 1H, CH), 7.50 (s, 2H, NH_2), 7.62 (s, 1H, NH), 8.32 (s, 1H, CH).

4.1.2. Compound 1. O=N–HCTZ (98 mg, 0.3 mmol) and 18C6 (80 mg, 0.3 mmol) were dissolved in a mixture of methanol/ethylacetate (1:2, 9 ml). The colorless, transparent crystals were obtained in a quantitative yield by slow evaporation of the solvents at room temperature for several days, mp>150 °C (with decomp., brown spot), found, %: C 34.09, H 4.22, Cl 7.71, N 12.30, S 14.07, required for $C_{26}H_{38}Cl_2N_8O_{16}S_4$: C 34.02, H 4.17, Cl 7.73, N 12.21, S 13.98. IR (cm^{-1}, peaks of strong absorption only): 3310–3100, 3070–3030, 3000–2790, 1580, 1560, 1550, 1530, 1430–1300, 1290, 1080. ^{1}H NMR ($CDCl_3$) δ ppm: 3.60 (s, 24H, CH_2O), 4.95 (s, 4H, CH_2), 7.07 (s, 2H, CH), 7.52 (s, 4H, NH_2), 7.64 (s, 2H, NH), 8.34 (s, 2H, CH).

Crystal data for **1**. monoclinic, $P2_1/c$, a=10.109 (2) Å, b=12.729 (2) Å, c=15.356 (3) Å, β=95.86 (1)°, V=1965.8 (6) Å^3, Z=2, Dx=1.551 g cm^{-3}, T=293 K, λ(Mo Kα) 0.71073 Å, μ=4.56 cm^{-1}, $F(000)$=952, GooF=0.934, R indices (all data) $R1$=0.0628, $wR2$=0.0960 for 3859 reflections and 262 parameters and R indices $R1$=0.0375, $wR2$=0.0868 for 2596 reflections obeying $I>2\sigma(I)$ criterion of observability.

4.1.3. Compound 2. O=N–HCTZ (98 mg, 0.3 mmol) and DCH6B (112 mg 0.3 mmol) were dissolved in the mixture methanol/ethylacetate (1:2, 9 ml). The colorless, transparent crystals were obtained in a quantitative yield by slow evaporation of the solvents at room temperature for several days, mp>160 °C (with decomp., brown spot), found, %: C 46.32, H 6.23, Cl 5.02, N 8.06, S 9.21, required for $C_{27}H_{43}ClN_4O_{11}S_2$: C 46.37, H 6.20, Cl 5.07, N 8.01, S 9.17. IR (cm^{-1}, peaks of strong absorption only): 3450–3100, 3070–3020, 3000–2780, 1590–1510, 1430 1300, 1280, 1080. ^{1}H NMR ($CDCl_3$) δ ppm: 1.46–1.21 (m, 16H, CH_2, CH), 3.61–3.46 (m, 20H, CH_2O), 4.95 (s, 2H, CH_2), 7.07 (s, 1H, CH), 7.52 (s, 2H, NH_2), 7.62 (s, 1H, NH), 8.34 (s, 1H, CH).

Crystal data for **2**. triclinic, $P-1$, a=14.326 (3) Å, b=15.458 (3) Å, c=16.757 (3) Å, α=68.04 (3), β=71.54 (3), γ=77.45 (3)°, V=3243.8 (11) Å^3, Z=4, Dx=1.432 g cm^{-3}, T=130 K, λ(Mo Kα) 0.71073 Å, μ=3.10 cm^{-1}, $F(000)$=1480, GooF=1.045, R indices (all data) $R1$=0.2769, $wR2$=0.3207 for 11190 reflections and 829 parameters and R indices $R1$=0.1121, $wR2$=0.2318 for 3749 reflections obeying $I > 2\sigma(I)$ criterion of observability.

Tables of crystal data, atomic coordinates and thermal parameters, full bond distances and angles, and structure factors may be obtained on request from the authors. CCDC reference numbers 256808 and 256809 for compounds (**1**) and (**2**), respectively.

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Додаток 44

Копія статті

“Structure of Dibenzocrown Ethers and their H-Bonded Adducts. Structure Peculiarities of Supramolecular Assemblages Formed by [1.5]Dibenzo-18-Crown-6 and Some NH-Donors”

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Structure of Dibenzocrown Ethers and their H-Bonded Adducts. 2. Structure Peculiarities of Supramolecular Assemblages Formed by [1.5]Dibenzo-18-Crown-6 and Some NH-Donors

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Key words: dibenzocrown ethers, H-bonded adducts, homo-and heterosynthons, supramolecular architecture, synthesis and crystal structure

Abstract

[1.5]Dibenzo-18-crown-6 ([1.5]DB18C6) forms the H-bonded supramolecular complexes with 3-nitro-1*H*-1,2,4-triazole (1:1), 2,4(1*H*,3*H*)-pyrimidinedithione (1:1), 1,2,5-oxadiazole-3,4-diamine monohydrate (1:1:1), ethanedithioamide (1:1) and 1,2-hydrazinedicarbothioamide (2:3). The first two complexes are discrete molecular adducts, two next complexes represent different types of tapes, while in the last complex the components are linked into 3D grid. In all cases, the formation of co-crystals results in the substitution of all or part of supramolecular homosynthons by heterosynthons and in the changing of supramolecular architecture.

Introduction

The research of organic molecules complexation *via* weak non-covalent interactions such as H-bonding, π-stacking and electrostatic interactions is a matter of a great concern. In biological systems, many heterocyclic bases such as imidazole, purine, uracil and their derivatives are very important and manifest their H-bonding abilities [1]. The biologically important planar heterocyclic bases and their analogues and derivatives are also promising in the exploring of π—π-stacking interactions with the macrocyclic receptors (crown ethers) containing the aromatic units [2]. The H-bonding remains the dominant component in the resulting complexes with neutral molecules although aromatic rings of the crown ethers decrease the electron density of the adjacent oxygen atoms. As a result the π—π-stacking interactions might exhibit themselves as a minor contribution in crystal packing.

In our previous communication [Kotlyar *et al.* submitted for publication], we reported the improved method of synthesis and crystal structures of [1.5]dibenzo-18-crown-6 ([1.5]DB18C6) and its complex with the zwitterion of amidosulfuric acid ($^{+}NH_3SO_3^{-}$). To the best of our knowledge, they are the first examples of structural characterizations of this crown ether and its complex with the neutral molecule bearing a pair of partitioned charges. This crown ether is a promising ligand in the complexation of both metal cations and neutral organic molecules, as it possesses the cavity comparable with the classic 18-crown-6 (18C6) in which only weak CH-O intramolecular interactions are easily disrupted in the adduct with amidosulfuric acid [Kotlyar *et al.*, submitted for publication]. The distinctive feature of [1.5]DB18C6 is a non-symmetric arrangement of aromatic rings along the macrocycle that could dictate a non-symmetric mode of coordination of neutral molecules. For this crown ether either one-face or different-face coordination is possible in dependence of the guest possibilities, the number and arrangement of its H-donor groups. The two aromatic rings that are in a close proximity to each other are also promising from the view point of possible cation (metal cation) – π (crown) interactions as well as π (neutral organic molecule) – π(crown) stacking interactions. In communication [Kotlyar *et al.*, submitted for publication] we revealed that [1.5]DB18C6 behaves very similar to the other of 18-membered crown ethers (18C6, benzo-18C6,

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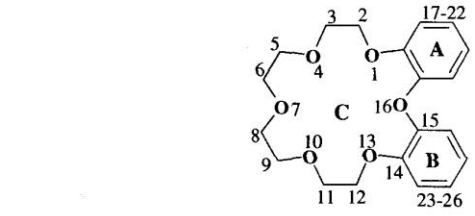
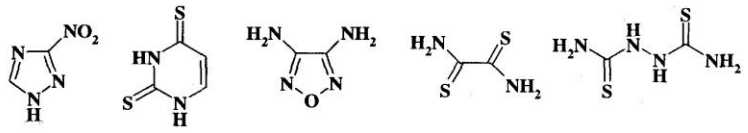


[1.5]DB18C6



1 2 3 4 5

Scheme 1. Structural formulas of crown ether (with the atomic numbering) and guest molecules **1–5**.

dicyclohexano-18C6) in the adduct with zwitterion of amidosulfuric that is arranged in the tripod binding mode above the macrocyclic cavity.

To study the interaction of [1.5]DB18C6 with neutral organic molecules from the crystal engineering point of view, its co-crystals with cyclic and non-cyclic molecules containing the different number of H-donor secondary and primary amino groups have been prepared (Scheme 1).

The cyclic molecules of 3-nitro-1*H*-1,2,4-triazole, **1** [3] and 2,4(1*H*,3*H*)-pyrimidinedithione, **2** [4] contain two and four H-donor centers correspondingly, that include one NH group and the neighboring CH group in **1** and two NH groups and two CH groups in **2**, incorporated in the rigid planar 5-membered and 6-membered cycles. In the molecules of 1,2,5-oxadiazole-3,4-diamine, **3** [5] and ethanedithioamide, **4** [6] two amino groups have *cis*- and *trans*-orientation, respectively. The molecule of 1,2-hydrazinedicarbothioamide, **5** [7] contains two NH_2 groups in *gauche*-conformation and two twisted NH groups inside the molecule. These molecules have been chosen to study their preferred mode of H-bonding, the nature of the H-bonded arrays, the observed supramolecular synthons and the resultant supramolecular architectures in the co-crystals with [1.5]DB18C6. It is interesting to clarify which of the supramolecular synthons are preserved and which are lost in the co-crystals with crown ether in comparison with initial crystalline pure guests. To answer this question the comparison of the crystal packing for the co-crystals with initial pure guests has been fulfilled.

Experimental

Synthesis

[1.5]DB18C6 was obtained as described in [Kotlyar *et al.*, submitted for publication]. Commercially available reagents **1–5** were used in their initial state. The thin layer chromatographic control of the substances purity was performed on Silufol UV-254 plates. All five complexes were analyzed for C, H, N and S in a Perkin Elmer 240C instrument.

*Synthesis of [1.5]DB18C6·***1**

28.5 mg (0.25 mmol) of **1** and 90 mg (0.25 mmol) of [1.5]DB18C6 were dissolved in 3 ml of acetone at 56 °C; 3 ml of *n*-hexane was added and the mixture was remained to crystallize at room temperature and spontaneous evaporation of solvents. Colorless transparent crystals M.P. 141–142 °C were obtained with the yield 111 mg (94%). Found, C, 55.64; H, 5.54; N, 11.86 for $C_{22}H_{26}N_4O_8$. Calculated, %: C, 55.69; H, 5.52; N, 11.81.

*Synthesis of [1.5]DB18C6·***2**

36 mg (0.25 mmol) of **2** and 90 mg (0.25 mmol) of [1.5]DB18C6 were dissolved in 5 ml of methanol at 64 °C; 15 ml of ethyl acetate and 0.3 ml of *n*-butanol were added. The treatment of the reaction mixture is similar to [1.5]DB18C6·**1**. Yellow transparent crystals M.P. 260–262 °C were obtained with the yield 116 mg (92%). Found, C, 57.15; H, 5.62; N, 5.59; S, 12.75 for $C_{24}H_{28}N_2O_6S_2$. Calculated, %: C, 57.12; H, 5.59; N, 5.55; S, 12.71.

*Synthesis of [1.5]DB18C6·***3**·H_2O

25 mg (0.25 mmol) of **3** and 90 mg (0.25 mmol) of [1.5]DB18C6 were dissolved in 3 ml of methanol at 64 °C, 3 ml of benzene and 7 ml of *n*-heptane were added. The treatment of the reaction mixture is similar to [1.5]DB18C6·**1**. Colorless transparent crystals M.P. 98–100 °C was obtained with the yield 101 mg (86%). Found, C, 55.26; H, 6.28; N, 11.74 for $C_{22}H_{30}N_4O_8$. Calculated, %: C, 55.22; H, 6.32; N, 11.71.

*Synthesis of [1.5]DB18C6·***4**

30 mg (0.25 mmol) of **4** and 90 mg (0.25 mmol) of [1.5]DB18C6 were dissolved in 5 ml of methanol at 64 °C; 15 ml of ethyl acetate and 0.3 ml of *n*-butanol

was added. The treatment of the reaction mixture is similar to [1.5]DB18C6·**1**. Red transparent crystals M.P. 128–130 °C were obtained with the yield 116 mg (92%). Found, C, 54.93; H, 5.84; N, 5.89; S, 13.38 for $C_{22}H_{28}N_2O_6S_2$. Calculated, %: C, 54.98; H, 5.87; N, 5.83; S, 13.34.

*Synthesis of [1.5]DB18C6·**5***

37 mg (0.25 mmol) of **5** and 90 mg (0.25 mmol) of [1.5]DB18C6 were dissolved in 1 ml of dimethylformamide at 150 °C and the mixture was remained to crystallize at room temperature. Colorless transparent crystals M.P. 223–224 °C were obtained with the yield 103.5 mg (90%). Found, 47.21; H, 5.65; N, 14.39; S, 16.48 for $C_{46}H_{66}N_{12}O_{12}S_6$. Calculated, %: C, 47.16; H5.68; N, 14.35; S, 16.42.

Data collection and structure refinement

The X-ray crystallographic data for [1.5]DB18C6·**1**, [1.5]DB18C6·**2** and [1.5]DB18C6·**4** were recorded with an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromatic CuK_α radiation using ω–2θ rotation scan mode, while for [1.5]DB18C6·**3**·H_2O and [1.5]DB18C6·**5** the data were recorded on a Bruker AXS CCD diffractometer equipped with graphite monochromatic MoK_α radiation using ω rotation with a sample-to-detector distance of 50 mm. The CCD data were processed with DENZO [8] and all reflections were corrected for polarization and Lorentz effects. An absorption correction was not applied. The structures were solved by direct methods (SHELXS-97) and refined on F^2 (SHELXL–97) [9]. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were treated anisotropically. In [1.5]DB18C6·**1** the oxygen atom O7 is disordered over two sites with occupancies of 0.933 and 0.067. In [1.5]DB18C6·**2**, three carbon atoms, C23, C24, C25 are disordered over two positions (site occupancies 0.607 and 0.393). In [1.5]DB18C6·**4** two carbon atoms of ethanedithioamide molecule occupy two positions with equal probability. In all structures C-bound hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 times the carbon temperature factor) and refined as riding atoms, while the N-bound and O-bound H-atoms were found from differential Fourier maps at an intermediate stage of the refinement and were refined isotropically.

The X-ray data and the details of the refinement for five complexes are summarized in Table 1.

Table 1. Crystallographic data for [1.5]DB18C6·**1**, [1.5]DB18C6·**2**, [1.5]DB18C6·**3**·H_2O [1.5]DB18C6·**4**, [1.5]DB18C6·**5**

Compound	[1.5]DB18C6·**1**	[1.5]DB18C6·**2**	[1.5]DB18C6·**3**·H_2O	[1.5]DB18C6·**4**	[1.5]DB18C6·**5**
Composition	$C_{22}H_{26}N_4O_8$	$C_{24}H_{28}N_2O_6S_2$	$C_{22}H_{30}N_4O_8$	$C_{22}H_{28}N_2O_6S_2$	$C_{46}H_{66}N_{12}O_{12}S_6$
Formula weight	474.47	504.60	478.50	480.58	1171.47
Wavelength (Å)	1.54178	1.54178	0.71073	1.54180	0.71073
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*C*2/*c*
a (Å)	10.859(3)	10.418(2)	9.923(2)	8.602(2)	22.200(4)
b (Å)	12.122(3)	11.674(2)	11.226(2)	17.796(3)	22.501(5)
c (Å)	10.350(3)	11.889(2)	12.238(17)	8.175(3)	13.286(3)
α (°)	98.02(2)	66.84(3)	68.35(1)	103.12(3)	90.0
β (°)	117.45(3)	77.34(3)	81.34(1)	104.24(3)	121.00(3)
γ (°)	93.52(3)	74.57(3)	75.48(1)	88.05(3)	90.0
V (Å^3)	1184.9(6)	1270.7(4)	1224.0(4)	1181.0(6)	5689(2)
Z	2	2	2	2	4
Dcalc (g cm^{-3})	1.330	1.319	1.298	1.351	1.368
μ (mm^{-1})	0.864	2.248	0.100	2.389	0.308
F(000)	500	532	508	508	2472
Reflections collected/ unique	4477/4477	4812/4812	11970/5049	4479/4479	28462/6452
Refinement method	Full–matrix least–squares on F^2				
Data/restraints/parameters	4477/0/317	4812/0/343	5049/3/332	4479/2/324	6452/0/379
Reflections with $I > 2\sigma(I)$	4029	4006	3328	3767	4330
Goodness–of–fit on F^2	1.046	1.072	1.079	1.219	0.938
R_1, wR_2 [$I > 2\sigma(I)$]	0.0599, 0.1697	0.0574, 0.1667	0.0592, 0.1938	0.0498, 0.1233	0.0371, 0.0925
R_1, wR_2 (all data)	0.0637, 0.1754	0.0647, 0.1754	0.0799, 0.2075	0.0702, 0.1677	0.0669, 0.1001
Extinction coefficient	0.0059(9)	–	0.031(6)	0.0138(9)	–
Largest diff. peak and hole e Å^{-3}	0.293/–0.319	0.467/–0.352	0.489/–0.342	0.420/–0.610	0.215/–0.342

Table 2. Selected geometric parameters for [1.5]DB18C6·1–[1.5]DB18C6·5

1	2	3	4	5	6		
					A/B	A/C	B/C
[1.5]DB18C6·1	2.577(2)–2.922(3)	0.345	0.059	0.927(3) O7 0.769(2) O16	77.9(1)	40.6(1)	47.2(1)
[1.5]DB18C6·2	2.563(3)–2.904(3)	0.341	0.002	0.218(3) O7 0.472(3) O16	69.2(5)	48.1(1)	31.4(1)
[1.5]DB18C6·3·H_2O	2.565(2)–2.951(3)	0.386	0.121	0.147(3) O7 0.511(2) O16	70.5(1)	46.9(1)	28.1(1)
[1.5]DB18C6·4	2.593(3)–2.888(3)	0.295	0.290	−1.192(4) O7 −0.322(3) O16	87.8(1)	81.1(1)	22.4(1)
[1.5]DB18C6·5	2.594(2)–2.946(2)	0.352	0.032	−0.778(2) O7 −1.192(2) O16	77.8(1)	45.3(1)	48.4(1)

1. Complex.
2. The range of O···O distances (Å) between the neighboring oxygen atoms in the cycle.
3. Δ O···O distances (Å).
4. The mean deviation (Å) from the least-squares plane through the atoms O1, O4, O10, O13.
5. The deviation of atoms O7 and O16 (Å) from the plane through O1, O4, O10, O13 atoms.
6. The angles between the planes (deg).

Results and discussion

[1.5]DB18C6 [Kotlyar *et al.*, submitted for publication] belongs to a family of different-faced crown ethers that differ by the mode of complexation on their different faces [10]. Its molecule consists of two rigid benzene rings denoted A (C17 > C22) and B (C14, C15, C23 > C26) and 18-membered crown ether loop (denoted C, further we refer to plane C as the mean least-square plane through 6 crown oxygens). Similar to other 18-membered crown ethers, in [1.5]DB18C6 the oxygen atoms form a distorted hexagon with the side (the distance between the adjacent O atoms) ranges from 2.565(2) to 2.946(2) Å (Table 2). This hexagon adopts a boat-like shape in [1.5]DB18C6·**1**, [1.5]DB18C6·**2** and [1.5]DB18C6·**5** with O1, O4, O10 and O13 atoms that define its bottom and O7, O16 atoms above this plane. The macrocycle in [1.5]DB18C6·3·H_2O and [1.5]DB18C6·**4** adopts a half-chair conformation with O7 and O16 atoms correspondingly being practically in the plane of four other oxygens, and one oxygen (O16 and O7) that strongly deviates from this plane. The A and B rings of the diphenyl oxide fragment are arranged approximately perpendicular to each other with the maximal deviation of 20.8° from the right angle in [1.5]DB18C6·**2** and both incline to plane C. In [1.5]DB18C6·**4**, the A ring is practically perpendicular to the plane C, while the B ring is approximately coplanar with this plane. The corresponding dihedral angles are summarized in Table 2. The conformation of [1.5]DB18C6 in the complexes is very similar and distincts only in details as show the torsion angles along

Table 3. Selected torsion angles [deg] in [1.5]DB18C6·1–[1.5]DB18C6·5

Angle	[1.5]DB18C6·1	[1.5]DB18C6·2	[1.5]DB18C6·3·H_2O	[1.5]DB18C6·4	[1.5]DB18C6·5
O1–C2–C3–O4	−61.2(2)	−71.4(2)	−81.1(3)	−74.1(3)	66.3(2)
C2–C3–O4–C5	−171.8(2)	−171.8(2)	−176.6(3)	173.2(2)	−176.3(2)
C3–O4–C5–C6	−175.3(2)	−173.6(2)	**−97.2(4)**	−173.5(3)	−173.7(2)
O4–C5–C6–O7	72.2(2)	56.6(3)	−53.4(5)	66.4(3)	−65.6(2)
C5–C6–O7–C8	−177.7(2)	173.0(3)	−177.4(3)	−175.7(3)	170.8(2)
C6–O7–C8–C9	**86.9(3)**	139.0(3)	−171.2(3)	170.2(3)	−171.5(2)
O7–C8–C9–O10	64.4(3)	52.8(5)	80.4(2)	−67.2(4)	59.5(2)
C8–C9–O10–C11	178.4(2)	179.0(4)	−173.9(1)	−166.8(3)	176.3(2)
C9–O10–C11–C12	−172.4(2)	179.0(3)	−167.0(1)	**−74.3(4)**	−175.0(2)
O10–C11–C12–O13	−69.5(2)	−70.2(4)	−62.3(2)	−56.6(4)	−71.6(2)
C11–C12–O13–C14	159.5(2)	177.6(3)	170.5(2)	−159.6(3)	**−80.1(2)**
C12–O13–C14–C15	−162.9(2)	−165.3(2)	−167.6(2)	175.9(3)	172.0(2)
O13–C14–C15–O16	2.2(2)	5.9(3)	2.6(3)	4.6(4)	−7.5(2)
C14–C15–O16–C17	**−108.0(2)**	**−118.8(2)**	**−115.3(2)**	**−84.6(3)**	**91.4(2)**
C15–O16–C17–C18	−175.2(2)	−175.5(2)	−174.9(2)	175.9(3)	−161.5(1)
O16–C17–C18–O1	0.9(2)	−0.8(3)	−1.2(3)	−4.7(4)	1.7(2)
C17–C18–O1–C2	−174.5(1)	179.3(2)	176.9(2)	−177.8(3)	179.2(1)
C18–O1–C2–C3	174.1(1)	174.4(2)	172.1(2)	151.7(3)	176.0(2)

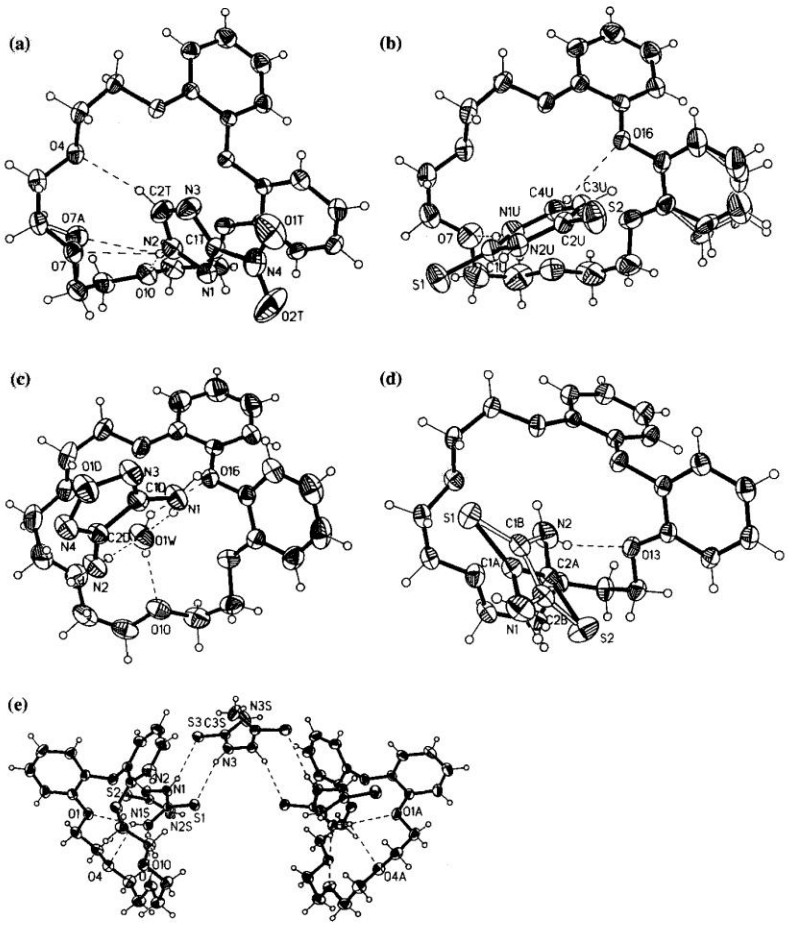


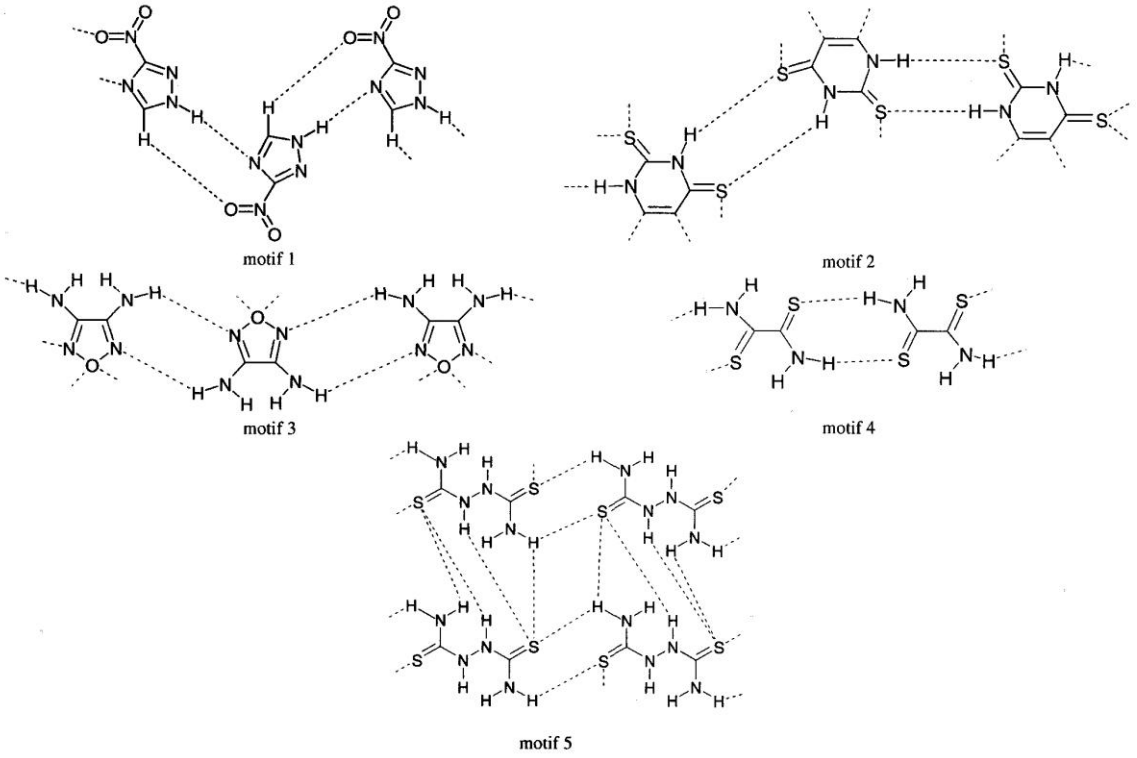
Figure 1. (a–e) ORTEP view of [1.5]DB18C6·**1**, [1.5]DB18C6·**2**, [1.5]DB18C6·**3**·H_2O, [1.5]DB18C6·**4** and [1.5]DB18C6·**5**. Ellipsoids for non-hydrogen atoms are drawn at the 30% probability level.

the macrocycle summarized in Table 3. The diphenyl oxide fragment is described by one *trans*—C—O bond, C15—O16—C17—C18, that ranges from 161.5 to 175.9° and one *gauche*-C—O bond, C14—C15—O16—C17, that ranges from 84.6 to 118.8°. Besides this C—O bond in *gauche*-conformation in the diphenyl oxide fragment, in all complexes except [1.5]DB18C6·**2** one more Csp^3—O bond adopts *gauche* conformation in the different positions of the macrocyclic loop, while all Csp^3—Csp^3 bonds remain *gauche* and range from 52.8 to 81.1°.

[1.5]DB18C6·**1**, [1.5]DB18C6·**2** and [1.5]DB18C6·**4** are 1:1 anhydrous H-bonded adducts, [1.5]DB18C6·**3**·H_2O is a monohydrate of 1:1:1 stoichiometry and [1.5]DB18C6·**5** is an anhydrous H-bonded adduct with an unusual 2:3 stoichiometry. The ORTEP view for the compounds is depicted in Figure 1. The cyclic molecules of **1**, **2**, **3** and non-cyclic **4** possess the planar skeletons, while **5** has an angular shape with the dihedral angle of 103° between its two planar parts.

[1.5]DB18C6·**1** represents the 1:1 discrete adduct where the molecules are held together by one bifurcated NH···O and one CH···O hydrogen bonds (Table 4). The very similar mode of intermolecular interactions was found in the adducts of 18C6 with 1*H*-1,2,4-triazole [11] and symmetric [3.3]DB18C6 with 1,2,4-triazolium cation [12]. The molecule of **1** is inclined at an angle of 61.6(1)° to the C plane of [1.5]DB18C6. The triazole ring is arranged approximately parallel to the benzene ring A with the partial overlap of the cyclic moieties, the corresponding dihedral angle between the planes is 14.6°. The atoms of triazole ring are at the distances of 3.003–3.488 Å from plane A. The related by translation adducts are stacked in pseudo-chains (Figure 2) where the triazole and benzene rings alternate.

In the crystalline **1** [3] the molecules form the planar chains sustained by NH···N and CH···O(NO_2) hydrogen bonds, the corresponding H-bonded ring is designated as a $R_2^2(8)$ in graph-set notation [13], the schematic presentation of this chain is given in Scheme 2 (motif 1).



Scheme 2. The main supramolecular motifs in **1** (motif 1), **2** (motif 2), **3** (motif 3), **4** (motif 4, 1D tapes in all cases), **5** (motif 5, 3D grid).

It is evident, that the same neighboring H-donor centers, NH and CH groups, responsible for the H-bonding, act both in **1** itself and in its complex with [1.5]DB18C6, however, the $R_2^2(8)$ homosynthon is substituted by the heterosynthon with the involvement of crown oxygens in H-bonding.

Similar to [1.5]DB18C6·**1**, [1.5]DB18C6·**2** is of 1:1 ratio, and the molecules of [1.5]DB18C6 and **2** are held together again by one NH···O and one CH···O hydrogen bonds of the neighboring NH and CH groups (Table 4). Compare **2** is arranged approximately perpendicular to the plane C of the crown ether, the corresponding dihedral angle being 87.4(1)°. The molecules of **2** are centrosymmetrically paired *via* a couple of NH···S hydrogen bonds to form a $R_2^2(8)$ ring. This dimer is imprisoned between two crown molecules and the final adduct represents the molecular capsule shown in Figure 3.

It is a promising and encouraged example of usage of rather simple crown ether to encapsulate the biologically important molecules. The crown ether used appears to be crucial for the final supramolecular architecture. Its two benzene rings arranged in a close proximity to each other excludes the symmetric mode of coordination on the both sides of the crown ether, as it was in the previously reported adduct of centrosymmetric *cis*-isomer of dicyclohexano-18-crown-6 (DCH18C6) with 2,4(1*H*,3*H*)-pyrimidinedithione (thiauracil) [14], where the H-bonded thiauracil dimer (quite identical to the dithiauracil dimer) alternate with the symmetric crown molecules in the infinite chains [15].

In the crystalline **2** itself [4], the molecules are associated in chains sustained by two similar alternating $R_2^2(8)$ synthons (Scheme 2, motif 2) built on NH···S hydrogen bonds. These chains are further aggregated into ladder-like layers due to ability of sulfur to yield short contacts (in this case weak CH···S contacts) in the perpendicular directions. The interaction with crown ether results in the break of the weakest guest–guest CH···S interactions and their substitution by the CH···O interactions with crown oxygens. These contacts occur in the plane of planar skeleton of **2** and are decisive for the molecular capsule formation.

In the first group of complexes, [1.5]DB18C6·**3**·H_2O stands separately, as the only ternary complex here. Water mediates [1.5]DB18C6 and **3**, taking advantage of both of its H-donors (two hydrogen atoms) in the interactions with crown oxygens and H-acceptors (two lone pairs) in the interactions with two amino groups of **3**, these latter interactions result in the 7-membered ring, $R_2^1(7)$ closed by two NH···O hydrogen bonds (Figure 4, Table 3).

Water molecule is perching at 1.686(2) Å above the plane C of the crown ether. The retrieval of CSD [16] revealed that the mediated function of water is a common case in the complexes of crown ethers with

Table 4. Hydrogen bonds in [1.5]DB18C6 1 – [1.5]DB18C6·5

D–H···A	d(H···A) (Å)	D(D···A) (Å)	∠(DHA) (deg.)	Symmetry transformation for H-acceptor
[1.5]DB18C6·**1**				
N2-H1N···O10	1.94(3)	2.836(2)	166(2)	*x*, *y*, *z*
N2-H1N···O7	2.57(3)	3.053(2)	114(2)	*x*, *y*, *z*
N2-H1N···O7A	2.66(4)	3.28(3)	126(2)	*x*, *y*, *z*
C2T-H2T···O4	2.52	3.420(3)	162	*x*, *y*, *z*
[1.5]DB18C6·**2**				
N1U-H1U···O7	1.89(4)	2.752(3)	168(3)	*x*, *y*, *z*
C4U-H4U···O16	2.49	3.174(3)	131	*x*, *y*, *z*
N2U-H2U···S1	2.47(3)	3.337(2)	167(2)	$-x+2, -y, -z+1$
[1.5]DB18C6·**3**·H_2O				
O1W-H1W1···O16	2.27(4)	2.887(3)	145(5)	*x*, *y*, *z*
O1W-H2W1···O10	2.17(3)	2.892(3)	168(5)	*x*, *y*, *z*
N1-H11N···O1W	2.28(2)	3.103(3)	158(2)	*x*, *y*, *z*
N1-H21N···N3	2.41(2)	3.227(3)	158(2)	$-x+2, -y+1, -z+1$
N2-H12N···N4	2.35(2)	3.140(3)	161(2)	$-x+2, -y, -z+1$
N2-H22N···O1W	2.05(2)	2.882(3)	177(3)	*x*, *y*, *z*
[1.5]DB18C6·**4**				
N1-H11N···O4	2.30(4)	3.109(4)	160(5)	*x*, *y*, $z+1$
N1-H21N···O10	2.18(4)	3.019(5)	168(6)	x, y, $z+1$
N2-H12N···O13	2.42(5)	3.224(5)	163(7)	*x*, *y*, *z*
[1.5]DB18C6·**5**				
N1S-H11S···O1	2.33(2)	3.161(2)	155(2)	*x*, *y*, *z*
N1S-H11S···O4	2.59(2)	3.150(2)	122(2)	*x*, *y*, *z*
N1S-H21S···O10	2.46(2)	3.290(2)	173(2)	*x*, *y*, *z*
N1S-H21S···O7	2.51(2)	2.998(2)	119(2)	*x*, *y*, *z*
N2S-H12S···O10	2.25(2)	3.045(2)	152(2)	$x, -y+1, z-1/2$
N2S-H22S···O4	2.17(2)	3.017(2)	168(2)	$x, -y+1, z-1/2$
N1-H1N···S3	2.48(2)	3.263(2)	164(2)	*x*, *y*, *z*
N2-H2N···S3	2.76(2)	3.467(2)	150(2)	$-x+1/2, -y+1/2, -z+1$
N3-H3N···S1	2.43(2)	3.310(2)	164(2)	*x*, *y*, *z*
N3S-H23S···S2	2.89(3)	3.514(2)	127(2)	$x-1/2, -y+1/2, z-1/2$

neutral molecules. In the case of centrosymmetric 18C6 and its centrosymmetric derivatives two water molecules display in an identical mode at two equal faces of macrocycle. Scarcely water molecule occupies only one face of the crown ether in the one-face [17] or different-face coordination [18]. Molecule **3** is arranged at an angle of 66.4(1)° to the C plane of [1.5]DB18C6. The H-bonding patterns and the final supramolecular architecture in [1.5]DB18C6·**3**·H_2O differ from the complexes of other crown ethers with **3** [19]. In the 1:1 anhydrous adducts with 15C5, B15C5 and DCH18C6, the components alternate in the H-bonded chains and each amino-group of **3** coordinates to its own crown molecule. In the 18C6·**3**·H_2O water molecules incorporate in the chain of composition···H_2O···18C6(A)···H_2O···**3**···18C6(B)···**3**···H_2O···18C6(A)···H_2O···. In contrary to these examples of two-face crown coordination, in [1.5]DB18C6·**3**·H_2O we observe the coordination of water molecule only on the concave face of the crown molecule. The related by inversion molecules of **3** formulate the H-bonded planar chains sustained by $R_2^2(8)$ supramolecular synthon. In a similar way the chains are organized in **3** itself [5] (Scheme 2), although there they are further combined in a ladder-like layer *via* cyclic oxygen and two free hydrogens of each amino groups. Thus, this synthon that acts between the planar chains appears to be weaker than that inside the chain and is broken first in the co-crystal of **3** with [1.5]DB18C6. The final supramolecular architecture represents the infinite tubes with the walls built of crown ethers and chains of **3** inside these tubes.

The planar skeleton of **4** is arranged approximately perpendicular to the C plane of crown ether, the twisted angle is 81.7(1)°. Figure 5 shows as [1.5]DB18C6 alternates with **4** in chains running along *c* direction in the unit cell.

Two arranged in *trans*-position terminal amino groups of **4** interact with the oxygens on both convex (two NH···O hydrogen bonds) and concave (one NH···O hydrogen bond) faces of the crown ether (Table 4). The same chain architecture was found in the 1:1 co-crystals with B15C5 [20], 15C5 [21], while the 1:2 stoichiometry in the co-crystals with 18C6 [22] or with *cis*-isomers of DCH18C6 [21] provided the sheets where the similar chains of alternative components are further combined into sheets

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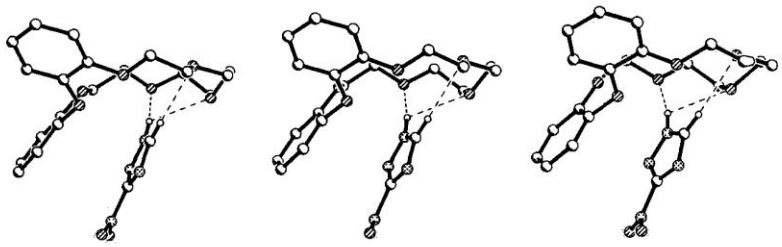

Figure 2. Arrangement of translated [1.5]DB18C6·**1** units in the crystal.

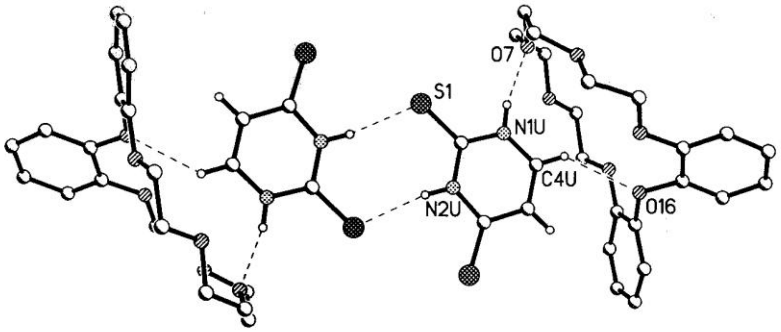

Figure 3. The centrosymmetric molecular capsule in [1.5]DB18C6·**2**.

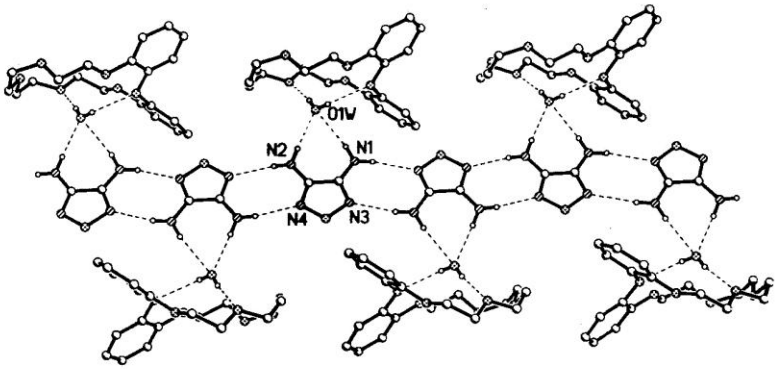

Figure 4. The fragment of the infinite chain in [1.5]DB18C6·**3**.

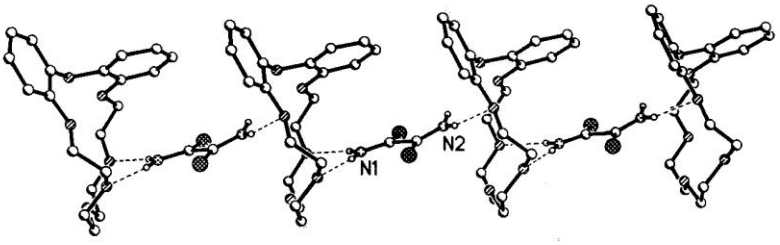

Figure 5. The fragment of the infinite chain in [1.5]DB18C6·**4**.

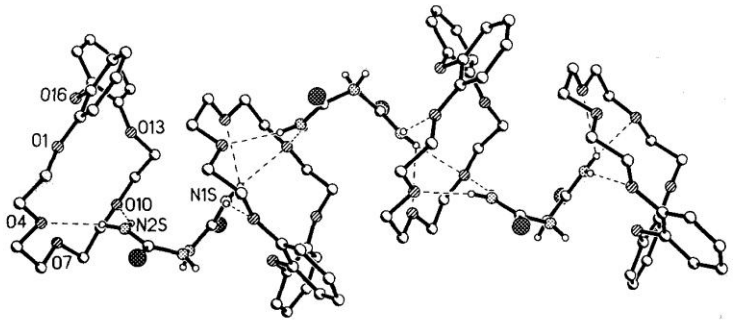

Figure 6. The fragment of the infinite chain in [1.5]DB18C6·**5**.

via H-bonded second molecule of **4**. In the crystalline **4** itself [6], the molecules are arranged into planar chains *via* $R_2^2(8)$ ring (Scheme 2, motif **4**) and further into 3D network *via* NH···S interactions in the perpendicular direction. None of homosynthons typical for **4** itself is preserved in any of its crown complexes. In all complexes only the heterosynthon crown ether – **4** exists.

Four above described adducts crystallise in *P*-1 space group with one formula unit in the asymmetric part of the unit cell, while [1.5]DB18C6·**5** crystallises in *C*2/*c* space group, and the asymmetric unit contains one molecule of [1.5]DB18C6, one molecule of **5** in general positions and half a molecule of **5** in a special position on the 2_1 screw axis, that provides the unusual 2:3 stoichiometry of this adduct. Two molecules of **5** reveal the different structural functions in the supramolecular architecture. One of the molecules alternates with [1.5]DB18C6 in the chains running along *c* direction (Figure 6) and bridges *via* its terminal amino groups two neighboring [1.5]DB18C6 molecules related by the glide plane. The amino group defined by N1S atom affords two bifurcated NH···O hydrogen bonds on the concave face of macrocycle, while the amino group defined by N2S atom affords two classic NH···O hydrogen bonds with crown oxygens on its convex face (Table 4). The diphenyl oxide fragment provides the rigidity of part of the crown ether loop and makes impossible the participation of O13 and O16 in hydrogen bonding. So, two secondary amino groups remain free for self-assembly and take this opportunity in the interaction with the second **5** molecule.

Each of two secondary amino groups defined by N1 and N2 atoms and two sulfur atoms S1 and S2 interact with two related by inversion **5** molecules of the second type (that resides on the 2_1 screw axis and does not have any direct contacts with the macrocycle) *via* $R_2^2(8)$ and $R_2^2(11)$ rings that result in the infinite ribbon built of three alternate rows of molecules of the first and second types depicted in Figure 7a. So, the second molecule of **5** serves as a peculiar binding node at the intersection of the fragments of four alternate chains.

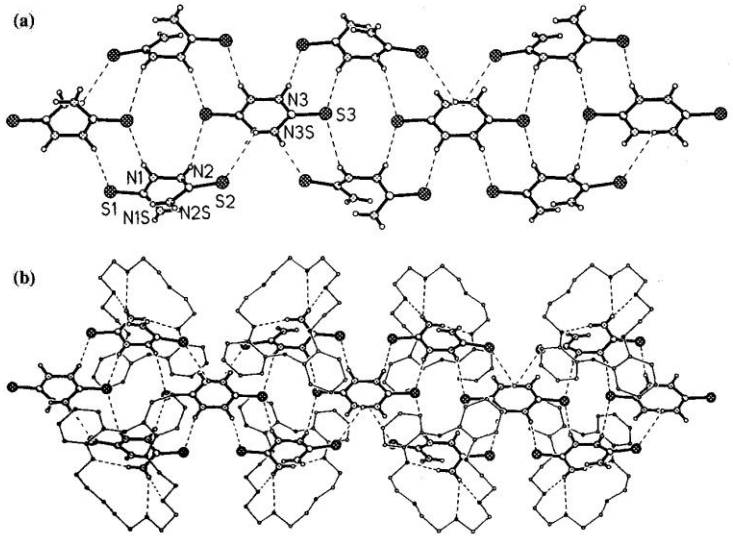

Figure 7. (a) The fragment of the ribbon built on **5** molecules. (b) The fragment of the crystal packing along *a* direction in [1.5]DB18C6·**5**.

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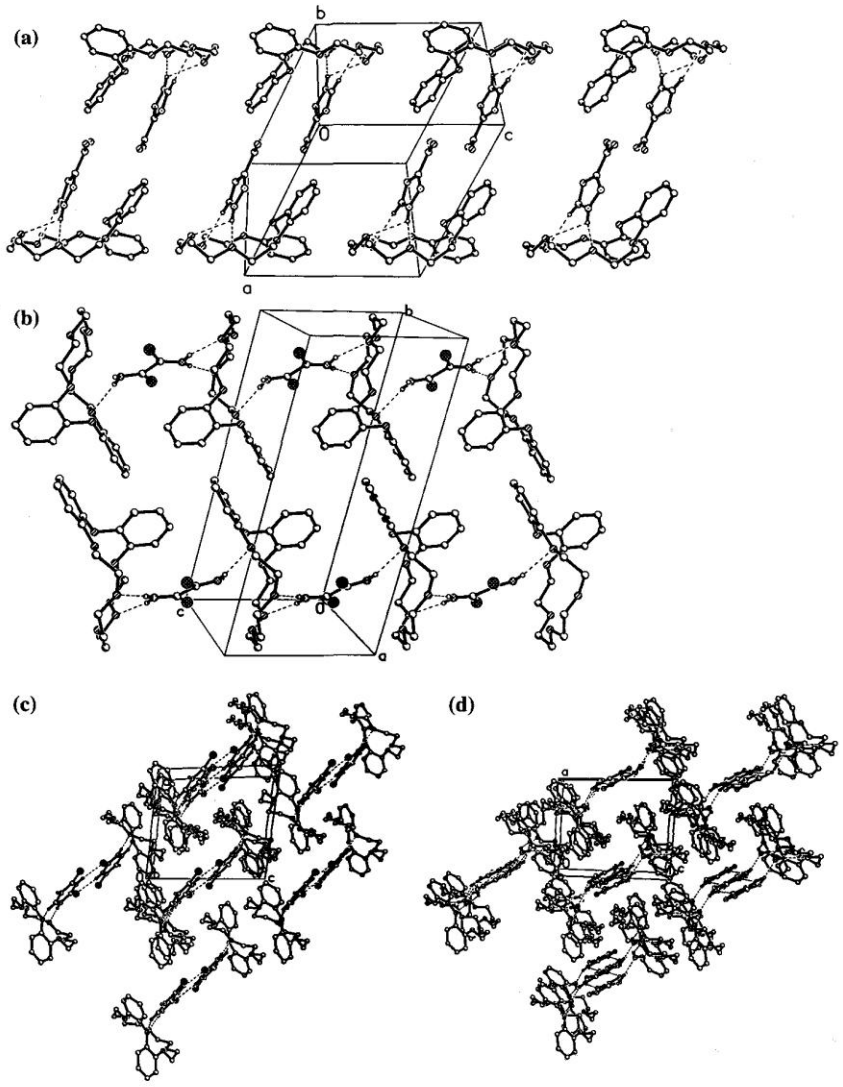

Figure 8. The fragments of crystal packing in **(a) [1.5]DB18C6·1**, (b) [1.5]DB18C6·**4**, (c) [1.5]DB18C6·**2**, (d) [1.5]DB18C6·**3**·H_2O.

The final supramolecular architecture of [1.5]DB18C6·**5** represents the 3D grid where the [1.5]DB18C6···**5**···[1.5]DB18C6···**5**···[1.5]DB18C6 chains running in *a* direction are interconnected along *c* direction *via* second **5** molecule (Figure 7b). Previously [20] we reported the co-crystals of **5** with 18C6, DCH18C6, 12C4 (1:1 ratio in all cases) and 15C5 (2:1 ratio). In the first two cases the components alternate in the chains *via* NH···O interactions that involve all four NH-donors of **5** and all crown oxygens of the flexible hexadentate backbone. That is the reason of a simple supramolecular architecture when no any opportunities remain for sulfur to use its pronounced acceptor functions. In the case of small 12C4 cavity which is capable to dispose only one NH···O hydrogen bond of the terminal NH_2 group, the molecules of **5** are combined into chains *via* two central NH groups and sulfur atoms forming the traditional $R_2^2(8)$ homosynthon. In the case of 15C5 the larger macrocyclic cavity is capable to dispose two terminal NH_2 groups in pseudo centrosymmetric mode, while all the other H-donor and acceptor functions of **5** are used inside its layer. It is an example of the most complete self-assembly of **5** among all of its crown ethers' adducts. So, the ribbon built of **5** molecules in [1.5]DB18C6·**5** represents the truncated fragment of the layers in 15C·**5**. The most stable for **5** is a planar $R_2^2(8)$ homosynthon closed by two NH···S hydrogen bonds which preserves in the co-crystals with 12C4, 15C5 and [1.5]DB18C6 spacers. All the other homosynthons are substituted by the powerful heterosynthons with the participation of crown oxygens.

Some concluding remarks should be addressed to the crystal packing. Molecular complexes in [1.5]DB18C6·**1** and infinite chains in [1.5]DB18C6·**4** are packed in a very similar way, with the aromatic rings being arranged in parallel planes (Figure 8a,b). The crystal packing of the molecular capsules in [1.5]DB18C6·**2** is rather similar to the packing of the infinite supramolecular tubes in [1.5]DB18C6·3·H_2O, thus in both cases the supramolecular units are adjoined by their hydrophobic surfaces (Figure 8c,d).

Conclusion

For the first time the complex formation between the non-symmetric [1.5]DB18C6 and neutral organic molecules, 3-nitro-1*H*-1,2,4-triazole, 1,2,5-oxadiazole-3,4-diamine monohydrate, ethanedithioamide and 1,2-hydrazinedicarbothioamide has been studied and final crystalline adducts were structurally characterized. Molecules of 3-nitro-1*H*-1,2,4-triazole and 2,4(1*H*,3*H*)-pyrimidinedithione **2** with the close arrangement of donor centers and water in the monohydrate of 1,2,5-oxadiazole-3,4-diamine are displayed in corresponding complexes at the concave face of the [1.5]DB18C6 forming the molecular adducts or tapes. Molecules of ethanedithioamide and 1,2-hydrazinedicarbothioamide *via* two NH_2 groups interact with oxygens both of the concave and convex faces of [1.5]DB18C6 molecule giving rise to alternate chains. In adduct of [1.5]DB18C6 with 1,2-hydrazinedicarbothioamide due to multiple NH···S interactions these chains are interconnected into 3D grid. H-bonding is the main type of interaction in these complexes. The competition of powerful O-containing macrocyclic H-acceptor with H-acceptor centers (O and S) in studied organic molecules results in the substitution of part of H-bonded supramolecular homosynthons by supramolecular heterosynthons. But for all that only those homosynthons are preserved that have a predominantly planar structure.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre [deposition numbers CCDC 237014 ([1.5]DB18C6·**1**), CCDC 237015 ([1.5]DB18C6·**2**), CCDC 237016 ([1.5]DB18C6·3·H_2O), CCDC 237017 ([1.5]DB18C6·**4**), CCDC 237018 ([1.5]DB18C6·5). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1233-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Додаток 45

Копія статті

“Селективные взаимодействия краун-эфиров с фторокомплексными кислотами кремния”

Журнал общей химии. 2005. Т. 75. Вып. 9

УДК 547.89

СЕЛЕКТИВНЫЕ ВЗАИМОДЕЙСТВИЯ КРАУН-ЭФИРОВ С ФТОРОКОМПЛЕКСНЫМИ КИСЛОТАМИ КРЕМНИЯ

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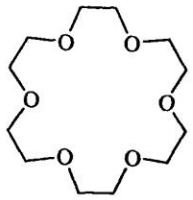
Согласно данным работы [1], 45%-ная кремнийфтористоводородная кислота представляет собой лабильную равновесную смесь SiF_6^{2-} (30–40%), $[SiF_5 \cdot H_2O]^-$ (60–70%), $SiF_4 \cdot 2\,H_2O$ (5%). Источники [2–4] указывают на содержание в растворах кремнийфтористоводородной кислоты единственного комплекса SiF_6^{2-}. При полном испарении воды из 45%-ной кремнийфтористоводородной кислоты, по данным работ [5, 6], образуется стабильный кристаллический фторокомплекс состава $(H_3O)_2SiF_6$.

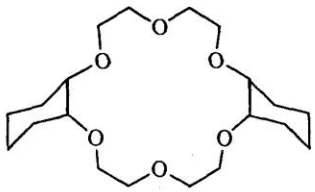
Одной из приоритетных задач супрамолекулярной химии является выявление селективных взаимодействий и стабилизации краун-эфирами («хозяевами») малоустойчивых соединений («гостей») в стабильные кристаллические соединения включения [7, 8]. В связи с этим в данной работе изучена возможность селективного синтеза кристаллических супрамолекулярных комплексов краун-эфиров с фторокомплексными кислотами кремния из растворов краун-эфиров во фтористоводородной кислоте в условиях самопроизвольного образования в них кремнийфтористоводородной кислоты.

Установлено, что при испарении растворов 1,4,7,10,13,16-гексаоксациклооктадекана (18К6) и *цис-син-цис*-пергидродибензо[*b*,*k*][1,4,7,10,13,16]-гексаоксациклооктадецина (А-ДЦГ-6) во фтористоводородной кислоте в стеклянном эксикаторе над серной кислотой селективно образуются кристаллические супрамолекулярные комплексы: нейтральный $[(SiF_4 \cdot 2\,H_2O) \cdot 18K6 \cdot 2\,H_2O]$ (I) и ионный $[H_3O^+ \cdot (A\text{-ДЦГ-}6)]SiF_5^-$ (II) соответственно.

Из состава комплексов (I, II) видно, что смещение равновесия и селективность связывания «гостевых» компонент кремнийфтористоводородной кислоты контролируется пространственным строением краун-эфиров 18К6 и А-ДЦГ-6.



18К6



А-ДЦГ-6

Описанные превращения являются первым примером селективного синтеза кристаллических супрамолекулярных комплексов (I, II) в условиях самопроизвольного образования на границе раздела фаз (газообразная–твердая) тетрафторида кремния и антинаправленным транспортом его в газовой фазе, и их результатом становится образованием равновесной смеси «гостевых» компонент в жидкой фазе по следующей схеме.

$$HF + SiO_2 \rightarrow SiF_4 + H_2O \rightarrow$$
$$\rightarrow SiF_4 \cdot 2\,H_2O + H_3OSiF_5 + (H_3O)_2SiF_6$$

Это может быть учтено в качестве химической основы при моделировании самоорганизационных природных процессов, согласно данным работ [7, 8]. Кристаллические супрамолекулярные соединения (I, II) стабильны и могут представлять интерес в качестве контейнеров [7] фторокомплексных кислот кремния.

Кристаллические супрамолекулярные комплексы (I, II). Раствор 0.25 ммоля 1,4,7,10,13,16-гексаоксациклооктадекана или *цис-син-цис*-пергидродибензо[*b*,*k*][1,4,7,13,16]гексаоксациклооктадецина в 15 мл 45%-ной фтороводородной кислоты помещали в стеклянный эксикатор над серной ки-

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слотой. После полного испарения растворителей с количественным выходом получали кристаллы комплексов (I, II).

Комплекс дигидрата 1,4,7,10,13,16-гексаоксациклооктадекана с *транс*-диакватетрафторсиликатом кремния, 2:1:2 (I), т. пл. 92–93°C (литературные данные [9]: т. пл 91–92°C). ИК спектр, ν, $см^{-1}$: 3430 (HO), 1145–1095 (COC), 775, 702 (SiF). Найдено, %: C 32.85; H 7.47; F 17.60; Si 6.45. $C_{12}H_{32}F_4O_{10}Si$. Вычислено, %: C 32.72; H 7.32; F 17.25; Si 6.38.

Комплекс *цис-син-цис*-пергидродибензо[*b,k*]-[1,4,7,10,13,16]гексаоксациклооктадецина с пентафторсиликатом гидроксония, 1:1 (II), т. пл. 101–103°C. ИК спектр, ν, $см^{-1}$: 3600–3500, 1650 (H_3O^+), 1165–1000 (COC), 875, 785 (SiF). Найдено, %: C 46.73; H 7.61; F 18.52; Si 5.55. $C_{20}H_{39}F_5O_7Si$. Вычислено, %: C 46.67; H 7.64; F 18.46; Si 5.46.

ИК спектры регистрировали на приборе Specord M-80 в вазелиновом масле, стекла KRS-5.

Работа финансировалась в рамках проекта NCS 94-2811-M-032.

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Додаток 46.

Копія доповіді Molecular Complexes of Homologous Alkanedicarboxylic Acids and D-Tartaric acid with Isoniazid


23rd European Crystallographic Meeting
6-11 August 2006
Leuven, Belgium
ecm
Leuven 2006
ABSTRACTS

m26.p12

Synthesis and Crystal Structure of Layered Zinc Phosphates: Accurate Hydrogen bonding in $(NH_4)Zn_2(PO_4)(HPO_4)$.

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Keywords: H-bonding, phosphates, intercalation

In the family of metal phosphates, zinc phosphates occupy a relevant position. The design and synthesis of these structures have become the focus of much interest due to their vast structural and compositional diversities. The crystal structure of a new layered ammonium zinc phosphate, $(NH_4)Zn_2(PO_4)(HPO_4)$, has been reported by Bircsak and Harrison in 1998, obtained as a sub-product from hydrothermal synthesis. Recently, $(NH_4)Zn_2(PO_4)(HPO_4)$ has been synthesized from hydrothermal conditions as a unique product in the system H_3PO_4-$(NH_2)CO$-$ZnCl_2$-H_2O and the hydrogen atoms positions have been determined by X-ray single crystal diffraction, allowing us to accurately determine the hydrogen bonding network. The chemical and structural features of this material make it potentially interesting in fields such proton conduction, ion exchange and intercalation. It is especially interesting to highlight the reaction of $(NH_4)Zn_2(PO_4)(HPO_4)$ when placed in an ammonia vapor atmosphere at room temperature. Ammonia molecules are inserted into the interlayer space and a new layered zinc phosphate is formed containing $N_2H_7^+$ units beetwen the layers. Although several ammonium ions with varying degrees of clustering can be described in the gas phase, at the moment, only a crystalline stable compound containing this unit-type has been partially resolved, N_2H_7I.

m26.p13

Molecular Complexes of Homologous Alkanedicarboxylic Acids and D-Tartaric acid with Isoniazid

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Keywords: crystal engineering, molecular complexes, pharmaceutical compounds

Concepts of *crystal engineering* and *supramolecular synthons* represent a new paradigm toward the design of novel pharmaceutical multiple component crystalline phases with desired composition, physical and mechanical properties [1]. Supramolecular synthesis may be explored to obtain novel and improved pharmaceuticals from known active pharmaceutical ingredients and pharmaceutically accessible additives [2]. The directional nature of hydrogen bonds is the master key today in the desirable self-assembly of molecules in the solid state. Carboxylic acid-pyridine synthon has emerged as a reliable tool in design of molecular complexes of homologous alkanedicarboxylic acids with isonicatine amide [3]. We have utilize this approach as recurring design strategy in supramolecular synthesis of composition of pharmaceutical phases involving isoniazid. Isoniazid or isonicotinic acid hydrazide (**INH**) is used as a first-line treatment for tuberculosis, in combination with other drugs for the treatment of active disease and also used for prevention of tuberculosis in people who have been exposed to active disease. The supramolecular reaction of **INH** with dicarboxylic acids resulted in both genuine co-crystals and organic salts depending on the nature of the dicarboxylic acid. As the some of the used dicarboxylic acid are pharmaceutically acceptable additives this result may be considered novel potential pharmaceutical phases. X-ray diffraction study of five representatives of this supramolecular system reveals that crystallization isoniazid with adipic, succinic and malonic acids is carried out in co-crystals of 2:1 stoichiometry, while the crystalisation of **INH** with oxalic or D-tartaric acids is resulted in organic salts of 1:1 stoichiometry. In the structure of co-crystals adipic and succinic acids reside inversion center and malonic acid sits on the two-fold rotation axis and invariably form acid - pyridine O-H···N hydrogen bond synthons with two neighboring **INH** molecules. In the case of malonic acid these hydrogen bonds are very hard (O···N=2.527Å, O-H=1.217Å, H···N=1.316Å and O-H ...N=171.81deg) and hydrogen atom weakly connected with acid and closely approach to aromatic nitrogen of isaniazid. In the structure of organic salt of oxalic acid the **INH** molecule is twice protonated on aromatic nitrogen and terminal amino-group and alternate in the charge assisted N-H···O-bonded zigzag chain with oxalate di-anion. The aromatic nitrogen-oxalate and secondary amino-group-oxalate NH···O bonds equal 2.527 and 2.683 Å, respectively. Carboxylic acid-pyridine synthon has not been found in the structure of organic salt of D-Tartaric acid with **INH**. Bifurcated NH···O and NH···N bonds unite monoprotonated on aromatic moieties **INH** in head-to-tail fashion into the chain.

This study is supported by MRDA(Moldova) - CRDF(U.S.) award No. MRDA-008:BGP-III, MOC2-3063-CS-03.

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Додаток 47.

Копія доповіді Folded and extended conformation of N,N'-dibenzyl-4,13-diaza-18-crown-6 (DD18C6) in its complexes: structural approach

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ABSTRACTS

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Folded and Extended Conformation of N,N'-dibenzyl-4,13-diaza-18-crown-6 (DD18C6) in its Complexes: Structural Approach

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The nitrogen-pivot, N,N'-dibenzyl-4,13-diaza-18-crown-6 (DD18C6) lariat ether is a very perspective complexing agent both for the charged and neutral species due to: involvement of the macrocyclic nitrogen in coordination; possible protonation on N-places; involvement of side arms in interactions due to their π-electron component. Three novel complexes of the compositions: $(H_2DD18C6)\cdot 2BF_4\cdot H_2O$ (I), $DD18C6\cdot 2(4\text{–}O_2NPhSO_2NH_2)$, (II) and $DD18C6\cdot 2(H_2NCS)_2$, (III) were synthesized and studied. In (I) the ($H_2DD18C6$) dication has a folded conformation with two benzyl substituents arranged approximately perpendicular to the macrocyclic ring and methylene hydrogen being involved in CH···π interactions. In (II) and (III) the neutral DD18C6 molecule has an extended conformation similar to DD18C6 pure phase. The H-bond dependent complex organization is discussed in all cases.

Додаток 48.

Копія доповіді Structures and some properties of two new "onium" fluorosilicates, the product of fluorosilicic acid interaction with 12-membered macrocycles

Academy of Sciences of Moldova
Institute of Chemistry
Institute of Applied Physics
State University of Moldova
Institute of Physical Chemistry, Polish Academy of Sciences
Chemical Society of Moldova

The XV-th International Conference

"Physical Methods in Coordination and Supramolecular Chemistry"

The XVII-th Reading in memory of Academician A. Ablov



Book of Abstracts

Chişinău, Moldova, September 27 – October 1, 2006

O4

STRUCTURES AND SOME PROPERTIES OF TWO NEW "ONIUM" FLUOROSILICATES, THE PRODUCTS OF FLUOROSILICIC ACID INTERACTION WITH 12-MEMBERED MACROCYCLES

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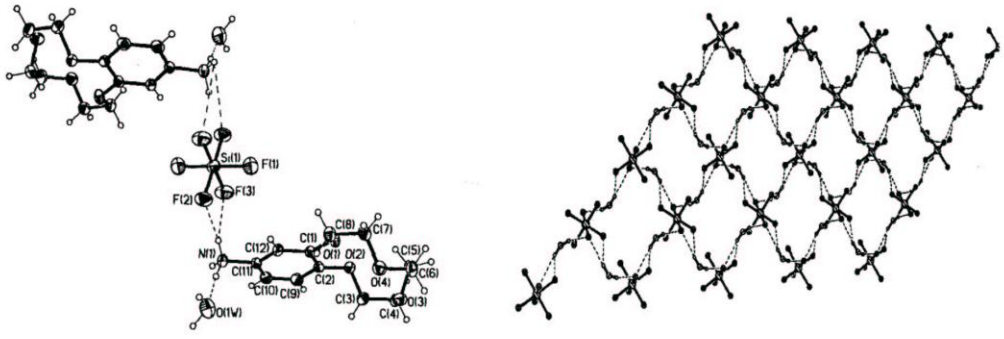
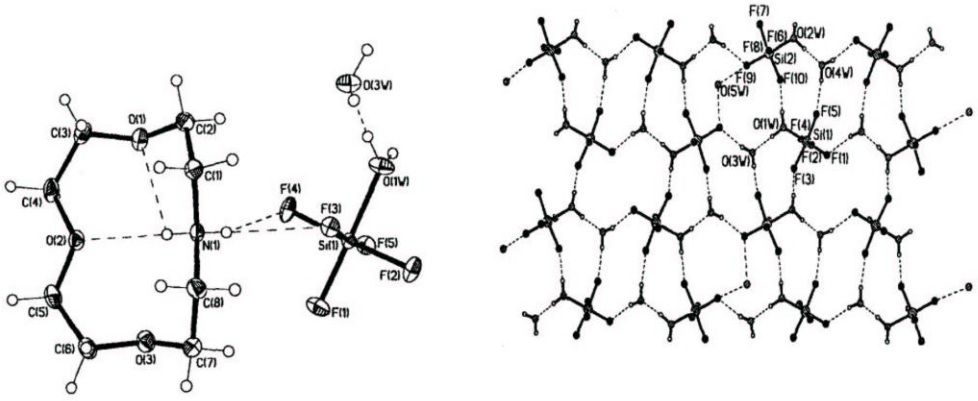
As a part of our systematic investigations of the macrocycles complexation with the fluorosilicic acid (FSA) [1] we have obtained the crystalline products of interaction in the system $H_2SiF_6 - H_2O$ – L, where L – 12-membered 2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecin-12-amine (L^1) and monoaza-12-crown-4 (L^2). The structures of these new compounds with the compositions $(L^1H)_2SiF_6 \cdot 2H_2O$ (**I**) and $(L^2H)[SiF_5(H_2O)] \cdot H_2O$ (**II**) were determined by X-ray analysis. The ionic structure **I** is composed of centrosymmetric SiF_6^{2-} anions (Si–F 1.6588(15) – 1.6719(11) Å), N-protonated cations L^1H^+, and two water molecules, which are bound by a system of H-bonds of NH···F, NH···O and OH···F types (fig. a). The SiF_6^{2-} anions and water molecules are assembled into negative layers via OH···F hydrogen bonds (fig. b). No interactions were registered between O-atoms of crown and H-donor fragments (H_2O, NH_3^+-groups of a symmetry-related cation), and thus **I** is not a "host-guest" (H-G) complex, but a simple arylammonium hexafluorosilicate.

The structure **II** demonstrated a new and quite rare example of stabilization of the complex anion $[SiF_5(H_2O)]^-$, the labile product of hydrolytic transformations of SiF_6^{2-} anion in the H-G complex. The components of **II**, i.e., $[SiF_5(H_2O)]^-$, L^2H^+, and water molecules are linked by a system of H-bonds, NH···F, NH···O, OH···F, OH···O (fig. c). In a way similar to **I**, in **II** the $[SiF_5(H_2O)]^-$ anions and water molecules form negative layers via OH···F and OH···O interactions (fig. d).



a b



c d

In the $[SiF_5(H_2O)]^-$ anion Si–F distances are 1.6424(12) – 1.6979(11) Å, Si–O – 1.8416(15) Å. The shortest Si–F bond (1.6424(12) Å) corresponds to F(2) atom which is not involved in H-bonds. For comparison, the average values of Si–F distances in $[SiF_5(H_2O)]^-$ anion of H-G compounds $(L^3H{\cdot}H_2O)[SiF_5(H_2O)]{\cdot}H_2O$ (L^3 – monoaza-18-crown-6) and $(L^4H_2)[SiF_5(H_2O)]_2$ (L^4 – diaza-18-crown-6) are 1.663 and 1.880 Å correspondingly [2]. The physicochemical characteristics of **I** and **II** will be discussed.

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Додаток 49.

Копія доповіді Novel bibracchial lariat ethers: folder conformation of free and complexed molecule

P27

NOVEL BIBRACCHIAL LARIAT ETHERS: FOLDED CONFORMATION OF FREE AND COMPLEXED MOLECULE

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Bibracchial lariat ethers (BiBLEs) [1] still attract relentless attention as smart macrocyclic ligands with the mixed set of donor-acceptor functions capable to effectively bind either cation or anion (doubly N-protonated dication). In continuation of our previous studies [2] we revealed that condensation of N,N'-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyl)-diacetohydrazide with acetone resulted in a novel BiBLE, **I**. In the triclinic sp. gr. *P*-1 molecule **I** resides on an inversion center with its two planar arms arranged above and below macrocyclic cavity that shield the macrocyclic N,O-atoms from any interactions. *P*-methoxydibenzyl-N,N'-diaza-18C6, **II** transforms in a doubly protonated dication in the reaction with boron trifluoride etherate resulting in the complex $[H_2\text{-}\mathbf{II}](BF_4)_2$ with the side arms again arranged above and below the macrocyclic cavity and two BF_4^- anions held *via* CH···F interactions.

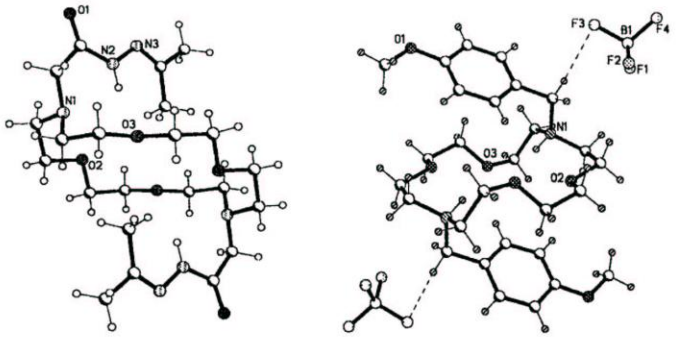

Fig. View of molecule **I** and complex $[H_2\text{-}\mathbf{II}](BF_4)_2$

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Додаток 50.

Копія доповіді Supramolecular isomerism in the system [crown-ether . H3O] MF6 (M = Ta, Nb)

P36

SUPRAMOLECULAR ISOMERISM IN THE SYSTEM [CROWN-ETHER·H_3O]MF_6 (M= Ta, Nb)

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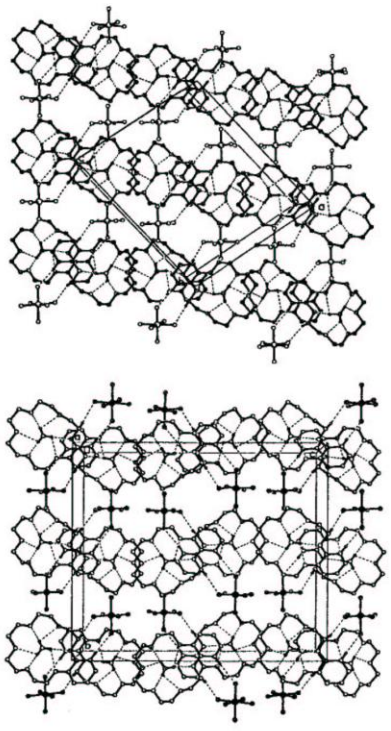
Supramolecular isomerism (SI) in coordination polymers has received increasing interest in recent years for fundamental and applied reasons [1]. The occurrence of SI implies superstructural diversity for a given building block. We report the crystal structures for the systems, [CE(crown-ether)·H_3O]MF_6 (M=Ta, Nb), where CE=benzo-18C6, *cis-syn-cis*-DCH18C6, which afford novel examples of SI. It was stated the influence of the synthetic route on the crystallography of the final product: the interaction of Ta_2O_5 with HF in the presence of corresponding CE results in the monoclinic modifications regardless of CE used ($P2_1/n$ both), while interaction of TaF_5 with CE in the medium of HF results in an orthorhombic isomer for [B18C6·H_3O]TaF_6 (*Pbca*) and triclinic one (*P*-1) for [DCH18C6·H_3O]TaF_6. For these latter complexes the isostructural Nb counterparts were obtained. For [B18C6·H_3O]TaF_6 the distinction between the isomers is dictated by the packing conditions of the quite similar building blocks (fig.), while in [DCH18C6·H_3O]TaF_6 the macrocyclic molecule exhibits strictly different conformations in monoclinic and triclinic modifications [2,3].



Monoclinic and orthorhombic isomers for [B18C6.H_3O]TaF_6

Acknowledgements. This study is supported by Russian Foundation for Basic Research (grant 06-03-90894-Mol_a).

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Додаток 51.

Копія доповіді Molecular complexes of mefenamic acid and tetraazamacrocycles

P38

MOLECULAR COMPLEXES OF MEFENAMIC ACID AND TETRAAZAMACROCYCLES

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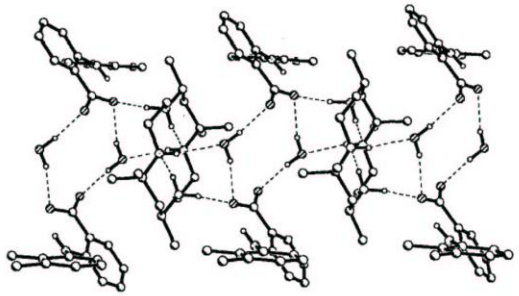
Multicomponent compounds have attracted attention from the pharmaceutical industry in recent years because of the role of carriers as solubilizers and stabilizers for poorly soluble drug molecules. Mefenamic acid, (**MF**) is a non-steroid drug with strong analgetic, antipyretic and anti-inflammatory properties. The very low aqueous solubility of **MF** causes undesirable side effects when administrated orally. These effects can be reduced by increasing the drug solubility *via* complexation with the suitable carrier. Only one such example for **MF** (with β-CD) is known so far[1], which reveals that although the inclusion complex is rather weak, the solubility and stability increase. It encouraged us within our ongoing efforts toward the crystal engineering of new multicomponent pharmaceutical solids to explore supramolecular synthesis for obtaining **MF** complexes with tetraazamacrocycles differing by ring size, but possessing the same number of incorporated nitrogen atoms predisposed for H-bonded interactions. The X-ray structure of two organic salts, $(MF)_2(H_2teta)\cdot 2H_2O$ (I, *P*-1) and $(MF)_2(H_2cyclen)\cdot 2H_2O$ (II, *C*2/*c*), reveals doubly protonated macrocycles. All four nitrogen atoms of the macrocycle are involved in hydrogen bonding with **MF** and water molecules in I and only three of them exclusively with **MF** in II. In I, H-bonding patterns are of the type $R_5^3(8)$, $R_4^4(12)$, $R_5^3(8)$, which combine the components into corrugated chains (fig.); whereas in II, only the $R_4^4(12)$ rings remain, which are shared with $R_4^3(8)$ rings.



Acknowledgements. This study is supported by MRDA(Moldova) – CRDF(U.S.) award No. MRDA-008: BGP-III, MOC2-3063-CS-03

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Додаток 52.

Копія доповіді Crystal structure of para-nintroanilinium hexafluorosilicate

P39

CRYSTAL STRUCTURE OF *para*-NITROANILINIUM HEXAFLUOROSILICATE

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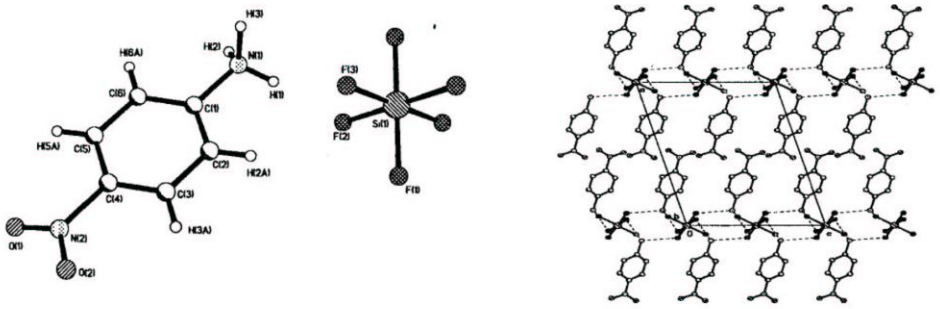
Arylammonium hexafluorosilicates with functionalised cations are convenient models for the investigation of H-bonds influence on the structure and properties of "onium" fluorosilicates. Here we discuss the crystal structure of $(p\text{-}O_2NC_6H_4NH_3)_2SiF_6$ (**I**), the product of hexafluorosilicic acid interaction with *para*-nitroaniline.

The structural units of crystal I are centrosymmetric SiF_6^{2-} anions (Si–F bond lengths are 1.668(3), 1.678(3) Å) and substituted anilinium cations, which are united by H-bonds of NH···F type. The geometric parameters of cation are typical for anilinium derivatives. Each of H-atoms of the cation $p\text{-}O_2NC_6H_4NH_3^+$ forms two or three bifurcated H-bonds, and one component of this (H···F 1.75–2.16, N···F 2.823–2.837 Å, ∠ NHF 151–176°) is much stronger than the others (H···F 2.48–2.60, N···F 3.054–3.205 Å, ∠ NHF 112–149°). In framework structure **I** there are three kinds of layers: one formed by SiF_6^{2-} anions, and two others formed by $p\text{-}O_2NC_6H_4NH_3^+$ cations. Cations from different layers are oriented in "head-to-head" position to each other.



Some interconnections between structural characteristics and thermochemical behaviour of structure **I** will be discussed.

Додаток 53.

Копія доповіді Crystal engineering of pharmaceutical co-crystals using different co-crystal formers and distinct hydrogen bonding sites of the drug molecule

P48

CRYSTAL ENGINEERING OF PHARMACEUTICAL CO-CRYSTALS USING DIFFERENT CO-CRYSTAL FORMERS AND DISTINCT HYDROGEN BONDING SITES OF THE DRUG MOLECULE

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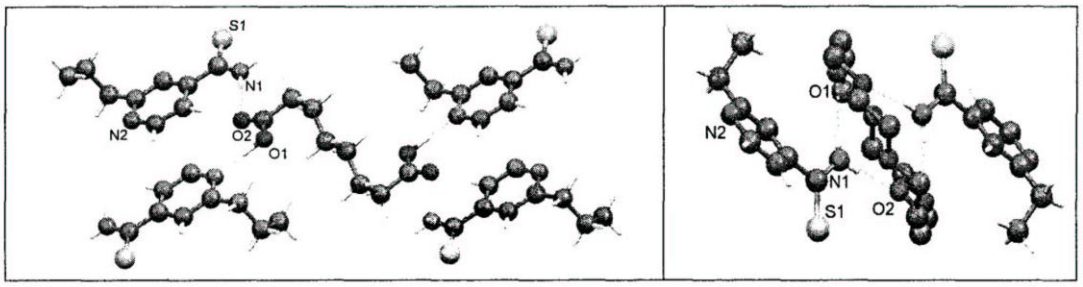
The concept of crystal engineering and supramolecular synthesis has enabled the generation of a diverse range of multicomponent crystalline pharmaceutical solids (i.e. co-crystals), which can improve the performance and functionality of known drugs [1]. The rational design of co-crystals is based on reliable supramolecular synthons and different co-crystal formers for fine-tuning the properties of new compositional matter, which are expected to be different from the pure form of the drug. This methodology is not routine still and understanding of factors which lead to successful or unsuccessful co-crystallization represents the challenge to modern crystal engineering. Two anti-tubercular drugs, 2-Ethyl- and 2-Propyl-4-thiocarbamoylpyridine were employed in two parallel series of co-crystallizations with homologous alkanedicarboxylic acids ($COOH-(CH_2)_n-COOH$, n=0-7) and 18-membered crown ethers. Co-crystals having 2:1 drug:co-crystal former stoichiometry have been obtained with adipic and suberic acids (n-4, 6) and 18-crown-6 and B isomer of DCH-18-crown-6. No co-crystals were isolated with other dicarboxylic acids. In the co-crystals, the dicarboxylic acid invariably interacts with both nitrogen atoms of drug molecules *via* O-H…N and N-H…O hydrogen bonds, resulting in the similar H-bonds pattern regardless of S-shape or linear conformation of dicarboxylic acid. Only the amino group of the drug participates in H-bonding with the crown ether, whereas the best acceptor of the drug (i.e. aromatic N) doesn't form any strong H-bond. The crown ether breaks the reliable homosynthon of thioamide group, which was found in co-crystals with dicarboxylic acids.



Acknowledgements. This study is supported by MRDA–CRDF award: MRDA-008: BGP-III, MOC2-3063-CS-03.

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Додаток 54.

Копія доповіді Crystal engineering of multicomponents pharmaceutical solids involving isonicotinic acid hydrazide and dicarboxilic asids

P49

CRYSTAL ENGINEERING OF MULTICOMPONENT PHARMACEUTICAL SOLIDS INVOLVING ISONICOTINIC ACID HYDRAZIDE AND DICARBOXYLIC ACIDS

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Crystal engineering as application of concept of supramolecular synthesis to generate the multiple-component crystalline phases represents an effective way to modify known active pharmaceutical ingredients and to improve its pharmaceutical profile [1]. Carboxylic acid-pyridine synthon has emerged as a reliable tool in design of molecular complexes of dicarboxylic acids with isonicotine amide [2]. We have utilized this approach as recurring design strategy in supramolecular synthesis of solid state composition of pharmaceutical phases. Isonicotinic acid hydrazide (INH) is used as a first-line treatment for tuberculosis, in combination with other drugs for the treatment of active disease and also used for prevention of tuberculosis in people who have been exposed to active disease. Crystallizations of INH with dicarboxylic acids resulted in six INH:dicarboxylic acid supramolecular systems: 2:1 co-crystals of with malonic, succinic and adipic acids, co-crystals 1:1 with glutaric acid and 1:1 organic salts with oxalic and D-tartaric acids. In co-crystals adipic, succinic and malonic acids invariably form acid – pyridine O-H···N hydrogen bond synthons with two neighboring INH molecules, glutaric acid forms different acid-pyridine and acid-hydrazide syntons. Malonic acid···INH strong O-H···N bonds (O···N=2.527Å, O-H=1.217Å, H···N=1.316Å) demonstrate the case of partial proton transfer. In the structure of INH : oxalic acid the INH molecules are doubly protonated on aromatic nitrogen and terminal aminogroup and alternate in the charge assisted N-H···O-bonded zigzag chain with oxalate di-anions. Acid-pyridine synthon has not been found in the structure of INH : D-Tartaric acid, but bifurcated N-H···O/N-H···N bonds unite protonated on basic nitrogen INH in the chains.

Acknowledgements. This study is supported by MRDA– CRDF award: MRDA-008:BGP-III, MOC2-3063-CS-03.

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Додаток 55.

Копія доповіді The association of p-aminobenzoic acid in the complex with azamacrocycles

3rd INTERNATIONAL CONFERENCE ON MATERIALS SCIENCE AND CONDENSED MATTER PHYSICS

Dedicated to the 85th and 80th anniversaries of outstanding Moldovan physicists Tadeusz Malinowski and Sergey Radautsan in the year of the 60th jubilee of the Academy of Sciences of Moldova

ABSTRACTS

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CHISINAU 2006

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THE ASSOCIATION OF *p*-AMINOBENZOIC ACID IN THE COMPLEXES WITH AZAMACROCYCLES

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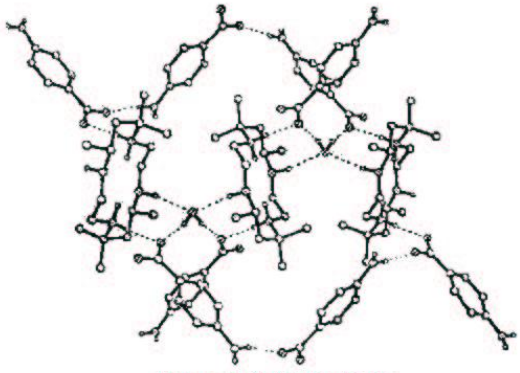
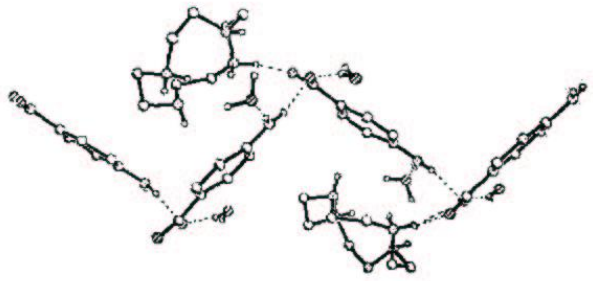
In the last decade we have witnessed an increased interest in the synthesis of co-crystals involving active pharmaceutical ingredients (API), with the aim to produce valuable new materials with improved solubility, dissolution rate, stability and bioavailability.[1] Crystal engineering and supramolecular synthesis are being widely explored to obtain new crystalline pharmaceutical formulations from known APIs and a benign additive used as a co-crystal former (CCF). Carboxylic and dicarboxylic acids have emerged as the leading candidates among CCFs used for this purpose. However, an increasing desire to develop a wider library of CCFs for fine tuning crystalline drug properties has motivated the search for new CCFs, capable of forming multiple-component pharmaceutical solids with APIs, namely, co-crystal, organic salts and their hydrates.

As part of our ongoing efforts toward the crystal engineering of new multicomponent pharmaceutical solids, we carried out the systematic investigation of the interaction of *p*-aminobenzoic acid (PABA) with azamacrocycles having different ring sizes (12, 14, 18 atoms in the ring) and a variable number of incorporated nitrogen atoms (n=1-4), which are predisposed to interactions with a carboxylic acid. PABA is an important biological molecule, being an essential bacterial growth factor involved in the synthesis of pteroylglutamic acid (folic acid), which has been shown to form *in vitro* in the presence of ATP and Mg^{2+}. In another unrelated application, PABA and its ether are used as sunscreen agents. As such, PABA is one of the most interesting small molecules for use in syntheses based on hydrogen bonding interactions with a variety of organic acids and bases. Furthermore, due to the presence of two favorably arranged functional groups, PABA can generate advantageous hydrogen-bonded arrays.

Crystallographic studies of four novel supramolecular multicomponent complexes with the compositions $(H_2teta)\cdot(PABA)_2\cdot H_2O$, $(H_2cyclen)\cdot(PABA)_2\cdot 2H_2O$, $(H\text{-}aza\text{-}18C6)\cdot(PABA)\cdot 3H_2O$, $(H_2\text{-}diaza\text{-}12C4)\cdot(PABA)_2\cdot 2H_2O$, reveal that they are all organic salts formed due to proton transfer from the carboxylic acid group of PABA to the amino group of the macrocycle, and thus are comprised of a PABA anion, a macrocyclic mono- or dication and a variable number of water molecules. In all complexes, the cations and anions are associated via $NH^+\cdots O^-$ charge-assisted hydrogen bonds, while the PABA anions self-assemble into helical chains due to interactions between their primary amino and carboxylate functionalities. Water molecules add diversity into the supramolecular architecture and offer promise in regards to fine tuning bulk solubility.



$(H_2teta)\,(PABA)_2\cdot H_2O$



$(H_2cyclen)\,(PABA)_2\cdot 2H_2O$

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Додаток 56

Копія статті Hierarchy of hydrogen bonding in bis(1,4,7-trioxa-10-azoniacyclodo-decane)bis(4-aminobenzoate) trihydrate

organic compounds

Acta Crystallographica Section C
Crystal Structure Communications
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Hierarchy of hydrogen bonding in bis(1,4,7-trioxa-10-azoniacyclododecane) bis(4-aminobenzoate) trihydrate

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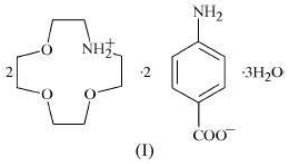
In the title compound, $2C_8H_{18}NO_3^+\cdot 2C_7H_6NO_2^-\cdot 3H_2O$, proton transfer occurs from the carboxylic acid group of the 4-aminobenzoic acid (PABA) molecule to the amine group of the macrocycle, resulting in the formation of a salt-like adduct. The anions are combined into helical chains which are further bound by the water molecules into sheets. The macrocyclic cations are situated between these layers and are bound to the anions both directly and *via* bridging water molecules. The structure exhibits a diverse system of hydrogen bonding.

Comment

The title compound, (I), was investigated as part of a study of hydrogen bonding in systems containing biologically important molecules and macrocyclic ligands. A search of the Cambridge Structural Database (Version 5.26, plus three 2005 updates; Allen, 2002) revealed a number of 4-aminobenzoic acid (PABA) cocrystals in neutral (Lynch *et al.*, 1992*b*; Lynch & McClenaghan, 2001; Moreno-Fuquen *et al.*, 2003), cationic (protonated on the amino group; Benali-Cherif *et al.*, 2002; Lynch *et al.*, 1992*a*) and anionic forms (deprotonated on the carboxylic acid group; Smith *et al.*, 1999). Only three examples are known so far for PABA cocrystals with O-containing crown ethers, *viz.* with 18-crown-6 (Elbasyouny *et al.*, 1983) and with two *cis* isomers of dicyclohexyl-18-crown-6 (Fonari *et al.*, 1994), which revealed that both complexes are adducts with a 1:2 stoichiometry, with the amino group of PABA responsible for the N—H···O(crown) hydrogen bonds. A robust dimeric carboxyl $R_2^2(8)$ homosynthon (Desiraju, 1995) was responsible for the PABA molecules associating into dimers. We report here the first example, (I), of a PABA cocrystal with the mixed N,O-macrocycle 1,4,7-trioxa-10-azacyclododecane.

Compound (I) is a salt-like adduct due to protonation of the macrocycle by PABA molecules. The asymmetric unit contains two tightly held cation–anion pairs, designated as *A* and *B*, and three water molecules (Fig. 1). Molecular dimensions are unexceptional.



(I)

The macrocyclic cations have an *exo–endo* orientation of the $>NH_2^+$ ammonium functionality, with one H atom involved in an intramolecular bifurcated N—H···O hydrogen bond inside the macrocycle and the second H atom involved in intermolecular hydrogen bonding with the PABA anions. The macrocycles have slightly different conformations and shapes, the heteroatoms being coplanar to within 0.39 Å in macrocycle *A* and 0.14 Å in macrocycle *B*. The mutual arrangement in the cation–anion units is described by the dihedral angle between the planes through the planar PABA skeleton and through four heteroatoms of the macrocycle, with a value of 48.9 (1)° in unit *A* and 62.9 (1)° in unit *B*.

In the *A* and *B* cation–anion units, the components are held together through a pair of N—H($>NH_2^+$)···O(COO^-) and C—H···O(COO^-) hydrogen bonds (Table 1). The N—H···O hydrogen bonds, with N2···O2 separations of 2.697 (2) and 2.735 (2) Å in units *A* and *B*, respectively, are the shortest of all those that sustain the structure. Each carboxylate group acts in a chelate mode *via* an $R_2^2(8)$ ring. This heterosynthon substitutes the planar robust centrosymmetric $R_2^2(8)$ homosynthon typical for two carboxyl groups. The environments of the macrocyclic cations are different in this structure, and whilst cation *A* does not have any direct contacts with water molecules, water molecule O1*W* interacts with cation *B* as a single H-atom donor and a single H-atom acceptor.

Although the mode of cation–anion interaction is similar in the *A* and *B* units, the structural functions of the *A* and *B* PABA anions are quite different in the supramolecular structure organization. PABA *A* anions are linked *via* N—

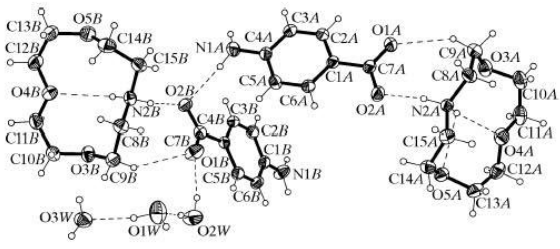


Figure 1
The asymmetric unit of (I), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and hydrogen bonds are indicated by dashed lines.

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H···O hydrogen bonds to form a $C(8)$ helical chain running parallel to the [010] direction (Fig. 2). Each PABA *B* anion, acting as a single H-atom donor and a single H-atom acceptor, links a pair of PABA *A* anions separated by translation along the same direction, thus forming the outer surface of the helix. Propagation of these four hydrogen bonds generates a chain of fused $R_4^4(22)$ rings. Water molecule O3*W* acts as a double hydrogen-bond donor to atom O1*A* at $(x, y, z+1)$ and atom O2*B* at $(-x, y+\frac{1}{2}, -z+1)$, thus generating a second type of ring, *viz.* $R_4^2(8)$, to stabilize the helix further (Fig. 2). Water molecule O2*W* acts as a single donor towards atom O1*B* at $(-x, y+\frac{1}{2}, -z+1)$ and as a single acceptor towards atom N2*B* at $(-x, y-\frac{1}{2}, -z+1)$, combining two neighbouring helices into an anionic sheet *via* $R_6^6(26)$ fused rings (Fig. 2).

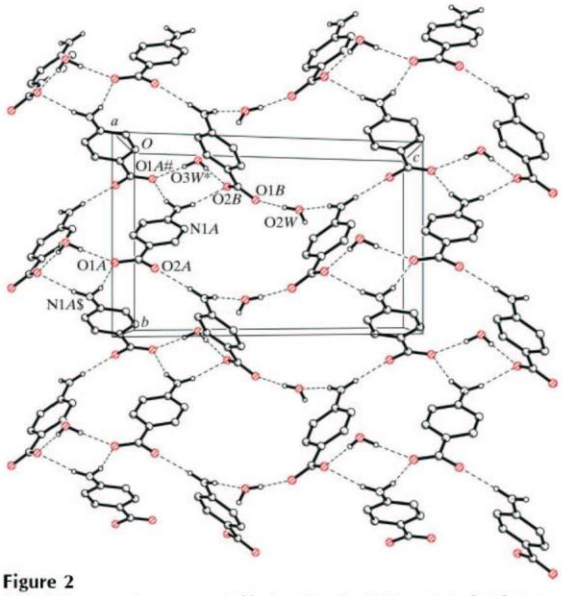

Figure 2
Part of the crystal structure of (I), showing the linking of the [010] chains by the water molecules. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(-x, y-\frac{1}{2}, -z+1)$, $(-x, y-\frac{1}{2}, -z)$ and $(-x, y+\frac{1}{2}, -z)$, respectively.

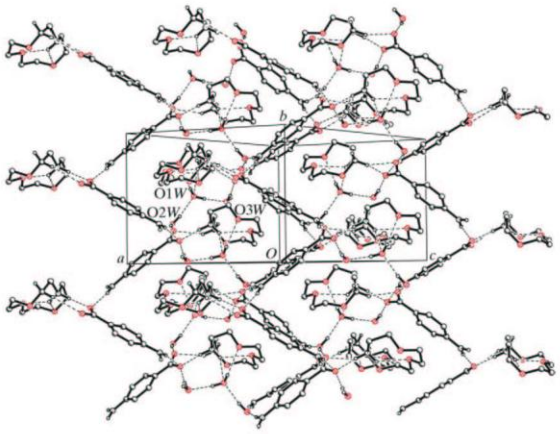

Figure 3
Part of the crystal structure of (I), showing the linking of the sheets by the cations. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Dashed lines indicate hydrogen bonds.

The anionic sheets are linked into a continuous framework by the cations and the water molecules, which play a vital role in the association of the cationic and anionic components into a three-dimensional network. Three water molecules themselves formulate a three-membered water cluster, *viz.* O3*W*···O1*W*···O2*W*, with O···O separations of 2.736 (3) and 2.846 (3) Å, whose terminal members contact with PABA anions, while the bridging O1*W* water molecule is associated with the *B* macrocyclic cation *via* O1*W*···O5*B* and N1*B*···O1*W* hydrogen bonds (Table 1). Thus, the incorporation of the macrocyclic cations between the anionic sheets occurs *via* direct cation–anion contacts (for *A* and *B* pairs) and *via* a mediating water molecule for the macrocyclic *B* cation (Fig. 3).

Experimental

To obtain complex (I), 1,4,7-trioxa-10-azacyclododecane (175 mg, 0.1 mmol) and PABA (137 mg, 1 mmol) were dissolved in a water–methanol (6 ml, 1:5 *v*/*v*) mixture at 337 K. The reaction mixture was then allowed to stand until crystals were deposited. These were filtered off and recrystallized from a mixture of methanol (2 ml), butanol (1 ml), ethyl acetate (2 ml) and heptane (2 ml) to give yellow crystals of (I) (m.p. 387–388 K). Analysis calculated for $C_{30}H_{54}N_4O_{13}$: C 53.08, H 8.02, N 8.25%; found: C 53.02, H 8.09, N 8.30%. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.48 (*m*, 32H, CH_2N, CH_2O, aza-12-crown-4), 7.11 (*m*, 8H, CH, Ph).

Crystal data

$2C_8H_{18}NO_3^+\cdot 2C_7H_6NO_2^-\cdot 3H_2O$
M_r = 678.77
Monoclinic, $P2_1$
a = 12.541 (3) Å
b = 9.5315 (19) Å
c = 15.989 (3) Å
β = 110.91 (3)°
V = 1785.4 (7) Å^3
Z = 2
D_x = 1.263 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5927 reflections
θ = 1.4–24.2°
μ = 0.10 mm^{-1}
T = 293 (2) K
Prism, yellow
0.29 × 0.23 × 0.21 mm

Data collection

Bruker SMART CCD diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical using intensity measurements (*SADABS*; Sheldrick, 1996)
T_{min} = 0.745, T_{max} = 1.000
17540 measured reflections
3714 independent reflections
2856 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 26.0°
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.062
S = 1.00
3714 reflections
480 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}

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Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1···O2B	0.89 (2)	2.14 (2)	3.015 (3)	168 (2)
N1A—H2···O1A^{i}	0.88 (2)	2.18 (2)	3.024 (3)	159 (2)
N2A—H3···O2A	0.94 (2)	1.77 (2)	2.697 (2)	170 (2)
N2A—H4···O4A	0.92 (2)	2.09 (2)	2.847 (2)	139 (2)
N2A—H4···O5A	0.92 (2)	2.45 (2)	2.839 (2)	106 (1)
C9A—H9A···O1A	0.97	2.46	3.305 (3)	146
N1B—H5···O2A^{ii}	0.90 (2)	2.12 (2)	3.011 (3)	169 (2)
N1B—H6···O2W^{iii}	0.90 (2)	2.18 (2)	3.065 (3)	167 (2)
N2B—H7···O4B	0.91 (2)	2.46 (2)	3.126 (2)	131 (2)
N2B—H7···O1W^{iv}	0.91 (2)	2.55 (2)	3.183 (3)	127 (2)
N2B—H8···O2B	0.94 (2)	1.80 (2)	2.735 (2)	170 (2)
N2B—H8···O1B	0.94 (2)	2.60 (2)	3.324 (3)	134 (2)
C9B—H9C···O1B	0.97	2.48	3.280 (3)	140
O1W—H11W···O5B^{v}	0.92 (2)	2.20 (3)	2.943 (3)	138 (4)
O1W—H12W···O3W	0.93 (2)	1.83 (2)	2.736 (3)	166 (4)
O2W—H21W···O1B	0.86 (2)	1.92 (2)	2.770 (3)	167 (3)
O2W—H22W···O1W	0.88 (2)	1.98 (3)	2.846 (3)	171 (3)
O3W—H31W···O2B^{v}	0.84 (2)	1.92 (2)	2.751 (3)	170 (3)
O3W—H32W···O1A^{vi}	0.83 (2)	1.94 (2)	2.770 (3)	173 (3)

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z$; (ii) $x, y-1, z$; (iii) $-x+1, y-\frac{1}{2}, -z+1$; (iv) $-x, y-\frac{1}{2}, -z+1$; (v) $-x, y+\frac{1}{2}, -z+1$; (vi) $x, y, z+1$.

C-bound H atoms were placed in calculated positions, with C H distances of 0.93 or 0.97 Å, and were treated using a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C). N-bound and water H atoms were located in a difference Fourier map and were then allowed to refine isotropically, subject to similarity restraints for N H and O H distances in amino groups, ammonia groups and water molecules, and with an angular H O H restraint for the O2W molecule (H···H = 1.46 Å), as well as a floating origin restraint. In the absence of species heavier than oxygen, no significant anomalous dispersion was observed. Friedel pairs were therefore merged.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3002). Services for accessing these data are described at the back of the journal.

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Додаток 57

Копія статті cis-anti-cis-Dicyclohexyl-18-crown-6-thiacetazone-methanol (1/2/2)

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

cis-anti-cis-Dicyclohexyl-18-crown-6–thiacetazone–methanol (1/2/2)

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In the title compound [systematic name: 2,5,8,15,18,21-tricyclo[20.4.0.0^{9,14}]hexacosane–4-acetylaminobenzaldehyde thiosemicarbazone–methanol (1/2/2)], $C_{20}H_{36}O_6{\cdot}2C_{10}H_{12}N_4OS{\cdot}2CH_3OH$, the *cis-anti-cis*-dicyclohexyl-18-crown-6 molecule resides on an inversion center, and two thiacetazone molecules are linked to the macrocycle *via* N—H···O hydrogen bonds of the terminal amino group [N···O = 3.017 (2) and 3.092 (2) Å]. These units are further associated into chains *via* bridging methanol molecules acting both as an H-atom donor [*via* an O—H···S contact, with O···S = 3.182 (3) Å] and as an H-atom acceptor [*via* an N—H···O contact, with N···O = 2.848 (3) Å].

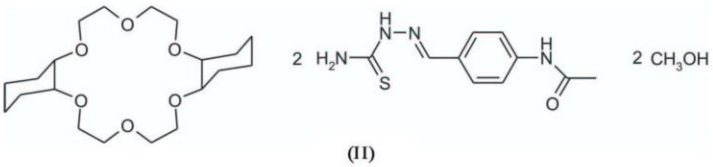
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.123
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In continuation of our earlier research devoted to the interaction of macrocyclic ligands with drug molecules, we studied the system that includes the 18-membered classic crown ether, *cis-anti-cis*-dicyclohexyl-18-crown-6 (DCH6B) and the antimicrobial drug thiacetazone, (I). The aim of our study was to elucidate the mode of interaction of the drug molecule with the macrocycle and to compare the crystal packing of the complex with the crystal packing of the pure drug form. Previously we have shown that the primary amino group of streptocide (Dvorkin *et al.*, 1989), diacarb (Fonari *et al.*, 1989), hypothiazide (Dvorkin *et al.*, 1990) and 4-aminobenzoic acid (Fonari *et al.*, 1994) always interacts with the classic 18-membered crown ethers *via* a pair of N—H···O hydrogen bonds. The mode of mutual interaction is more predictable in the case of DCH6B, as its geometry is predisposed to the generation of an inversion center within the molecule and an equal-face coordination. This is not always the case for 18-crown-6, which, for example, in the complex with hypothiazide (Dvorkin *et al.*, 1990) reveals C_1 symmetry and different-face coordination of the drug molecule.



(II)

The structure of thiacetazone, (I), itself has been reported previously [Karlsen *et al.*, 1988; refcode GANGEH in the Cambridge Structural Database (Version 5.26, plus three 2005 updates; Allen, 2002)]. In (I), the self-assembly of the molecules occurs *via* a diverse system of hydrogen bonding; the

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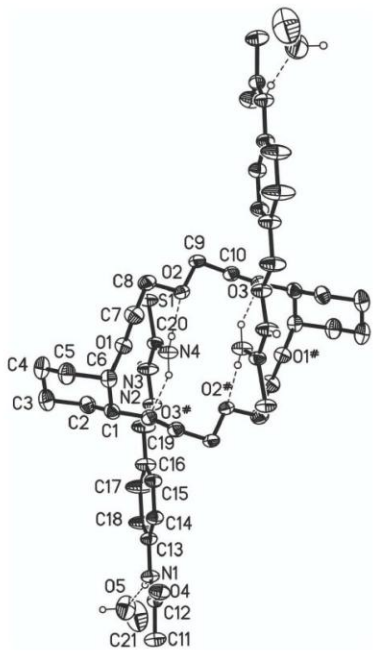

Figure 1
A view of the molecular structure of (II), showing the atomic labeling scheme and displacement ellipsoids drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines. Atoms marked with a hash (#) are in the symmetry position $(2-x, 2-y, 1-z)$ [C-bound H atoms have been omitted for clarity].

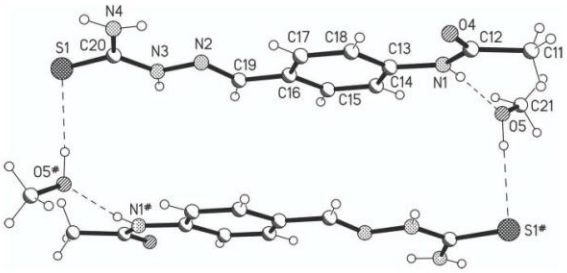

Figure 2
The centrosymmetric heterotetramer in the structure of compound (II), sustained by N—H···O and O—H···S hydrogen bonds (dashed lines). Atoms marked with a hash (#) are in the symmetry position $(2-x, 2-y, 1-z)$.

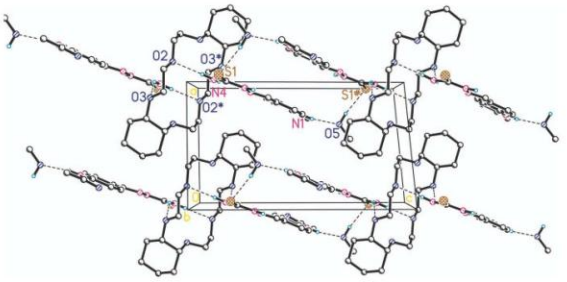

Figure 3
The crystal packing of the chains in compound (II) viewed along the *b* axis. Atoms marked with an asterisk (*) and a hash (#) are at the symmetry positions $(2-x, 2-y, -z)$ and $(2-x, 2-y, 1-z)$, respectively [C-bound H atoms have been omitted for clarity].

molecules form the centrosymmetric dimer *via* a pair of N—H···O hydrogen bonds with the participation of the NH group of the thiourea fragment and an $R_2^2(22)$ ring is generated. These dimers are further associated into chains, again *via* N—H···O hydrogen bonds, with the participation of the terminal amino groups; $R_2^2(26)$ rings are generated. These chains are combined into layers *via* typical thiosemicarbazone centrosymmetric planar $R_2^2(8)$ synthons, based on two N—H···S hydrogen bonds. In the title compound, (II), a complete rearrangement of the hydrogen bonds occurs.

The structure of (II) is shown in Fig. 1, and selected geometric parameters are given in Table 1. The crown ether lies on an inversion center. The geometry of all the molecules forming the complex is in reasonable agreement with the precise data obtained for crown ethers and for (I) (Karlsen *et al.*, 1988). The thiacetazone molecule adopts an almost planar conformation, all the non-H atoms being coplanar within ±0.079 Å. The macrocycle in (II) adopts a C_i symmetric conformation with the O atoms coplanar within ±0.15 Å. The torsion angles of the DCH6B ring are given in Table 1. The dihedral angle between the least-squares planes through all the crown O atoms and the thiacetazone molecular skeleton is 89.70 (4)°. In the 1:2 centrosymmetric unit DCH6B–thiacetazone, the components are held together *via* two pairs of N—H···O hydrogen bonds involving the primary amino group, with atom N4 displaced by 2.057 (2) Å from the least-squares plane of the DCH6B O atoms. The NH H atom of the thiourea group is blocked by the methanol molecule *via* a N—H···O hydrogen bond.

Two symmetry-related thiacetazone and methanol molecules form a centrosymmetric tetramer *via* a pair of N—H···O and a pair of O—H···S hydrogen bonds (Fig. 2). Thus, the methanol molecule acts as a single donor and a single acceptor, and an approximate regular rectangle is formed with the short axis between the planar fragments equal to 3.53 Å, and a long axis of *ca* 12.1 Å. The alternation of these tetramers and macrocyclic molecules forms corrugated chains packing along [100] in the unit cell (Fig. 3).

In conclusion, we underline again the complete rearrangement of the hydrogen bonding in complex (II) compared with that in the crystal structure of the pure drug, compound (I); neither of the supramolecular synthons remains in the ternary complex, (II), discussed above.

Experimental

A solution of DCH6B (0.372 g, 1 mmol) and thiacetazone (0.236 g, 1 mmol) in methanol (25 ml), and ethyl acetate (25 ml), was stored for 3–4 d at 293–298 K in an open flask. Colorless transparent crystals of (II) separated out in a yield of 81% (0.370 g). Compound (II) is soluble in methanol, ethanol and acetone [m.p. > 513 K (decom-

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position)]. ^{1}NMR (DMSO-d6, 300 MHz): 2.04 (*s*, 6H, CH_3-thiacetazone), 1.22 1.71 (*m*) and 3.55 (*m*, 36H, B-isomer DCH-6), 7.58 (*d*) and 7.69 (*d*, 8H, CH-thiacetazone), 7.97, 10.05 and 11.31 (*s*, 8H, HN). Analysis calculated for $C_{42}H_{68}N_8O_{10}S_2$: C 55.48, H 7.54, N 12.33, S 7.05%; found: C 55.53, H 7.51, N 12.37, S 7.09%.

Crystal data

$C_{20}H_{36}O_6{\cdot}2C_{10}H_{12}N_4OS{\cdot}2CH_4O$
M_r = 909.16
Triclinic, $P\overline{1}$
a = 9.6712 (18) Å
b = 9.9236 (18) Å
c = 14.849 (4) Å
α = 93.17 (3)°
β = 91.38 (2)°
γ = 118.649 (7)°
V = 1246.7 (5) Å^3
Z = 1
D_x = 1.211 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 4.4–12.5°
μ = 0.17 mm^{-1}
T = 153 (2) K
Prism, colorless
0.42 × 0.26 × 0.20 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
T_{min} = 0.928, T_{max} = 0.967
4658 measured reflections
4371 independent reflections
3488 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 25.0°
$h = 1 \rightarrow 11$
$k = 11 \rightarrow 10$
$l = 17 \rightarrow 17$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.123
S = 1.03
4371 reflections
302 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.2974P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C20	1.7034 (18)	C11—C12	1.509 (3)
O4—C12	1.214 (2)	C13—C18	1.384 (3)
O5—C21	1.310 (4)	C13—C14	1.386 (3)
N1—C12	1.358 (2)	C14—C15	1.380 (3)
N1—C13	1.409 (2)	C15—C16	1.387 (3)
N2—C19	1.262 (3)	C16—C17	1.388 (3)
N2—N3	1.384 (2)	C16—C19	1.464 (3)
N3—C20	1.339 (2)	C17—C18	1.376 (3)
N4—C20	1.313 (3)		
C12—N1—C13	128.89 (17)	C14—C13—N1	115.93 (17)
C19—N2—N3	115.99 (17)	C15—C14—C13	120.16 (19)
C20—N3—N2	119.86 (17)	C14—C15—C16	121.4 (2)
O4—C12—N1	123.72 (18)	C15—C16—C17	117.58 (18)
O4—C12—C11	122.43 (18)	C18—C17—C16	121.50 (17)
N1—C12—C11	113.83 (19)	C17—C18—C13	120.34 (16)
C18—C13—C14	118.96 (17)	N2—C19—C16	122.59 (19)
C18—C13—N1	125.11 (17)	N4—C20—N3	117.77 (17)
C1—C6—O1—C7	−160.6 (2)	O2—C9—C10—O3	−65.4 (2)
C6—O1—C7—C8	−177.5 (2)	C9—C10—O3—C1^i	112.0 (2)
O1—C7—C8—O2	−70.1 (2)	C10—O3—C1^i—C6^i	140.9 (2)
C7—C8—O2—C9	−171.5 (2)	O3—C1^i—C6^i—O1^i	96.9 (2)
C8—O2—C9—C10	−177.8 (2)		

Symmetry code: (i) $-x+2, -y+2, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1O···S1^i	0.89 (2)	2.30 (2)	3.182 (3)	174 (4)
N1—H1A···O5	0.85 (2)	2.01 (2)	2.848 (3)	169 (2)
N3—H3A···O4^{ii}	0.84 (2)	2.15 (2)	2.980 (2)	167 (2)
N4—H4A···O3^{iii}	0.86 (3)	2.38 (2)	3.092 (2)	140 (2)
N4—H4B···O2	0.86 (2)	2.16 (2)	3.017 (2)	175 (2)

Symmetry codes: (i) $-x+2, -y+2, -z+1$; (ii) $x, y+1, z$; (iii) $-x+2, -y+2, -z$.

C-bound H atoms were placed in calculated positions, with C H distances of 0.95-1.00 Å, and were treated using a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C) for all H atoms except methyl H atoms, for which U_{iso}(H) = 1.5U_{eq}(C). NH and OH H atoms were located in difference Fourier maps and allowed to refine isotropically, with the O H distance restrained to 0.86 (3) Å.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Копія статті The 1:1 adduct of antimony trifluoride with[1.5]dibenzothia-18-crown-6

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The 1:1 adduct of antimony trifluoride with [1.5]dibenzothia-18-crown-6

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.019
wR factor = 0.045
Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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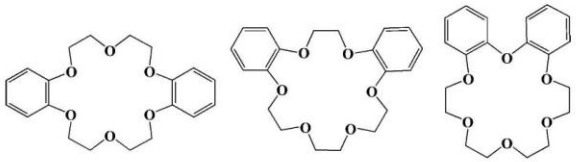
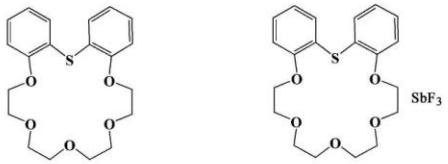
In the title compound [systematic name: 6,7,9,10,12,13,15,16-octahydrodibenzo[n,q][1,4,7,10,13,16]pentaoxathiacyclooctadecine antimony(III) trifluoride clathrate], ($C_{20}H_{24}O_5S$)-SbF_3], the components are held together *via* electrostatic interactions between the antimony lone pair and the collective electron system of the macrocycle. The antimony trifluoride molecule is situated in a perching mode above the macrocyclic cavity, its coordination being completed by three crown ether O atoms at distances in the range 2.737 (1)–3.136 (1) Å. Neighboring 1:1 adducts are linked into chains *via* C—H···F hydrogen bonds.

Comment

For SbF_3 a number of complexes with crown ethers (CEs) have been synthesized and structurally characterized (Schafer *et al.*, 1990; Lipkowski *et al.*, 1996). They are perching complexes, where the neutral components are held together *via* electrostatic interactions between the antimony lone pair, pointed towards the center of the crown ring, and the collective electron system of the macrocyclic O atoms.



(I) (II) (III)



(IV) (V)

The peculiarities of the complex formation between antimony trifluoride and dibenzocrown ethers have not been studied yet. To fill this gap, we have studied the isomers of dibenzo-18-crown-6, (I)–(III), and 18-membered diphenyl sulfide CE, (IV). Under similar synthetic conditions, only crystals of complex (V) were suitable for X-ray examination. We report here the crystal structure of the title complex, (V).

It is known (Wolf *et al.*, 1987) that, when incorporated into a macrocyclic framework, sulfur prefers an exocyclic orientation of its lone pair and does not participate in the metal coordination (Campbell & Dalley, 1981; Campbell, Dalley & Simonsen, 1981; Campbell *et al.*, 1981*a*,*b*).

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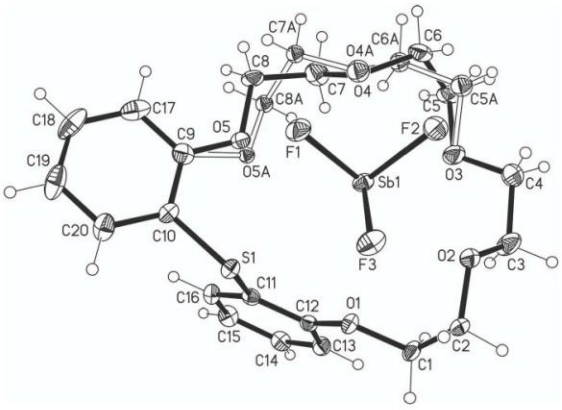

Figure 1
Top view of the title compound, with the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. The minor component of the disordered fragment is shown by open lines.

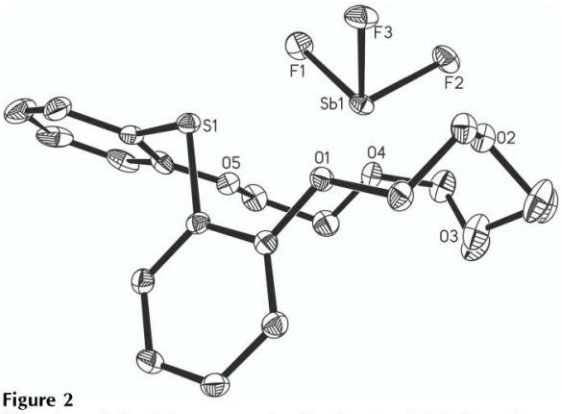

Figure 2
Side view of the title compound, with the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. The minor component of the disordered fragment and C-bound H atoms have been omitted for clarity.

Figs. 1 and 2 show the top and side *ORTEP-3* (Farrugia, 1997) views, respectively, of the title compound. The antimony trifluoride molecule is situated in a perching mode above the macrocyclic cavity and deviates 1.273 (2) Å from the least-square plane through the six (5O + 1S) heteroatoms, which are coplanar within 0.480 Å. The antimony first coordination sphere comprises three covalently bound F atoms at distances of 1.928 (1)–1.942 (1) Å, two CE O atoms, O2 and O4, at approximately equal distances of 2.737 (1) and 2.801 (9) Å, and atom O3 at a distance of 3.136 (1) Å.

The twist angle between the benzene rings in (V) is 85.06 (6)° [for comparison, the same angle is 69.2 (5)° in (III) in its complex with dithiouracil (Ganin *et al.*, 2005) and 87.5 (1)° in molecule (III) itself (Kotlyar *et al.*, 2005)].

Neighboring complexes, *via* C—H···F hydrogen bonds (Table 2), are linked into chains running along the [010] direction (Fig. 3).

Experimental

To a stirred solution of antimony trifluoride (89 mg, 0.5 mmol) in methanol (10 ml) a solution of (IV) (188 mg, 0.5 mmol) in methanol (10 ml) was added at a room temperature. The reaction mixture was allowed to stand until crystals were deposited. Transparent colorless crystals of (V), suitable for X-ray investigation [m.p. 463 K (decomposition)], were obtained by evaporation of a methanol solution. Analysis calculated for $C_{20}H_{24}F_3O_5SSb$: C 39.24, H 3.95, S 5.24%; found: C 39.66, H 4.04, S 5.40%.

Crystal data

$(C_{20}H_{24}O_5S)[SbF_3]$	$Z = 4$
$M_r = 555.20$	$D_x = 1.726$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.598$ (2) Å	$\mu = 1.44$ mm^{-1}
$b = 16.293$ (2) Å	$T = 123$ (2) K
$c = 13.286$ (2) Å	Prism, yellow
$\beta = 111.760$ (9)°	0.15 × 0.12 × 0.10 mm
$V = 2136.32$ (6) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	4190 independent reflections
φ–ω scans	3952 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.026$
16182 measured reflections	$\theta_{max} = 26.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 2.0901P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.046$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.42$ e Å^{-3}
4190 reflections	
296 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Sb1—F2	1.9277 (11)	Sb1—F1	1.9418 (11)
Sb1—F3	1.9299 (11)		
F2—Sb1—F3	88.00 (5)	F3—Sb1—F1	87.01 (5)
F2—Sb1—F1	88.83 (5)	C10—S1—C11	103.83 (8)
O1—C1—C2—O2	−66.91 (18)	O4—C7—C8—O5	−72.4 (6)
C1—C2—O2—C3	−77.18 (19)	C7—C8—O5—C9	−176.7 (3)
C2—O2—C3—C4	176.81 (16)	C8—O5—C9—C10	−170.4 (2)
O2—C3—C4—O3	−70.5 (2)	O5—C9—C10—S1	2.8 (3)
C3—C4—O3—C5	−173.0 (2)	C9—C10—S1—C11	−76.52 (16)
C4—O3—C5—C6	−99.1 (3)	C10—S1—C11—C12	158.81 (14)
O3—C5—C6—O4	−61.7 (6)	S1—C11—C12—O1	−4.0 (2)
C5—C6—O4—C7	−63.3 (9)	C11—C12—O1—C1	−179.65 (15)
C6—O4—C7—C8	−163.8 (6)	C12—O1—C1—C2	160.99 (14)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···F1^{i}	0.99	2.45	3.368 (2)	155
C13—H13A···F1^{i}	0.95	2.40	3.244 (2)	147

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Atoms O4, O5, C5, C6, C7 and C8 are disordered over two positions, with site occupancies of 0.628 (1) and 0.372 (1). The minor

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component was refined in an isotropic approximation. All H atoms were placed in calculated positions, with C—H distances of 0.95 or 0.99 Å, and were treated using a riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT* and *DENZO* (Otwinowski & Minor, 1997); data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr Yu. Simonov for fruitful discussions.

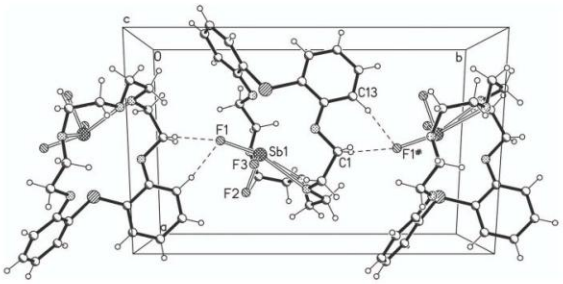

Figure 3
Part of the crystal structure of (V), showing the linking of the complexes into chains *via* C—H···F hydrogen bonds. The F atom marked with a hash (#) is at the symmetry position $(1 - x, y - \frac{1}{2}, -z + \frac{1}{2})$.

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Додаток 59

Копія статті Structure of Dibenzocrown Ethers and Their H-Bonded Adducts. 3. Isolation of Oxonium Ions by Biphenyl-20-crown-6 and [1.5]Dibenzo-18-Crown-6 in Complexes with [NbF6] and [TaF6]

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Structure of Dibenzocrown Ethers and Their H–Bonded Adducts. 3. Isolation of Oxonium Ions by Biphenyl–20–crown–6 and [1.5]Dibenzo–18–Crown–6 in Complexes with $[NbF_6]^-$ and $[TaF_6]^-$

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Abstract

The products of Nb_2O_5 and Ta_2O_5 reaction with an aqueous solution of hydrofluoric acid, HF at the presence of biphenyl–20–crown–6 (BP20C6, L^1) or [1.5]dibenzo–18–crown–6 ([1.5]DB18C6, L^2) are complexes $[L^1 \cdot (H_3O)][NbF_6]$ (**1**), $[L^1 \cdot (H_3O)][TaF_6]$ (**2**), $[2L^2 \cdot (H_7O_3)][NbF_6]$ (**3**) and $[2L^2 \cdot (H_7O_3)][TaF_6]$ (**4**). Complexes **1**–**4** were identified by ultimate analysis, IR spectroscopy and the X-ray structure analysis. According to the last one, complexes **1** and **2** are isostructural, and the H_3O^+ oxonium ion is embedded in one crown molecule *via* OH···O hydrogen bonds, The infrequent complexes **3** and **4** represent the supramolecular isomers distinctive by the crown conformations and crystal packing, where the $(H_7O_3)^+$ cation is enclosed in the cage of two crown molecules. Being poor H–bond acceptors, NbF_6^- and TaF_6^- anions do not compete with the crown oxygen atoms for the oxonium hydrogen atoms, but are involved in the numerous C–H···F short contacts responsible for the expended supramolecular architectures in the all cases. A change of crown ethers' conformation in complexes **1**–**4** and a correlation between the degree of proton hydration and an accessibility of the crown ether oxygen atoms is observed.

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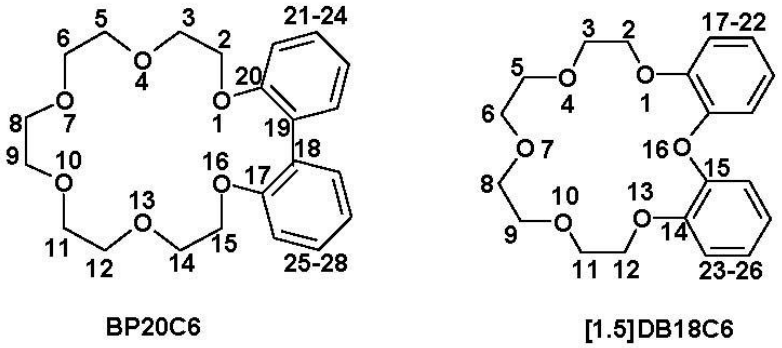
Introduction

An interest to the chemistry of Nb(V) and Ta(V) fluoride complexes is essentially connected with the development of suitable methods of concentration (separation) of these elements, the processes being based on the recrystallization or extraction of the proper complexes from acidic aqueous solutions [1]. So far there is no any data in the literature concerning the structure and properties of the products of Nb(V) and Ta(V) fluorocomplexes interaction with crown ethers in aqueous solutions [2] and a very few structurally studied complexes of Nb(V) and Ta(V) fluorides where they present in the forms of $[NbF_6]^-$ [3,4] and $[TaF_6]^-$ [5,6] monoanions. Meantime taking into account the complexing properties of the crown ethers, such data could be useful from the viewpoint of interaction types modeling in the extraction systems with the participation of neutral oxygen-containing extragents. Available investigations [7] permit to forecast a «fixation» of hydroxonium ion (H_3O^+) by crown ethers in the «extractable» forms of the fluorometallate complexes. Moreover, the results of work [8] indicate that in the series of crown ethers the most effective interaction with the proton donor component is realized in the cases of 18– и 20–membered cyclic polyethers containing six oxygen atoms.

In this work we wish to examine the «host-guest» complexes formed as a result of interaction between the products of Nb_2O_5 and Ta_2O_5 reaction with an aqueous hydrofluoric acid at the presence of biphenyl–20–crown–6 (BP20C6) and [1.5]dibenzo–18–crown–6 ([1.5]DB18C6). Essential structural features of these crown ethers are, on the one hand, a presence of the conformationally rigid biphenyl or diphenyloxide fragments, and, on the other hand, a different ratio of the so-called "aromatic" and "aliphatic" oxygen atoms (2:4 and 3:3, respectively).



Scheme 1. Structural formulas of studied crown ethers (with the atomic numbering).

In the first article in this series [9] we have shown the capability of these two crown ethers to interact with the amidosulfuric acid, H_2NSO_2OH. In the proper 1:1 adducts the amidosulfuric acid molecule in a zwitterion form coordinates to three alternative crown oxygen atoms in a near–ideal "tripod" arrangement *via* NH···O hydrogen bonds, and the conformations of crown molecules are different in the complexes and in the initial macrocyclic ligands. In the next presentation [10] we have revealed that [1.5]DB18C6 forms the H–bonded (*via* $NH\cdots O_{crown}$ and/or $CH\cdots O_{crown}$ hydrogen bonds) supramolecular complexes with 3–nitro–1H–1,2,4–triazole (1:1), 2,4(1H,3H)–pyrimidinedithione (1:1), 1,2,5–oxadiazole–3,4–diamine monohydrate (1:1:1), ethanedithioamide (1:1) and 1,2–hydrazinedicarbothioamide (2:3). In the all cases, during the co–crystals formation, the competition of the O–containing macrocyclic H–acceptor with H–acceptor (O and S) centers in the mentioned neutral molecules results in the substitution of all or part of supramolecular homosynthons by the heterosynthons and as a consequence, in the changing of supramolecular architecture.

Our search of CSD [11] revealed neither complexes of [1.5]DB18C6 and BP20C6 with the cations nor built on the cation–anion type interactions, and only a very few examples of the complexes of the BP20C6 close derivatives with the metal [12] or organic cations [13] which are sustained by the ion–dipole interactions or charge–assisted hydrogen bonds.

A significant amount of works on crown ethers complexes with the hydrated proton (oxonium ions, $H(H_2O)_n^+$, n=1 to ca. 20) [14] has shown that crown ethers act as excellent acceptors for strong, charge–assisted H-bonds with oxonium ions and a choice of the crown ether and a counterion has a decisive influence on the identity of the oxonium ion available in the crystal. The decisive factor is the crown oxygen atoms accessibility for the interaction with the oxonium cation, while the counter–ion should be (i) sterically inaccessible and (ii) a poor H–acceptor in comparison with the crown ether. A series of oxonium–containing crown complexes of the composition $[CE{\bullet}H(H_2O)_n^+{\bullet}An]$ (where CE – crown ether, An – halogen-containing anion, n = 1 and 2), are summarized in Table 1. The analysis of these structures shows that predominantly 18C6 and its benzo–, dicyclohexano– and tetracarboxylic derivatives are highly selective for H_3O^+ because of the size and symmetry fit between them, allowing the inclusion of the oxonium ion within the 18-membered crown ether cavity with the formation of three strong OH···O hydrogen bonds [15a–u]. Less in size benzo–15C5 and 12C4 are also capable to fix oxonium ion either in a sandwich fashion [15v], or through additional contact with the anion [15w], while the large in size dibenzo–30C10 is capable to

display simultaneously two H_3O^+ cations inside the cavity [15x]. In contrary, the fixation of $H_7O_3^+$ cation by crown ether is relatively uncommon and only two examples are known so far (Table 1), where $H_7O_3^+$ oxonium cations alternate with crown ether in the hydrogen-bonded chains with the long-range interactions to the anions [15j].

In this article we report the synthesis, spectroscopic and structural studies of four complexes separated from the reaction systems M_2O_5 (M = Nb, Ta) – HF – H_2O – L, where L^1 – BP20C6 and L^2 – [1.5]DB18C6.

Experimental

Dibenzocrown ethers BP20C6 (L^1) and [1.5]DB18C6(L^2) were obtained as described in [9]. Complexes $[L^1(H_3O)][NbF_6]$ (**1**), $[L^1(H_3O)][TaF_6]$ (**2**), $[2L^2(H_7O_3)][NbF_6]$ (**3**) and $[2L^2(H_7O_3)][TaF_6]$ (**4**) were obtained by the interaction of the corresponding oxides with the 40% aqueous HF and by the further treatment of the resulting solution by BP20C6 or [1.5]DB18C6. All four complexes were analyzed for C, H and F in a Perkin Elmer 240C instrument. IR spectra (Table 2) of the complexes (samples as suspensions in Nujol mulls between KRS-5 windows) were measured on Specord 75-IR spectrometer in the range 4000-400 cm^{-1}.

Synthesis of $[BP20C6(H_3O)][NbF_6]$ (**1**).
Nb_2O_5 (133 mg, 0.5 mmol) was dissolved in 10 mL of 45% hydrofluoric acid. The resulting solution was evaporated up to 2 mL and BP20C6 (388 mg, 1 mmol) in 5 mL of methanol was added, then the mixture was stored to crystallize at room temperature and spontaneous evaporation of solvents. Colorless transparent crystals M.P. 114-116°C (decomp.). Found, C, 43.06; H, 5.03; F, 18.61 for $C_{22}H_{31}F_6NbO_7$. Calculated, %: C, 43.01; H, 5.03; F, 18.61.

Synthesis of $[BP20C6(H_3O)][TaF_6]$ (**2**) was carried out analogously to (**1**) from Ta_2O_5 (221 mg, 0.5 mmol) and BP20C6 (388 mg, 1 mmol). Colorless transparent crystals M.P. 155-157°C (decomp.). Found, C, 37.57; H, 4.48; F, 18.19 for $C_{22}H_{31}F_6TaO_7$. Calculated, %: C, 37.62; H, 4.45; F, 16.23.

Synthesis of $[2[1.5]DB18C6{\cdot}(H_7O_3)][NbF_6]$ (**3**) was carried out analogously to (**1**) from Nb_2O_5 (133 mg, 0.5 mmol) and [1.5]DB18C6·(360 mg, 1 mmol). Colorless transparent crystals M.P. 155-157°C (decomp.). Found, C, 48.89; H, 5.65; F, 11.56 for $C_{40}H_{55}F_6NbO_{15}$. Calculated, %: C, 48.89; H, 5.64; F, 11.60.

Synthesis of [2[1.5]DB18C6·(H_7O_3)][TaF_6] (**4**) was carried out analogously to (**1**) from Ta_2O_5 (221 mg, 0.5 mmol) and [1.5]DB18C6·(360 mg, 1 mmol). Colorless transparent crystals M.P. 165-166°C (decomp.). Found, C, 44.83; H, 5.22; F, 10.69 for $C_{40}H_{55}F_6TaO_{15}$. Calculated, %: C, 44.87; H, 5.18; F, 10.65.

Data collection and structure refinement.

The X–ray intensity data for complexes **1**–**4** were recorded at 123 K with a Nonius Kappa CCD four–circle diffractometer equipped with graphite monochromatic MoKα radiation using ω–2θ rotation scan mode [16]. Final unit cell dimensions and positional data were obtained and refined on the entire data set. Integration and scaling resulted in a data set corrected for Lorentz and polarization effects using DENZO [17]. The scaling as well as the global refinement of crystal parameters were performed by SCALEPACK, multi-scan absorption correction was applied [17]. The structure solution and refinement proceeded similarly using SHELX–97 program package [18] for all four structures. Direct methods yielded all non–hydrogen atoms of the asymmetric unit. These atoms were treated anisotropically (full–matrix least squares method on F^2). In complexes **1** and **2** the oxygen atom of oxonium cation is disordered over two positions with the occupancies equal 0.646(8) and 0.354(8) in **1** and 0.657(12) and 0.343(12) in **2**, correspondingly. The minor components of oxonium oxygen atom were refined isotropically in the both complexes. In complex **3** the oxonium ion occupies the position on the two–fold axis being equally disordered. C–bound H atoms were placed in calculated positions, with C–H distances of 0.93 or 0.97 Å, and were treated using a riding–model approximation, with $U_{iso}(H)=1.2U_{eq}(C)$. H–atoms of water molecules and oxonium ions were determined from a difference Fourier map and were then allowed to refine isotropically with $U_{iso}(H)=1.5U_{eq}(O)$ and O–H distances subjected to DFIX restraints.

The X–ray data and the details of the refinement for four complexes are summarized in Table 3, selected bond distances and angles – in Table 4, hydrogen bonding geometry – in Table 5, torsion angles – in Table 6.

Results and discussion

The presence of oxonium cations and water molecules in the complexes **1**–**4** determines the appearance in their IR spectra the average intensity bands of the ν(OH) and δ(HOH)

vibrations (Table 2) in the ranges 3480–3030 cm^{-1} and 1685–1620 cm^{-1} respectively, and the diffused contours of last ones agree with the fact of the OH···O type hydrogen bonding systems realization [19]. The comparative analysis of the complexes **1**–**4** IR spectra with the ones of corresponding ligands in the area of the conformationally sensitive vibrations of the macrocycles (1300-800 cm^{-1}) permits to conclude the certain changing of the initial macrocyclic conformation under the complexation. Thus, in the spectra of complexes **1** and **2** (Table 2) the splitting of the intense band ν_{as}(COC) of the initial BP20C6 (1090 cm^{-1}) on two components (1095 and 1080 $см^{-1}$) is observed, and the bands of ν_s(COC) vibrations at 1000 and 955 cm^{-1} change in intensity. Instead of the intense band of ν_{as}(COC) with the maximum at 1105 cm^{-1} and the shoulder at 1075 cm^{-1} observed in the spectrum of [1.5]DB18C6 ($\mathbf{L^2}$), the intense doublets with the maximum at 1110 и 1085 cm^{-1} in the spectra of complexes **3** and **4** are registered. In the area of ν_s(COC) vibrations for these complexes the intensification and low-frequency (bathochromic) shift (~ 20 cm^{-1}) of the ligand band at 955 cm^{-1} (Table 2) was found, with practically unchanged position of the ligand band at 1000 cm^{-1}. The stretching vibrations ν(M–F) for hexafluorometallate monoanions [19] in the spectra of complexes **1** and **2** become apparent in the form of the very intense bands at 588 and 565 cm^{-1} respectively, and in the spectra of complexes **3** and **4** these vibrations are registered at 595 and 560 cm^{-1}.

As it is evident from Table 3, complexes **1** and **2** are isostructural, so the structural discussion will be carried out only for complex **1**, while Tables 3–6 contain the essential geometric and hydrogen bonding parameters for both complexes. Compounds **3** and **4** differ by the unit cell dimensions, although they crystallize in the same monoclinic crystal system, structure solution for both of them was found in the same *C*2/*c* space group, and having the identical composition of the complexes, $[L^2(H_7O_3)][MF_6]$ (M = Nb, Ta), the asymmetric unit of **4** represents the four–time increased content of **3**. Below we will show the distinctive features of these two supramolecular isomers.

The NbF_6^- anions in the complexes**1** and **3** adopt the usual octahedral geometry with Nb–F distances ranging from 1.867(2) up to 1.891(2) Å and with the F–Nb–F valent angles between *cis*–fluorine atoms being in the range 87.9(1)–91.8(1)° and between *trans*–fluorine atoms being in the range 176.7(1)–179.8(2)°. The geometry of the NbF_6^- anion is in a close concern with that found in 3-chloro-1,3,4,2,5-thiadiselenadiazolium hexafluoroniobium [3] and in *bis*(pyrazine)dicopper *bis*(hexafluoroniobium) piperazine solvate [4].

The TaF_6^- anions in the complexes **2** and **4** also adopt the usual octahedral geometry with Ta–F distances ranging from 1.859(3) up to 1.895(2) Å and with the F–Ta–F valent angles between *cis*-fluorine atoms being in the range 87.9(1)–91.9(1)° and between *trans*- fluorine atoms

being in the range 176.8(1)–180.0(1)°. This geometry is in a close concern with that found in catena-[(μ-chloro)-*bis*(μ-fluoro)tetrafluoro-hexamethyltantalum)] ditin [5] and in methyltriphenylphosphonium hexafluorotantalate [6].

The ORTEP view of complex **1** is shown in Figure 1. In the complex cation $[BP20C6{\cdot}H_3O]^+$, oxygen atom of oxonium ion is disordered over two positions, O(1w) and O(1wa) with the common hydrogen atoms, the both images being of the pyramidal geometry. The major component, O(1w) deviates at –0.212(3) Å, while the minor component, O(1wa) deviates at 0.703(6) Å from the plane through six oxygen atoms [–0.215(5) and 0.69(1) in complex **2**, correspondingly]. Further only the major position of the disordered oxonium ion will be discussed. Three $O_{(1w)}\cdots O_{crown}$ distances for the hydrogen bonds range from 2.504(3) to 2.589(3) Å, while three other $O_{(1w)}\cdots O_{crown}$ separations are longer and equal to 2.615(3) (O4), 2.859(3) (O10) and 3.061(3) Å (O16) [2.618(4) (O4), 2.864(4) (O10) and 3.060(4) Å (O16) in complex 2]. It is reasonable that an "aromatic" oxygen atom O16 connected with the biphenyl moiety, appears to be shielded for the interaction with the oxonium ion. On the other hand, the size of the crown ether ring is sufficient for the displacement of oxonium cation and accumulation of all of its hydrogen atoms.

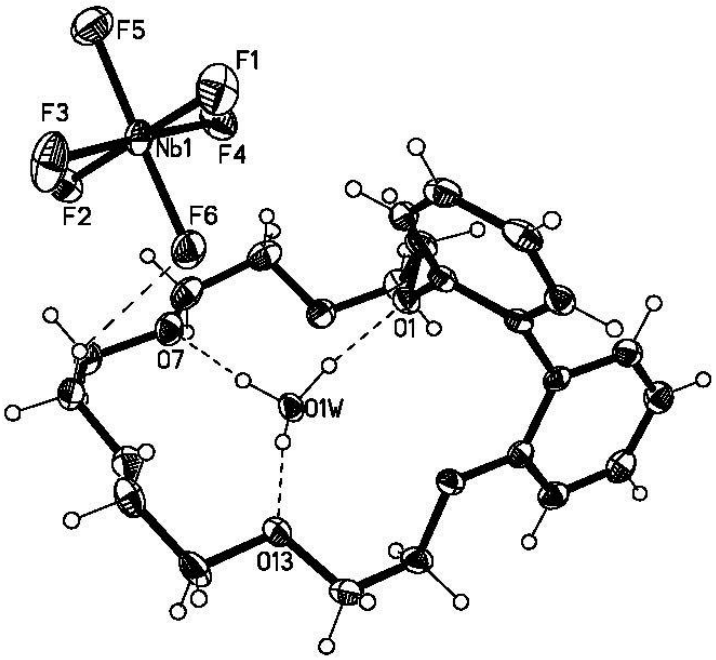


Figure 1. ORTEP drawing of **1** with the partial numbering scheme and hydrogen bonding shown by dashed lines. Thermal ellipsoids are shown at the 50% probability level.

The benzene rings of the BP20C6 molecule are arranged with the twist angle between their mean planes equal to 69.4(1)° [69.1(1)° in **2**], this value is close to that one found in the complex of BP20C6 with amidosulfuric acid [65.9(2)° and 69.7(2)° in two independent formula units], and a slightly higher than in a pure BP20C6 itself [63.8(1)°] [9]. The conformation of BP20C6 molecule is described by six *gauche*– torsion angles along five Csp^3–Csp^3 and one Csp^2–Csp^2 bonds, two *cis*– torsion angles along two Csp^2–Csp^2 bonds that belong to the aromatic rings, and ten *anti*– and two *gauche*– C–O angles, and differs from the crown conformation in its complex with amidosulfuric acid by two C–O bonds in *gauche*-conformation.

The supramolecular architecture in **1** is sustained by weak C–H···O and C–H···F interactions, which combine the components into 3D network (Fig. 2).

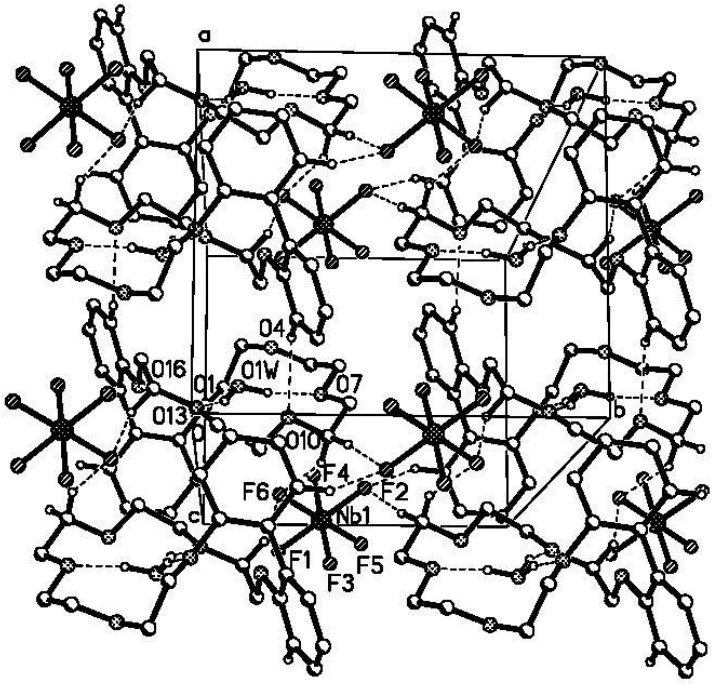


Figure 2. Fragment of crystal packing for **1**. Only hydrogens involved in hydrogen bonds are shown. Along *a* direction the inversion-related macrocycles are linked by CH···O hydrogen bonds, C(25)-H(25A)···O(10)(*-x*, *-y*+1, *-z*) 3.131(3), H···O 2.42 Å, CHO angle 133.0°, while along *b* direction the NbF_6^- anions are bridging the neighboring macrocycles *via* weak CH···F hydrogen bonds into 3D network, C···F contacts being in the range 3.185(3) – 3.462(3), H···F 2.48 – 2.54 Å, CHF angles 128 – 168°.

The ORTEP view for complex **3** is shown in Figure 3. The asymmetric unit of **3** comprises one [1.5]DB18C6 crown molecule and one O1w water molecule, both located in general positions, O2w oxonium cation, and NbF_6^- anion, both located in special positions, on the two-fold axis. The pyramidal geometry of the oxonium cation conflicts with the two-fold axis symmetry, so oxonium cation appears to be disordered. Water molecule O1w deviates at 1.499(2) Å from the plane of six crown oxygen atoms, which are coplanar within 0.403 Å, it donates both of its hydrogen atoms for two bifurcated OH···O hydrogen bonds with "aliphatic" and "aromatic" crown oxygens, O···O separations being in the range 2.859(3) – 3.014(3) Å. This water molecule, acting as H-acceptor, donates one of its lone pairs for the OH···O hydrogen bond with the oxonium hydrogen, O···O separation being 2.438(3) Å, by which, in its turn, oxonium cation bridges two related by the two-fold axis ([1.5]DB18C6·H_2O) units. The third hydrogen atom of oxonium cation alternately contacts with O(10) crown oxygens of two related by the two-fold axis crown molecules, $O_{oxonium}\cdots O(10)_{crown}$ separation being 2.935(2) Å. The three–membered O1w···O2w···O1w(-*x*, *y*, -*z*+1/2) chain of the alternating water···oxonium···water entities of the composition $H_7O_3^+$ is closed in the cage of two crown molecules.

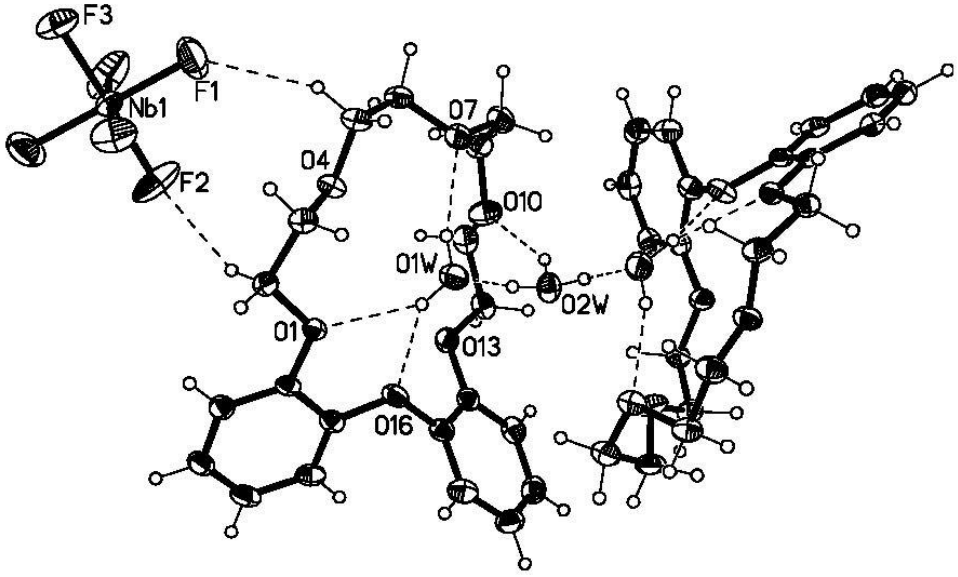


Figure 3. ORTEP drawing of **3** with the partial numbering scheme and hydrogen bonding shown by dashed lines. Thermal ellipsoids are shown at the 50% probability level. Only major position for oxonium ion (O2w) is shown.

The benzene rings of the [1.5]DB18C6 molecule are arranged with the twist angle between their mean planes equal to 66.1(1)° (for comparison, the same angle is equal to

69.2(5)° in the [1.5]DB18C6 complex with dithiouracil and 87.5(1)° in the [1.5]DB18C6 molecule itself [9,10]). The macrocyclic 18–membered skeleton is described by four *gauche*–Csp^3–Csp^3 and two *cis*- Csp^2–Csp^2 torsion angles, eleven *anti*– and one *gauche*– C–O torsion angles. The specific feature of complex **3** (as in the above–mentioned complex with dithiouracil), is that two [1.5]DB18C6 molecules in the same conformation formulate a supramolecular capsule with the charged $(H_7O_3)^+$ unit inside.

Figure 4 reveals how NbF_6^- anion *via* four C–H···F hydrogen bonds bridges the neighboring related by the two–fold axis 5-membered cations, $[([1.5]DB18C6)_2{\cdot}H_7O_3^+]$ into chains propagated along *c* direction in the unit cell.

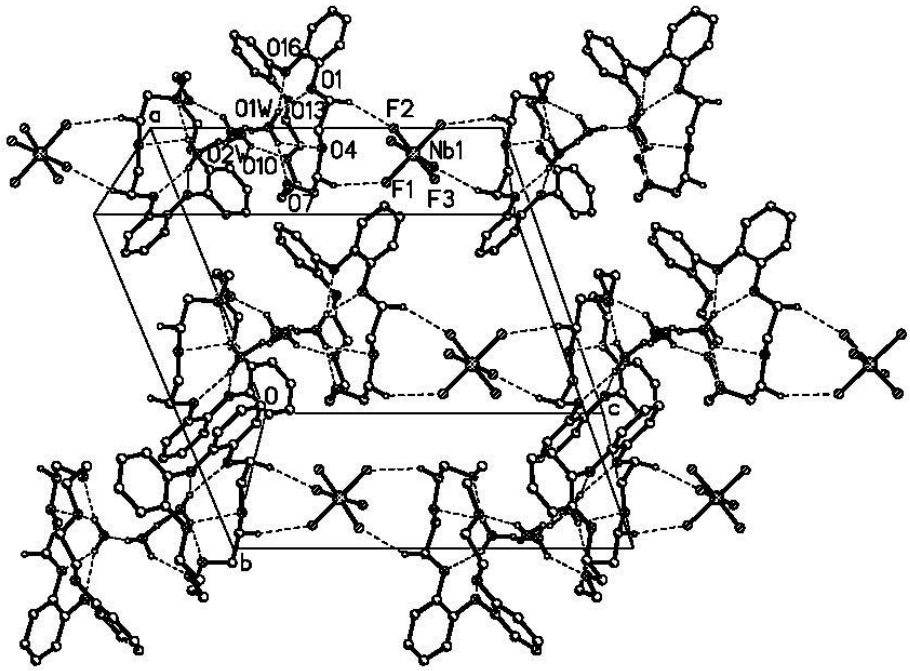
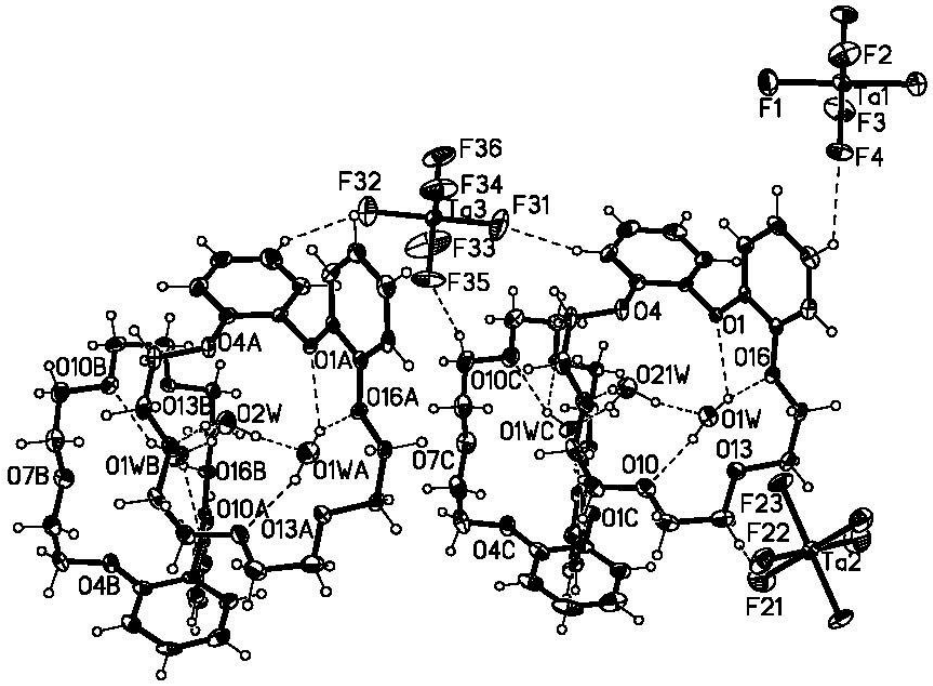


Figure 4. Fragment of crystal packing for **3**. Only hydrogens involved in hydrogen bonds are shown. Along *c* direction the related by two-fold axis units are linked by CH···F hydrogen bonds in the chains, C(2)-H(2B)···F(2) 3.296(3), H···F 2.43 Å, CHF angle 146°, and C(5)-H(5B)···F(1) 3.432(4), H···F 2.55 Å, CHF angle 149°.

In the asymmetric unit of complex **4** four [1.5]DB18C6 molecules (depicted by the numerical indexes, and indexes a, b and c), four water molecules (O1w, O1wa, O1wb, and O1wc), two oxonium ions (O2w and O21w), and one TaF_6^- anion occupy the general positions, while two other TaF_6^- anions reside on the two–fold axis. In contrary to complex **3**, the O2w and O21w H_3O^+ oxonium cations occupy general positions without distortion of

their pyramidal geometry. That results in two 5–membered associates, each composed of $H_7O_3^+$ cations enclosed inside the cage of two different crown molecules (in pairs: molecule a – molecule b; molecule c – molecule with numerical indexes). The organization of these associates is very close to **3**, the shortest are four $O_{water}\cdots O_{oxonium}$ distances which are in the range 2.424(5) – 2.521(4) Å, the next in length are two $O_{oxonium}\cdots O_{crown}$ distances that adopt the values of 2.615(4) and 2.636(4) Å, and the longest are $O_{water}\cdots O_{crown}$ distances which range from 2.712(4) to 3.036(4) Å. However, the main distinctive feature is that two these capsules occupy general positions in the asymmetric unit. It results in the different Owater···Ooxonium distances in the three-membered water clusters, equal to 2.521(5) and 2.438(5) Å in the chain O(1w)···O(21w)···O(1wc), and 2.509(5) and 2.428(5) Å in the chain O(1wa)···O(2w)···O(1wb). The oxonium cations have only one contact with the crown oxygen, O(21w)···$O(10)_{crown}$ being 2.614(4) Å, and O(2w)···$O(10A)_{crown}$ being 2.635(4) Å in two 5-membered capsules, correspondingly. As a sequence of the different mode of hydrogen bonding, both of these two capsules combine two crown molecules in different conformations, one of which is rather close to that one found in **3**. In each pair the conformations of two molecules differ only by C(6)–O(7)–C(8)–C(9) angle, which adopts the values of 85.4(4) and 174.5(4)° in the first pair, and 90.9(5) and 173.0(4)° in the second pair, the same torsion angle is equal to 78.5(3)° in complex **3** (Table 6).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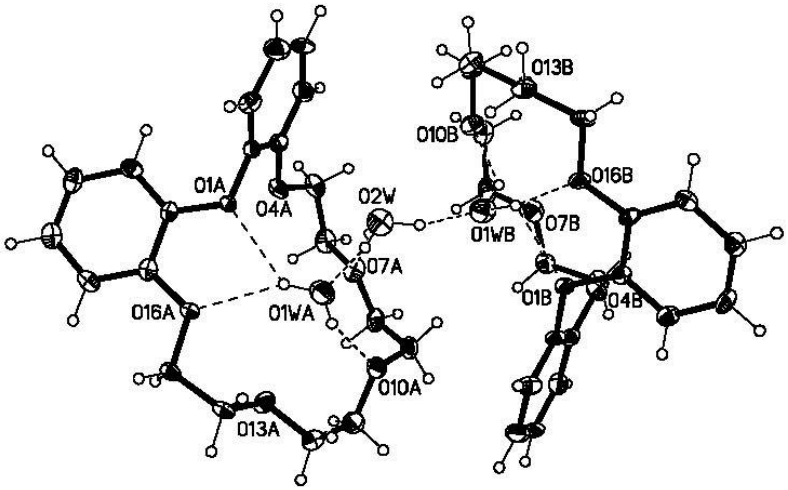
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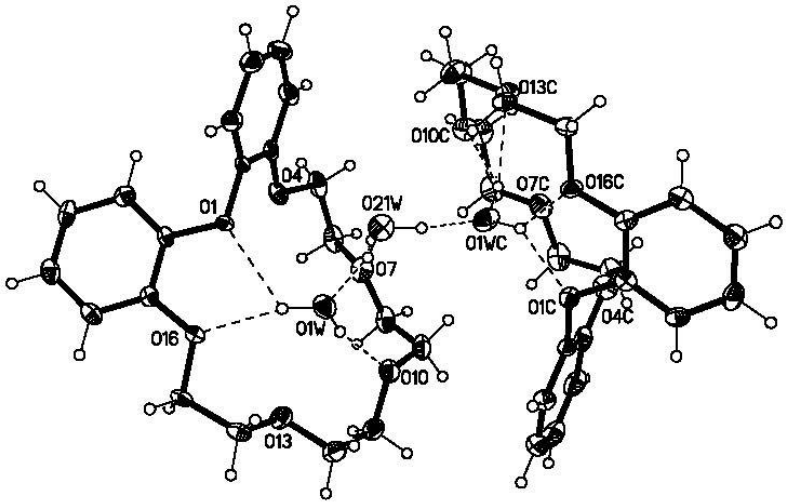
O1WB
O7A
O1B
O4B
O16A
O1WA
O10A
O13A

b).



c).

Figure 5. ORTEP drawing of **4** with the partial numbering scheme and hydrogen bonding shown by dashed lines. Thermal ellipsoids are shown at the 50% probability level. a) general view of the asymmetric unit with the shortest CH···F distances shown by dashed lines; b-c) two crystallographically independent 5–membered supramolecular capsules in the projection on the best plane.

The bridging TaF_6^- anion (Ta3), occupying the general position, fulfills the double function, *via* F(31) and F(35) atoms it participates in the short C–H···F contacts with two crown molecules that belong to one capsule, C(23)···F(31) 3.291(6), H···F 2.36 Å, CHF angle 166°, C(8c)···F(35) 3.492(6), H···F 2.52 Å, CHF angle 166°, and *via* F(32) atom it bridges two independent capsules, C(24a)···F(32) 3.345(6), H···F 2.57 Å, CHF angle 138°. The crystal packing for **4** keeps the main property typical for such previously studied crystals, built on the macrocycle – fluoride–containing anion (GeF_6^{2-}, SiF_6^{2-}, SiF_5^- etc), and water: the crystal is built as a napoleon, of the alternative organic (macrocycle) and inorganic (anions) rows in the 3D network (Fig. 6).

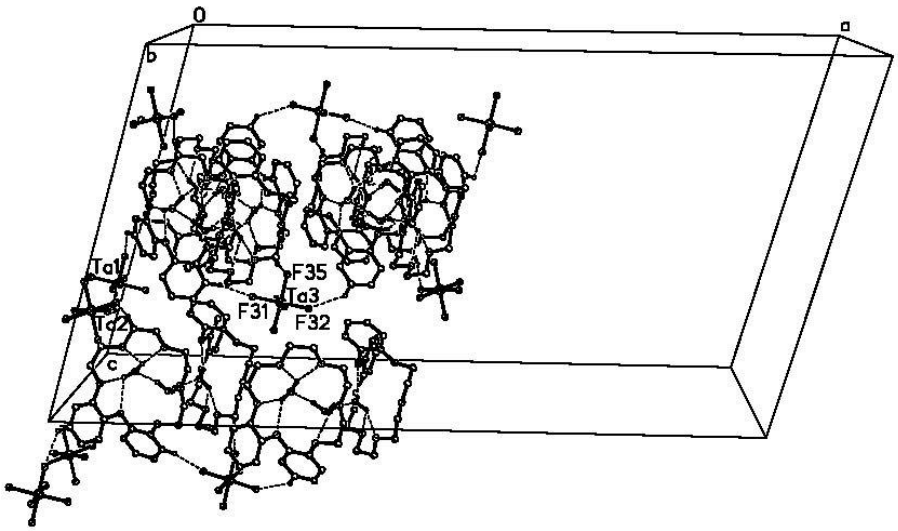


Figure 6. Fragment of crystal packing for **4**. Only hydrogens involved in hydrogen bonds are shown.

Thus, the list of the 18–membered hexadentate crown ethers presented in Table 1 can be supplemented by the 20–membered hexadentate crown ether, BP20C6 (L^1), containing biphenyl fragment, as complexes **1** and **2** demonstrate the similar suitable fit between the BP20C6 macrocycle cavity and H_3O^+ oxonium cation.

In contrary, the presence of the diphenyloxide fragment in the 18–membered hexadentate crown ether [1.5]DB18C6 (L^2) is a decisive condition for the $H_7O_3^+$ entity in complexes **3** and **4** within the cage formed by two crown molecules with the formation of the closed capsule with only very weak interactions with the NbF_6^- and TaF_6^- anions. And so, the complexes **3** and **4** fill up the scanty list (see Table 1) of the crown ethers complexes with $H_7O_3^+$ oxonium cations.

Conclusion

The interaction of Nb_2O_5 and Ta_2O_5 oxides with the hydrofluoric acid in the presence of biphenyl–20–crown–6, BP20C6 and [1.5]dibenzo–18–crown–6, [1.5]DB18C6 yield the complexes of the composition $[BP20C6{\cdot}(H_3O)][MeF_6]$ and $[2[1.5]DB18C6\ (H_7O_3)MeF_6]$ (Me = Ta, Nb). According to the X–ray data, in the first two isostructural adducts the H_3O^+ oxonium cation centers the crown cavity through a near–ideal 'tripod' arrangement of $OH\cdots O$ hydrogen bonding to alternate crown oxygen atoms. In the case of the rare complexes

[2[1.5]DB18C6·(H_7O_3)MeF_6] the $H_7O_3^+$ oxonium cation is enclosed inside the cage formed by two crown ethers. Complexes **3** and **4** represent a bright example of supramolecular isomerism (i.e., the existence of more than one network for the same building blocks) [20].

It is necessary to make a note that in the studied conditions the complexes of crown ethers with less symmetrical and carrying more negative charge (in comparison with NbF_6^- and TaF_6^-) oxofluoride anions are not formed, since the last ones are present in the reaction solutions Me_2O_5 (Me = Nb, Ta) – HF – H_2O. It seems, this fact demonstrates a tendency to stabilize the oxonium complexes of crown ethers in preference to the monoanions (Table 1).

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, deposition numbers CCDC 290090 (**1**), CCDC 290088 (**2**), CCDC 290089 (**3**), CCDC 290087 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1233-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Додаток 60

Копія статті Molecular complexes of thionicotinamide with 18-membered crown ethers: synthesis and crystal structure

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Molecular complexes of thionicotinamide with 18-membered crown ethers: Synthesis and crystal structures

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Abstract

The reaction of thionicotinamide (3-thioamidopyridine) with 18-membered crown ethers, 18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and *cis anti cis*-dicyclohexyl-18-crown-6 (D18C6) results in the molecular complexes of 1:1 ratio for 18C6 (complex **1**) and B18C6 (complex **2**) and monohydrate of 2:1:1 ratio for D18C6 (complex **3**), respectively. The complexes are sustained by combination of N H···O, O H···N and C H···O hydrogen bonds, and the components are associated into molecular adduct (**1**) or infinite chain (**2** and **3**).
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Keywords: H-bonded adducts; Thionicotinamide; 18-Membered crown ethers; Synthesis and crystal structure

1. Introduction

In the last decade we witnessed an increased interest to the co-crystals including active pharmaceutical ingredient (API) [1–3] with the aim to produce new valuable materials. Crystalline self-assemblies are promising for improving drug solubility, dissolution rate, stability and bioavailability. Supramolecular synthesis is now being widely explored to obtain new pharmaceuticals from known APIs and a benign solid component (cyclodextrins [4–6], carboxylic [7–10] and dicarboxylic acids [11–13], etc.). The recent findings in this topic are summarized in the fresh review paper by Zaworotko and co-workers [14].

Crown ethers (CEs) exhibit themselves as very useful model compounds capable to function as do more complex chemical structures. Moreover, some simple crown ethers exhibit biological activity. These two properties make them very attractive molecules that permit a detailed analysis of interactions that are thought to be important in biology [15]. For several years we are involved in the problem of the molecular recognition of biologically important molecules (nucleic bases, drugs) by macrocyclic molecules, as the model systems mimic substrate–receptor interactions [16,17]. We have analyzed series of complexes, e.g., streptocid (4-aminobenzenesulfonamide) – 18-membered CEs (18-crown-6, dicyclohexyl-18-crown-6, benzo, cyclohexyl-18-crown-6) [18–20], PABA (4-aminobenzoic acid) – CEs (isomers of dicyclohexyl-18-crown-6, aza-12-crown-4) [21,22], hypothiazide (6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide) – CEs (18-crown-6, dicyclohexyl-18-crown-6) [23,24]. It has been shown that the interaction with the neutral macrocycle results in the genius co-crystals with the primary amino-group involved in the coordination to macrocyclic molecule, while aza-macrocycle is easily protonated and interaction results in an organic salt. The self-assembly of the drug molecules via hydrogen bonds typical for their pure forms is destroyed and is substituted by the interaction with the

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macrocyclic molecule [25]. As the rule, the complete rearrangement of the hydrogen bonds occurs, and only the strongest homosynthons typical for the pure form (as that $R_2^2(8)$ combining two carboxylic groups [26]) remain in the complex [20] (Scheme 1).

In continuation of this research, we studied the system thionicotinamide (3-thioamidopyridine) – CE [18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and *cis–anti–cis*-dicyclohexyl-18-crown-6 (D18C6)] and report here on the X-ray crystal structures of three novel complexes.

The thioamide functional group is present in many drugs and agricultural chemicals, and exposure to man can result in inadvertent toxicity. Thus, a large number of potentially useful drugs containing the thioamide group are limited in their use due to the toxic side effects associated with these compounds. The diverse thioamide derivatives have been used as herbicides, antitubercular and antibacterial agents. The associated toxicity of the thioamides is explained to be linked to their oxidative metabolism, especially *S*-oxygenation [27]. Some recent studies were devoted to the synthesis of modified thionicotinamide to decrease its toxicity and maintain the useful medicinal properties [28]. Thionicotinamide is a known xenobiotic. It is a drug used for the treatment of *Chagas disease*, a common health problem in South America [29].

The crystallographic data [30] for this class of compounds are rather scanty. They are restricted by three isomeric thioamidopyridines of general formula $C_6H_6N_2S$, 2-thioamidopyridine [31], 3-thioamidopyridine [32] and 4-thioamidopyridine [33]. The structure of the 2-propyl derivative of 4-thioamidopyridine has also been reported [34]. The structural interest to these compounds has centered on the parameters of the thioamide group and the consequent electron arrangement within the group. Additional features of interest are the non-coplanarity of the pyridine ring with the thioamide group and the hydrogen-bonding schemes. The isomers have three possible coordination sites, and the packing of all of them reveals some common features. The molecules lie in the layers via $R_2^2(8)$ centrosymmetric rings built on NH···S contacts (N···S ~ 3.4 Å, a bit longer than the sum of van der Waals radii) and C(7) chains (contacts NH···N, N···N about 2.96 Å), and then these layers stack along the shortest axis (Scheme 2).



Scheme 1. Homosynthon $R_2^2(8)$ typical for carboxylic acids.

As for the multicomponent adducts involving isomers of thionicotinamide, only its S-oxide monohydrate [35] and thionicotinamidium 3,5-dinitro-4-methylbenzoate 3,5-dinitro-4-methylbenzoic acid adduct [36] are reported. From the viewpoint of crystal packing, it is interesting that only NH···N contact (N···N distance of 2.954 Å) remains in the crystal packing of the first adduct, while weaker NH···S contacts are substituted by the interaction with water molecule as a more powerful H-acceptor, while in the second compound the full rearrangement of the intermolecular interactions occurs, and two homosynthons typical for 3-thionicotinamide itself are substituted by the heterosynthons between thionicotinamidium cations and 3,5-dinitro-4-methylbenzoate anions (or 3,5-dinitro -4-methylbenzoic acid molecules).

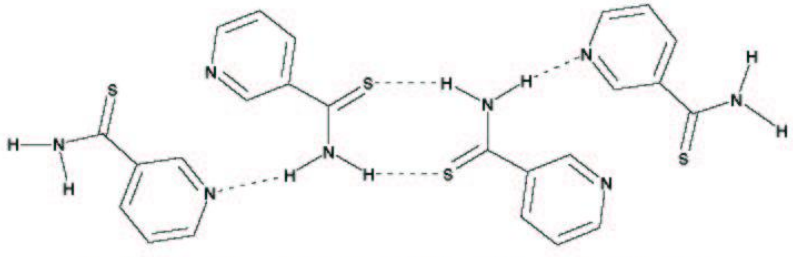
The aim of our study is to elucidate the mode of interaction of the drug molecule with the macrocycles and to compare the crystal packing motifs in the complexes.

2. Experimental

Commercially available reagents were used as received. Compounds **1–3** were analyzed for C, H, N and S in a Perkin-Elmer 240 C. The thin-layer chromatographic control of the substance purity was performed on Silufol UV-254 plates. ^{1}H NMR spectra were recorded at 300 MHz on a Varian Oxford 300 NMR spectrometer.

2.1. Synthesis

Compound 1. A solution of 18C6 (0.264 g, 1 mmol) and thionicotinamide (0.138 mg, 1 mmol) in 2 ml of methanol and 3 ml of ethyl acetate was stored for 3–5 days at 20 °C in an open flask. The crystals, separated in a yield of 91% (0.365 g), were suitable for X-ray analysis. Yellow crystals, soluble in methanol, ethanol, acetone, m.p. 120–122 °C. Analysis: found C, 53.71; H, 7.51; N, 6.96; S, 7.97%. $C_{18}H_{30}N_2O_6S$ requires C, 53.68; H, 7.54; N, 6.93; S, 7.94%. ^{1}H NMR (CD_3OD_{d4}, 300 MHz): 3.60 s (24H, 18C6), 7.45 m, 8.26 m, 8.60 m, 9.00 m (4H, CH).



Scheme 2. The mode of association of 3-thionicotinamide molecules in the crystal.

Compound 2. A solution of B18C6 (0.312 g, 1 mmol) and thionicotinamide (0.138 mg, 1 mmol) in 7 ml of methanol and 15 ml ethyl acetate was stored ~3 days at 20 °C in an open flask. The crystals, separated in a yield of 96% (0.430 g), were suitable for X-ray analysis. Yellow crystals, soluble in methanol, ethanol, acetone, m.p. 140–142 ° C. Anal. found C, 58.59; H, 6.83; N, 6.31; S, 7.12%. $C_{22}H_{30}N_2O_6S$ requires C, 58.65; H, 6.71; N, 6.22; S, 7.19%. ^{1}H NMR ($DMSO_{d6}$, 300 MHz): 3.55 m, 3.73 m, 4.05 m (20H, CH_2) and 6.90 m (4H, CH – B18C6), 7.43 m, 8.18 m, 8.64 m, 8.99 m (4H, CH).

Compound 3. A solution of D18C6 (0.372 g, 1 mmol) and thionicotinamide (0.138 g, 1 mmol) in 5 ml of acetone and 5 ml hexane was stored for 3–5 days at 20 °C in an

Table 1
Crystal data summary for complexes **1–3**

Complex	1	2	3
CCDC number	601910	601911	601909
Empirical formula	$C_{18}H_{30}N_2O_6S$	$C_{22}H_{30}N_2O_6S$	$C_{32}H_{50}N_4O_7S_2$
Formula weight	402.50	450.54	666.88
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*Cc*	*P-1*	*Pccn*
Unit cell dimensions			
a (Å)	17.228(2)	8.471(2)	16.880(1)
b (Å)	8.525(1)	9.866(2)	18.685(1)
c (Å)	14.866(1)	15.111(2)	11.331(1)
α (deg.)	90.0	84.37(1)	90.0
β (deg.)	102.75(2)	84.69(2)	90.0
γ (deg.)	90.0	65.78(2)	90.0
Cell volume (Å^3)	2129.4(3)	1144.2(4)	3573.7(5)
Formula units/unit cell	4	2	4
D_{calc} (g/cm^{-3})	1.256	1.308	1.239
μ (mm^{-1})	0.186	0.181	0.198
$F(000)$	864	480	1432
Crystal dimensions (mm)	$0.55\times0.53\times0.40$	$0.58\times0.46\times0.38$	$0.42\times0.34\times0.25$
θ Range for data collection (deg.)	2.42–27.51	2.27–25.00	2.18–27.00
Limiting indices	$22\leqslant h\leqslant17$, $10\leqslant k\leqslant11$, $18\leqslant l\leqslant19$	$0\leqslant h\leqslant9$, $10\leqslant k\leqslant11$, $17\leqslant l\leqslant17$	$15\leqslant h\leqslant21$, $23\leqslant k\leqslant23$, $14\leqslant l\leqslant14$
Reflections collected/unique	6608/3703 [R(int) – 0.0274]	4304/4008 [R(int) – 0.0103]	20874/3909 [R(int) – 0.0287]
Reflections with $I>2\sigma(I)$	1667	3505	1865
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3703/2/253	4008/0/289	3909/0/216
Goodness-of-fit on F^2	0.881	1.020	0.849
Final R indices [$I>2\sigma(I)$] %	R_1 – 0.0401, wR_2 – 0.0721	R_1 – 0.0332, wR_2 – 0.0930	R_1 – 0.0350, wR_2 – 0.0782
R indices (all data) %	R_1 – 0.0886, wR_2 – 0.0763	R_1 – 0.0390, wR_2 – 0.0960	R_1 – 0.0829, wR_2 – 0.0854
Largest diff. peak and hole (eÅ^{-3})	0.179/ 0.209	0.208/ 0.214	0.187/ 0.232

Table 2
Hydrogen bonding in complexes **1–3**

D–H···A	r(D–H) (Å)	r(H···A) (Å)	r(D···A) (Å)	∠(DH···A) (deg)	Symmetry transformation for acceptor
1					
N2–H1N2···O2	0.90(3)	2.10(3)	2.998(4)	176(3)	x, y, z
N2–H2N2···O6	0.93(3)	2.59(3)	3.294(4)	132(2)	x, y, z
2					
N2–H1N2···O4	0.88(2)	2.11(2)	2.989(2)	173(2)	x, y, z
N2–H2N2···O1	0.87(2)	2.43(2)	3.231(2)	153(2)	x, y, z
N2–H2N2···O6	0.87(2)	2.48(2)	3.218(2)	144(2)	x, y, z
3					
N2–H1N2···O2	0.90(2)	2.07(2)	2.934(2)	161(2)	x, y, z
N2–H2N2···O1	0.88(2)	2.10(2)	2.975(2)	170(2)	$x+1, y+1, z+2$
O4–H1O4···N1	0.81(2)	2.16(2)	2.957(2)	165(3)	$x+1/2, y+3/2, z$

open flask. The crystals, separated in a yield of 71% (0.235 g), were suitable for X-ray analysis. Yellow crystals, soluble in methanol, ethanol, acetone, m.p. 115–116 °C. Anal. found C, 57.61; H, 7.59; N, 8.38; S, 9.67%. $C_{32}H_{50}N_4O_7S_2$ requires C, 57.63; H, 7.56; N, 8.40; S, 9.62%. ^{1}H NMR ($DMSO_{d6}$, 300 MHz): 1.19–1.71 m and 3.55 m (36H, D18C6), 7.44 m, 8.19 m, 8.65 m, 8.99 m (8H, CH), 9.68 s, 10.04 s (2H, NH; 2H, SH).

2.2. X-ray crystallography

The X-ray intensity data were collected at room temperature on a Bruker CCD diffractometer for **1** and **3** and on a Siemens P4 diffractometer for **2**. The recorded data were corrected for polarization and Lorentz effects. The structure solution and refinement proceeded similarly for all structures using SHELX-97 program package [37]. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were treated anisotropically (full-matrix least-squares method on F^2). C-bound hydrogen atoms were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while the N- and O-bound H-atoms were found from difference syntheses at an intermediate stage of the refinement and were treated isotropically. The X-ray data and the details of the refinement for **1–3** are given in Table 1, H-bonding data are given in Table 2, geometry of thionicotinamide molecule in **1–3** is summarized in Table 3.

Table 3
Selected bond lengths (Å) and angles (deg) for thionicotinamide molecule in complexes **1–3**

	1	2	3
S1–C6	1.653(3)	1.667(2)	1.652(2)
N1–C1	1.297(5)	1.337(2)	1.333(3)
N1–C5	1.361(4)	1.330(2)	1.340(2)
N2–C6	1.318(4)	1.324(2)	1.314(2)
C1–C2	1.367(6)	1.367(3)	1.361(3)
C2–C3	1.381(5)	1.368(2)	1.368(3)
C3–C4	1.369(4)	1.391(2)	1.375(2)
C4–C5	1.378(4)	1.384(2)	1.372(2)
C4–C6	1.465(4)	1.492(2)	1.483(2)
C1–N1–C5	116.1(4)	116.5(2)	116.0(2)
N1–C1–C2	125.2(4)	123.8(2)	123.4(2)
C1–C2–C3	117.4(4)	118.8(2)	119.2(2)
C4–C3–C2	120.5(3)	119.4(2)	119.5(2)
C3–C4–C5	116.5(3)	117.0(1)	117.0(2)
C3–C4–C6	122.3(3)	121.1(1)	121.3(2)
C5–C4–C6	121.1(3)	121.9(1)	121.7(2)
N1–C5–C4	124.2(3)	124.5(2)	124.8(2)
N2–C6–C4	116.1(3)	116.7(1)	115.5(2)
N2–C6–S1	122.8(3)	122.2(1)	122.7(1)
C4–C6–S1	121.0(2)	121.1(1)	121.8(1)

Crystallographic data (cif files) for complexes **1–3** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 601909 (complex **3**), 601910 (complex **1**), and 601911 (complex **2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336 033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

3. Results and discussion

Complexes **1** and **2** represent anhydrous co-crystals of 1:1 ratio of thionicotinamide and corresponding crown ether, while **3** is a monohydrate of 2:1:1 stoichiometry. As all three complexes reveal a lot of common features in the complex organization, we present the comparative analysis for **1–3**. Fig. 1 reveals the ORTEP view for complexes **1** and **2**.

These two complexes are very close in structure organization: in **1** the formula unit is sustained by two NH···O hydrogen bonds, with the involvement in these interactions

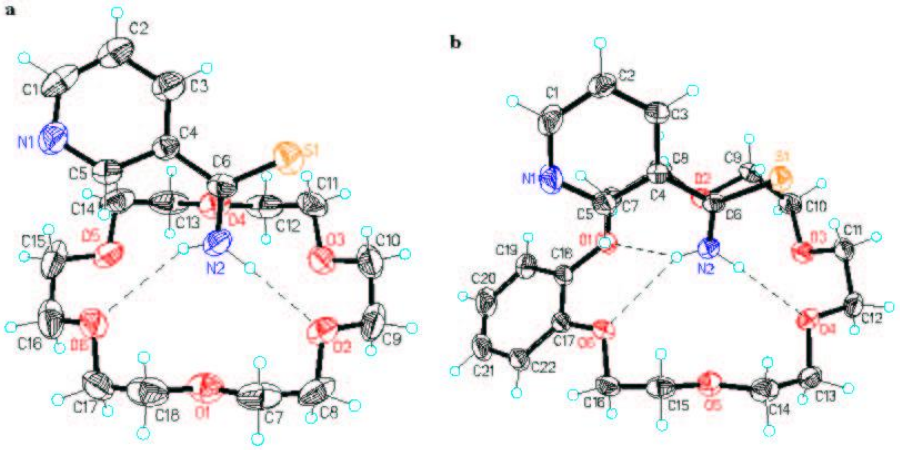


Fig. 1. (a and b). ORTEP view of complexes **1** and **2** with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown by dashed lines.

of two crown oxygen atoms, O2 and O6 separated by the oxyethylene fragment. The N···O distances adopt the values 2.998(4) and 3.294(4) Å. It is evident that the second value is rather long as well as the corresponding H(N)···O6 distance, however, this contact contributes to the complex stability. In complex **2** thionicotinamide and B18C6 molecules are held together again through two NH···O hydrogen bonds, single one with the N···O separation of 2.989(2) Å, and the second one which is bifurcated, with two aromatic oxygen atoms O1 and O6 of B18C6, the corresponding N···O distances being 3.218(2) and 3.231(2) Å. The nitrogen atom of thioamide group is situated at 1.720(3) and 1.748(2) Å from the mean plane of six oxygen atoms of the macrocycles in the complexes 1 and **2**, correspondingly. 18C6 in 1 has a crown-like shape typical for D_{3d} conformation with the mean deviation of six oxygen atoms from their least-square plane being within ±0.23 Å. B18C6 in **2** has a more distorted shape with the maximal deviations for O3 and O4 atoms equal to 0.40 and 0.42 Å, correspondingly from the mean plane through all six oxygen atoms where they are fitted within ±0.26 Å. The molecules in the complexes are arranged in such a way that the dihedral angle between the mean planes of crown oxygen atoms and the pyridine ring of thionicotinamide molecule is equal to 36.4(1)° in 1 and 58.8(1)° in **2**, correspondingly. The subtle differences in 1 and **2** are connected with the nature of the CE used, namely with the availability of the phenyl ring in the molecule of B18C6. These differences exhibit themselves in the crystal packing. The packing of 1 does not reveal any specific features besides van der Waals interactions between the neighboring complexes. In contrary, in **2** one may note two short C–H···O contacts, one, C5···O6 functions within the complex (C···O 3.445(2) Å, CHO angle is 164°), while the second one, C3···O3(x 1, y, z) functions between the neighboring complexes translated along a direction (C···O 3.281(2) Å, CHO angle is 133°). These weak interactions combine the complexes in the chains (Fig. 2).

Fig. 3 depicts the ORTEP view of complex **3**. The asymmetric part of the unit cell comprises of one molecule of CE that resides on the inversion center, one thionicotinamide molecule in general position and one water molecule that resides on twofold screw axis. It results in the common

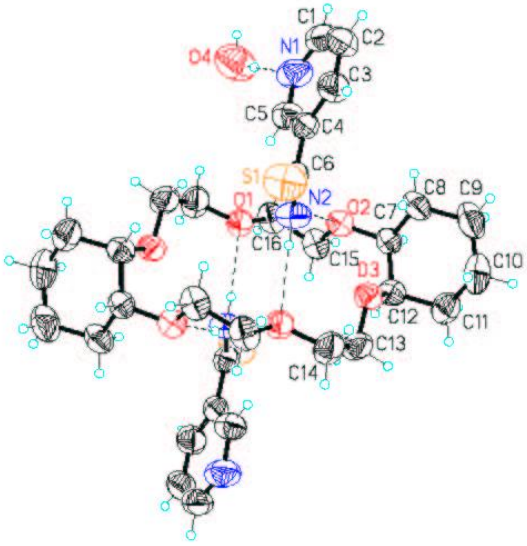


Fig. 3. ORTEP view of complex **3** with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown by dashed lines.

complex stoichiometry of 1:2:1. Due to CE position on an inversion center, two thionicotinamide molecules approach its two faces in a similar manner. The molecules in a 1:2 molecular unit are held together by four single inversion-related NH···O hydrogen bonds, N···O distances being 2.957(2) and 2.975(2) Å. These H-bonds are the shortest amongst three studied complexes. In the complex the nitrogen atom of thioamide group deviates at 1.883(2) Å from the mean plane of six oxygen atoms of the D18C6, which are coplanar within ±0.14 Å. The molecules in the complex are arranged in such a way that the dihedral angle between the mean planes of crown oxygen atoms and the pyridine ring of the thionicotinamide molecule is equal to 60.8(1)°.

Water molecule occupies position on twofold screw axis. Via OH···N hydrogen bond with the pyridine nitrogen it binds two neighboring complexes in the corrugated chain. The fragment of the chain is shown in Fig. 4.

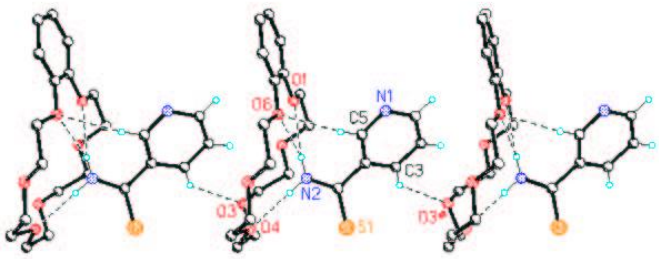


Fig. 2. Chain organization in **2**. C-bound H-atoms of B18C6 molecule are omitted for clarity. Atom marked with a hash (#) is at the symmetry position x 1, y, z.

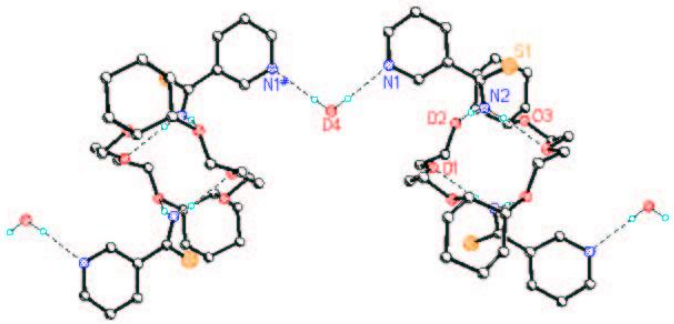


Fig. 4. Chain organization in 3. C-bound H-atoms are omitted for clarity. Atom marked with a hash (#) is at symmetry position $x + 1/2$, $y + 3/2$, z.

The geometry of thionicotinamide molecule is consistent in 1–3 and in pure 3-thionicotinamide [32] (Table 3). The molecule is characterized by the planar pyridine ring with S1 and N2 atoms of the side chain considerably displaced from the plane of the pyridine ring, but C6 atom of the thioamido-group is not significantly displaced from this mean plane. The mean plane through the pyridine ring and the mean plane through the thioamide group [S1/N2/C6] are inclined at an angle of 40.8(1)° in **1**, 24.0(1)° in **2**, and 34.7(1)° in **3** to one another, the same angle in thionicotinamide itself is equal to 33.8°. This non-coplanarity is not uncommon and due to [38] it arises from the steric hindrance between the atoms in the side chain and the ring atoms *ortho* to the side chain.

4. Conclusion

Three molecular complexes of thionicotinamide with 18-membered crown ethers were synthesized in approximately the same conditions and their crystal structures were described. As we noted in Section 1, the molecules of isomers of thionicotinamide are held in the crystal via $R_2^2(8)$ supramolecular synthon (Scheme 2). In the supramolecular adducts with the macrocycles this synthon is destroyed. In all studied complexes the H-donor amino-group forms NH···O hydrogen bonds with the crown ethers' oxygen atoms. The availability of sterically bulky sulfur atom in the thioamide fragment does not permit to create a system of equal NH···O hydrogen bonds that is especially pronounced in complexes **1** and **2**.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.04.034.

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Додаток 61

Копія статті The 1:2 and 1:1 molecular complexes of N,N'-dibenzyl-4,13-diaza-18-crown-6 with 4-nitrobenzenesulfonamide and dithiooxamide

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The 1:2 and 1:1 molecular complexes of *N,N'*-dibenzyl-4, 13-diaza-18-crown-6 with 4-nitrobenzenesulfonamide and dithiooxamide

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Abstract

The reaction of diazacrown ether, *N,N'*-dibenzyl-1,7,10,16-tetraoxo-4,13-diazacyclooctadecane (DD18C6) with 4-nitrobenzenesulfonamide, 4-$O_2NPhSO_2NH_2$ and dithiooxamide, $(H_2NCS)_2$ results in the molecular complexes of 1:2 (complex **1**) and 1:1 (complex **2**) ratios, correspondingly. The crystals of **1** are monoclinic, space group $P2_1/c$, $a-9.256(2)$, $b-9.214(2)$, $c-24.379(5)$ Å, $\beta-100.87(3)°$, $V-2041.9(7)$ Å^3, $Z-2$. The crystals of **2** are triclinic, space group $P\text{-}1$, $a-8.458(2)$, $b-9.314(1)$, $c-20.098(5)$ Å, $\alpha-87.51(1)$, $\beta-85.46(1)$, $\gamma-67.52(1)°$, $V-1458.2(5)$ Å^3, $Z-2$. The complexes are sustained by N H···O and N H···N hydrogen bonds and exhibit zero-dimensional molecular complex and one-dimensional chain structures, correspondingly.
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Keywords: 0D and 1D H-bonded adducts; *N,N'*-dibenzyl-4, 13-diaza-18-crown-6; Synthesis and crystal structure; Conformation

1. Introduction

The crown ether family of macrocyclic compounds has attracted a huge interest, since their discovery in 1967 [1,2], especially in the fields of host–guest and coordination chemistry. The nitrogen-pivot, bibracchial (two-armed) and tribracchial (three-armed) lariat ethers (BiBLEs and TriBLEs) [3–5] were modeled on valinomycin complexation and designed to be flexible and dynamic when unbound and to be enveloping when a guest is complexed [5,6]. In the course of studying the coordination properties of macrocyclic ligands, and in particular *N,N'*-disubstituted diaza-18-crown-6, the exciting interactions have surfaced. For example, in *N,N'*-dibenzyl-4,13-diaza-18-crown-6 (DD18C6) complexes, a range of C–H···O and C–H···N interactions significantly affects the conformation of the macrocyclic ring and the ability of the crown to bind ions and neutral molecules.

A search of the Cambridge Structural Database (August 2005 update) [7] revealed the complexes that incorporate DD18C6 molecule both in a neutral and in a doubly protonated form. Previous studies have indicated that the alkaline and lighter lanthanoid species (La-Sm) tend to form inclusion-type compounds, with a metal salt incorporated into the macrocyclic cavity. It results in rather different crown conformations, the asymmetric 'basket-like' shape with two phenyl substituents situated at the same side of the macrocyclic cavity in the cases of NaI·DD18C6 [8] and $Ln(NCS)_3$·DD18C6 (Ln=La, Nd, Eu) [9], T-shape arrangement of two phenyl substituents in the complex $AgPF_6$·DD18C6 [10], and more symmetric conformation with benzyl arms splayed up from both sides of the macrocyclic ring in catena-((μ_2-isothiocyanato-*N,S*)-(μ_2-thiocyanato-*N,S*)-bis(DD18C6)-di-potassium) [4]. In contrast, the protonation of the azacrown ether inhibits the inclusion of the lanthanoid species, affording complex metal-containing anion species interspersed between a network of crown molecules [11]. In a similar way, the recently reported structures

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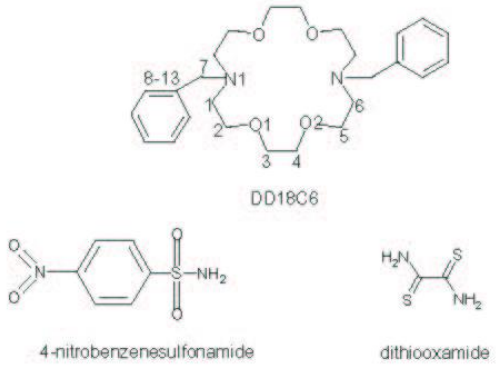
of $(H_2DD18C6)\cdot 2(BF_4)\cdot H_2O$ [12] and $(H_2DD18C6)\cdot I_3$ [13] revealed the unusual C–H···π interactions between the phenyl substituents and two macrocyclic methylene protons which effectively anchor the ring into its folded conformation and inhibits flexing, which has often been observed with the macrocycles of this type. This type of interaction is quite unusual as a methylene hydrogen is participating in this interaction, rather than the hydrogen of a water molecule [12].

Two other reported structures, [DD18C6·2(2,4,6-trinitrophenol)] [14] and $[H_2DD18C6\cdot 2(H_2O)][UO_2Cl_4]$ [11] reveal the guest species, 2,4,6-trinitrophenolate anions or water molecules residing on either side of the doubly protonated macrocycle, the first complex being sustained by two NH···O(phenolate) hydrogen bonds with the benzyl arms arranged approximately perpendicular to the macrocyclic cavity, while in the second complex the $[H_2DD18C6\cdot 2H_2O]$ unit is stabilized by two OH···O and two NH···O hydrogen bonds with benzyl arms arranged outward the macrocyclic cavity. This last example demonstrates that by the incorporation of water molecules into macrocyclic ring, hydrogen bonding within the azacrown ligand is introduced, and these interactions disrupt the intramolecular C–H···π bonding.

Surprisingly, so far there are no examples of genuine host–guest complexes of DD18C6 with neutral molecules where the macrocycle incorporates in its neutral form. In order to fill this gap, we have tried 4-nitrobenzenesulfonamide, $4\text{-}O_2NPhSO_2NH_2$, 4-aminobenzenesulfonamide, $4\text{-}H_2NPhSO_2NH_2$, dithiooxamide, $(H_2NCS)_2$ and dithiobiurea, $(H_2NNHCS)_2$ molecules for complex formation. All these molecules are rich in proton-donor functions to facilitate the hydrogen-bonding with the H-acceptor centers of DD18C6 molecule and previously exhibited themselves as very suitable candidates for complex formation with sterically hindered macrocycles [15]. All the reactions were carried out in the same synthetic conditions, however, only two complexes, with 4-nitrobenzenesulfonamide and dithiooxamide were obtained in the form of the crystals suitable for the X-ray analysis.

Here, we report on the X-ray crystal structures of 1:2 complex of DD18C6 host with 4-nitrobenzenesulphonamide (complex **1**) and 1:1 complex with dithiooxamide (complex **2**), both being composed of neutral molecules and sustained by the combination of NH···O and NH···N hydrogen bonding (Scheme 1).



Scheme 1. Schematic presentation of the DD18C6, 4-nitrobenzenesulfonamide and dithiooxamide molecules with the atomic numbering scheme in the crown molecule.

2. Experimental

Commercially available reagents were used as received. Complexes **1** and **2** were analyzed for C, H, N and S in a Perkin–Elmer 240C. The thin-layer chromatographic control of the substance purity was performed on Silufol UV-254 plates. ^{1}H NMR spectra were recorded at 300 MHz on a Varian Oxford 300 NMR spectrometer relative to $DMSO_{d6}$.

2.1. Synthesis

1. DD18C6 (44 mg, 0.1 mmol) and 4-nitrobenzenesulfonamide (40 mg, 0.2 mmol) were dissolved in methanol (1 ml) at 64 °C, following the addition of ethyl acetate (2 ml) and *n*-butanol (0.1 ml). The resulting clear solution was slowly reduced in volume by evaporating the solvents at room temperature. Colorless transparent crystals m.p. 140 °C. Analysis: found C 53.94, H 5.98, N 9.97%; $C_{38}H_{50}N_6O_4$ requires C 53.89, H 5.95, N 9.92%. ^{1}H NMR, δ: 3.52m (28H, CH_2N, CH_2O–DD18C6), 7.11m, 8.32m (18H, CH–Ph).
2. DD18C6 (44 mg, 0.1 mmol) and dithiooxamide (12 mg, 0.1 mmol) were dissolved in methanol (2 ml) at 64 °C, following the addition of ethylacetate (4 ml), *n*-butanol (0.1 ml). The resulting clear solution was slowly reduced in volume by evaporating the solvents at room temperature. Red transparent crystals, mp 118–120 °C. Analysis: found C 52.73, H 6.82, N 12.37%; $C_{28}H_{42}N_4O_4S_2$ requires C 52.76, H 6.79, N 12.30%.^{1}H NMR, δ: 2.05s (8H, NH_2-dithiooxamide), 3.52m (28H, CH_2N, CH_2O–DD18C6), 7.11m (10H, CH–Ph).

2.2. X-ray crystallography

The X-ray intensity data for **1** and **2** were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo Kα radiation using ϕ–ω scans [16]. Unit cell parameters were obtained and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO [17]. The scaling and the global refinement of crystal parameters were performed by SCALEPACK [17]. The recorded data were corrected for polarization and Lorentz effects. The structure solution and refinement proceeded similarly for both structures using SHELX97 program package [18]. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were treated anisotropically (full-matrix least squares method on F^2). In complex **2** O(2B) and C(5B) atoms were assumed to be disordered over two orientations. The occupancy factors refined to 0.759(1) for the major component and 0.241(1) for the minor component, the minor position was treated

Table 1
Crystal data summary for complexes **1** and **2**

Complex	1	2
CCDC number	294975	294976
Empirical formula	$C_{38}H_{50}N_6O_{12}S_2$	$C_{28}H_{42}N_4O_4S_2$
Formula weight	846.96	562.78
Temperature (K)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\text{-}1$
Unit cell dimensions		
a (Å)	9.256(2)	8.458(2)
b (Å)	9.214(2)	9.314(1)
c (Å)	24.379(5)	20.098(5)
α (°)	90.0	87.51(1)
β (°)	100.87(3)	85.46(1)
γ (°)	90.0	67.52(1)
Cell volume (Å^3)	2041.9(7)	1458.2(5)
Formula units/unit cell	2	2
D_{calc} (g/cm^{-3})	1.378	1.282
μ (mm^{-1})	0.200	0.222
F (000)	896	604
Crystal dimensions (mm)	0.25×0.25×0.20	0.30×0.25×0.15
θ Range for data collection (°)	2.37–24.15	2.37–22.38.
Limiting indices	$-10\le h\le 10$, $-10\le k\le 10$, $-27\le l\le 27$	$-8\le h\le 8$, $-9\le k\le 9$, $-21\le l\le 21$
Reflections collected/unique	10771/3192 [R(int) = 0.0857]	5761/3414 [R(int) = 0.0695]
Reflections with $I>2\sigma(I)$	2609	1926
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3192/0/270	3414/3/364
Goodness-of-fit on F^2	1.191	0.983
Final R indices [$I>2\sigma(I)$] %	R_1 = 0.0872, wR_2 = 0.1719	R_1 = 0.0998, wR_2 = 0.2553
R indices (all data) %	R_1 = 0.1124, wR_2 = 0.1809	R_1 = 0.1651, wR_2 = 0.2869
Largest diff. peak and hole (eÅ^{-3})	0.499/−0.321	0.923/−0.326

isotropically. C-bound hydrogen atoms were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while the N-bound H-atoms were found from differential Fourier maps at an intermediate stage of the refinement and were treated isotropically subject to SADI restraint in complex **2**. The X-ray data and the details of the refinement for **1** and **2** are given in Table 1, H-bonding data are given in Table 2, the torsion angles in DD18C6 in **1** and **2** are summarized in Table 3.

3. Results and discussion

3.1. Complex I

Fig. 1 reveals the ORTEP view of molecular complex **1**, comprised of one DD18C6 and two 4-nitrobenzenesulphonamide molecules. The macrocyclic molecule resides on the inversion center and adopts a C_i extended conformation with the phenyl groups splayed outward the macrocyclic cavity (the torsion angles for the independent part of the molecule are given in Table 3). The 1:2 unit is sustained by two N–H···N and two N–H···O hydrogen bonds, N(2)···O(2) 2.960(6) and N(2)···N(1) 3.009(6) Å. The N–S bond is arranged approximately perpendicular to the mean plane of six heteroatoms of the macrocycle, which are coplanar within ± 0.237 Å, and N(2) atom deviates at 1.536(4) Å from the same plane. The dihedral angle between the least-square planes through the six heteroatoms of DD18C6 and phenyl ring of the guest molecule is equal to 26.9(2)°, while the dihedral angle between the aromatic rings of the host and guest molecules is equal to 38.5(2)°.

The complexes are packed in a herringbone motif along [100] direction in the crystal (Fig. 2) in such a way to maximize

Table 2
Hydrogen bonding in complexes **1** and **2**

D–H···A	r(D–H) (Å)	r(H···A) (Å)	r(D···A) (Å)	∠(DH···A) (°)
1				
N(2)–H(1N2)···N(1)	0.90(7)	2.11(7)	3.009(6)	177(6)
N(2)–H(2N2)···O(2)	0.80(5)	2.16(5)	2.960(6)	179(4)
2				
N(2A)–H(2N)···O(2A)	0.86(5)	2.37(6)	3.223(9)	167(8)
N(2A)–H(1N)···N(1A)	0.86(5)	2.27(5)	3.129(8)	172(8)
N(2B)–H(4N)···O(2B*)	0.99(3)	2.57(2)	3.54(3)	168(6)
N(2B)–H(3N)···N(1B)	0.98(4)	1.94(4)	2.913(8)	170(7)

Table 3
Selected torsion angles (°) in the DD18C6 molecule in complexes **1** and **2**

Complex	1[a]	2a[a]	2b[a]
N(1)–C(1)–C(2)–O(1)	72.2(5)	57.3(8)	−59.7(9)
C(1)–C(2)–O(1)–C(3)	−179.1(4)	−178.1(6)	−168.0(7)
C(2)–O(1)–C(3)–C(4)	174.6(4)	177.3(6)	177.7(7)
O(1)–C(3)–C(4)–O(2)	−64.2(5)	−61.8(9)	−84.3(9)
C(3)–C(4)–O(2)–C(5)	−158.1(4)	−77.0(8)	77.0(11)
C(4)–O(2)–C(5)–C(6)	174.5(4)	−178.9(6)	165.6(8)
O(2)–C(5)–C(6)–N(1)#1	−60.5(5)	−170.2(6)	−179.9(10)
C(5)–C(6)–N(1)#1–C(1)#1	172.3(4)	174.3(6)	60.3(9)
C(6)–N(1)#1–C(1)#1–C(2)#1	−72.1(5)	−51.8(8)	−163.1(6)

[a] Symmetry transformations used to generate equivalent atoms: $1-x+1, -y+1, -z+1$ (complex **1**); #1 $-x, -y+1, -z+2$ (complex **2a**); #1 $-x, -y+1, -z+1$ (complex **2b**).

the T-shape arrangement of the phenyl rings of the molecules that belong to the neighboring complexes.

3.2. Complex 2

DD18C6 and dithiooxamide molecules form molecular complex **2** of 1:1 ratio. Fig. 3 shows two crystallographically independent complexes (**a** and **b**) of complex **2**. Both DD18C6 and dithiooxamide molecules reside on the inversion centers. Complexes **a** and **b** differ by the disordering of two neighboring atoms, O(2B) and C(5B) of the oxyethylene chain in complex **b**. Similar to complex **1**, in complex **a** amino-group of dithiooxamide molecule is involved into one NH···O and one NH···N rather weak hydrogen bonds, N(2A)···O(2A) 3.223(9) and N(2A)···N(1A) 3.129(8) Å. While the NH···N hydrogen bond, N(2B)···N(1B) 2.913(8) Å also exists in complex **b**, the second hydrogen atom of amino-group is directed toward the minor position of O(2B) atom, O(2B*) at N(2B)···O(2B*) separation equal to 3.54(3) Å.

In the planar skeleton of dithiooxamide molecule, the non-hydrogen atoms are coplanar within ±0.004 Å in complex **a**, and within ±0.007 Å in complex **b**. The dithiooxamide molecules are arranged approximately perpendicular to the mean plane of six (2N+4O) heteroatoms of the corresponding



Fig. 1. ORTEP view of complex **1** with the partial numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown by dashed lines.

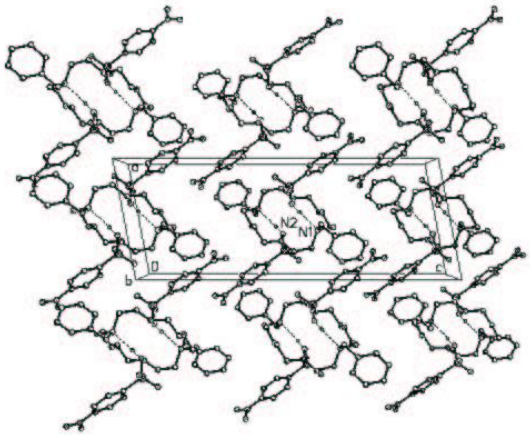


Fig. 2. Herringbone motif of packing of complexes **1** in the crystal. C-bound H atoms are omitted for clarity.

macrocycle, the dihedral angle is equal to 78.9(2)° in complex **a** and 76.6(2)° in complex **b**. N(2A) atom deviates at 2.358(8) Å from the mean plane of six heteroatoms of the macrocycle **a**, while N(2B) atom deviates at 2.357(8) Å from the mean plane of six heteroatoms of the macrocycle **b**. Through the above mentioned hydrogen bonds the molecules are combined into chains running along [110] direction in the crystal (Fig. 4).

The hydrogen bonding mode of the host–guest interactions is quite similar in **1** and **2a** as it involves in a similar way a pair of nitrogen and a pair of oxygen atoms of the DD18C6 molecule separated by the oxyethylene fragment.

The shape of the centrosymmetric DD18C6 molecule is very close in two complexes, with two phenyl substituents extended horizontally away from the macrocyclic ring, and being coplanar in a similar fashion to the uncoordinated ligand [4,8,12] (Fig. 5). In complex **1** the DD18C6 molecule has a rather regular shape with six heteroatoms alternatively deviating from the mean plane at ±0.237 Å, trans-annular

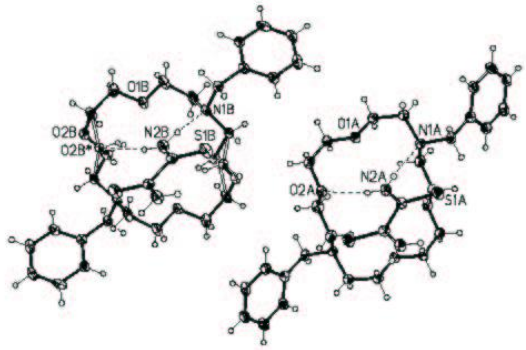


Fig. 3. ORTEP view of two independent complexes (a and b) in complex **2** with the partial numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown by dashed lines. The disordered fragment is shown by open lines.

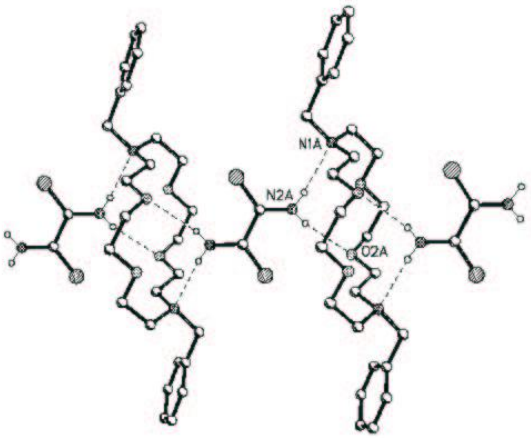


Fig. 4. Fragment of chain in complex **2** (chain a). C-bound H atoms are omitted for clarity.

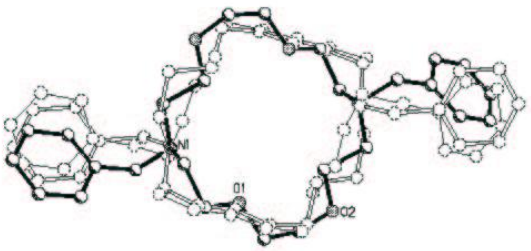


Fig. 5. Fitting of three DD18C6 molecules in complexes **1** and **2** on the plane of six (2N+4O) heteroatoms of macrocycle. The DD18C6 molecules are shown by: solid (complex **1**), open (complex **2a**) and dashed (complex **2b**) lines.

O···O distances being 5.114(6) and 5.772(6) Å and N···N distance being 6.414(8) Å. All C–C bonds are in an energetically preferable gauche-conformation, all C–O bonds are in an energetically preferable trans-conformation, one of two C–N bonds is in gauche- and one—in trans-conformation. In the **2a** unit, six heteroatoms of the DD18C6 molecule alternatively deviate from the mean plane at ±0.396 Å, trans-annular O···O distances being 5.54(1) and 6.214(9) Å and N···N distance being 6.70(1) Å. In the **2b** unit, the DD18C6 molecule has the most flatten shape with six heteroatoms alternatively deviating from the mean plane at ±0.145 Å, and trans-annular O···O distances being 5.30(1) and 7.18(2) Å and N···N distance being 6.32(1) Å. The distribution of C–C and C–O torsion angles is absolutely the same in **2a** and **2b** units, with two C–C bonds being in gauche- and one in trans-conformation, and three C–O bonds in trans-and one—in gauche-conformation. One of two C–N bonds is in gauche- and one—in trans-conformation and vice versa.

4. Conclusion

For the first time the host–guest complexes of bibracchial diazacrown ether, *N,N′*-dibenzyl-1,7,10,16-tetraoxo-4,13-diazacyclooctadecane (DD18C6) with 4-nitrobenzenesulfonamide, $4\text{-}O_2NPhSO_2NH_2$ and dithiooxamide, $(H_2NCS)_2$ were synthesized in approximately the same conditions and characterized by X-ray diffraction analysis. The molecular complexes are sustained by conventional NH···O and NH···N hydrogen bonds. The macrocyclic ligand conformation is slightly different from its uncomplexed form.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.01.040. Crystallographic data for the structural analysis of complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 294975 and 294976. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Додаток 62

Копія статті (4R)-4-Hydroxy-1-nitroso-L-proline: synthesis, X-ray structure, ab initio and conformational calculations

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(4*R*)-4-Hydroxy-1-nitroso-L-proline: synthesis, X-ray structure, ab initio and conformational calculations

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Abstract 4-Hydroxy-L-proline, an amino acid, an important component of collagen, was transformed into its *N*-nitroso-derivative, (4*R*)-4-hydroxy-1-nitroso-L-proline, **1** by butylnitrite in the acidic medium. The structure is a cyclic hydroxy-*N*-nitrosoacid with the carboxyl and hydroxyl groups trans to each other. The carboxyl group is in the *syn*-conformation. In the structure, the neutral molecules are connected via classical intermolecular O H···O hydrogen bonds involving the hydroxyl and carboxyl groups [O···O=2.6251(14) Å], and form chains along the *a*-axis direction. The chains are linked into sheets via O H···O hydrogen bond, [O···O=2.6813(15) Å] with participation of oxygen atom of nitroso group. Ab initio calculations based on density functional theory at the B3LYP/6-311++G(d, p) level of theory were performed to analyze the influence of 4-hydroxy-L-proline (Hyp) nitrosation on the conformation of the synthesized *N*-nitroso-compound. The geometry optimization of **1** and initial 4-hydroxy-L-proline was carried out in the gas phase and in solution using the polarizable continuum model. The single-point calculation was performed for the crystal structure of **1**. The most stable conformer of **1** is observed in an aqueous solution. In this state, the pyrrolidine ring adopts an envelope conformation, which is also maintained in the gas phase. The twisted conformation of the pyrrolidine ring is present in all states of Hyp and in the crystal structure of **1**. In **1** the interchange of five-membered ring conformation in solution and in the gas phase in comparison with the crystal is accompanied by an increase of the dipole moment of the molecule, which is maximal in solution.
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1. Introduction

The functional specificity of proteins and polypeptides depends on the conformational behavior of the initial amino acids, which are extensively studied by theoretical and experimental methods.[1] L-Proline (Pro) and 4(*R*)-hydroxy-L-proline (Hyp) are abundant amino acids in collagen and exceptional among amino acids, as they are the only ones that have the amino group fixed within a pyrrolidine ring, making it rigid and directional in biological systems despite its conformational flexibility. Due to its crucial biological role (it is the most abundant protein in vertebrates) and very peculiar structure, collagen has been deeply investigated, together with several related polypeptides. Collagen is composed of approximately 300 repeats of the sequence $X_{aa}Y_{aa}$Gly, where X_{aa} and Y_{aa} are in most cases Pro and Hyp, respectively. The occurrence of Pro and Hyp in collagen restricts the orientational freedom of the chain in relation to the fiber axis and permits only left-handed helices.[2]

The importance of Pro and Hyp explains the extensive theoretical and structural studies of these amino acids and their derivatives including several di- and polypeptides. Aside from recent electron-density studies and quantum chemical investigations, the study of amino acid clusters in the gas phase has attracted considerable attention. The stereoelectronic effects crucial for the collagen stability have been studied, as well as quantum mechanical calculations for Pro, Hyp, and fluorinated dipeptide analogues in aqueous solution and for the Pro gaseous isomers have been fulfilled.[3] Moreover, in a recent paper, Conticello et al. discuss in detail the stereoelectronic effects in elastin-mimetic polypeptides due to Pro substitution.[4]

The structural studies of vitally important amino acids are fundamentally important. With respect to the metal free Pro and Hyp, so far the crystal structures of L-Pro and DL-Pro,[5,6]

Keywords: Oxyproline; Nitrosation; X-ray structure; Theoretical calculations.
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the monohydrates of L-Pro and DL-Pro[7,8] and numerous other solvates and salts of Pro have been determined. For Hyp and its derivatives, structural data are available for the zwitterion of 4-hydroxy-L-proline itself defined by X-ray analysis[9,10] and precision neutron diffraction,[11] 4-hydroxy-L-proline hydrate,[12] 4-hydroxy-*N*-methylproline,[13] and *N*,*N*′-dimethylated 4-hydroxy-D- and 4-hydroxy-L-proline chloride.[14] The acyclic peptides, ALB*-ALB-PRO* (three residues) and PRO*-PRO* were also described.[15,16]

As the only amino acids with the imino group, Pro and Hyp were extensively studied to elucidate the conditions responsible for the generation of carcinogenic *N*-nitroso-derivatives. A dose–response study on the endogenous formation of *N*-nitrosoproline was performed in rats, dogs, and in smokers and non-smokers. Solutions containing nitrite, proline, and in some cases ascorbic acid (ASC) and/or SCN^- were infused into the stomach and samples taken to determine gastric [nitrite], [NPro], [ASC], [SCN^-], and pH as functions of time. The ability of ASC to inhibit nitrosation (by reaction with nitrite) was shown to be highly dependent on initial [ASC] and on the rate of entry of O_2 into the stomach from blood. The rate of *N*-nitroso-Pro formation in the absence of ASC and SCN^-, the inhibitory effects on nitrosation of ASC, and the catalytic effects of SCN^- were all accurately predicted by the mathematical model.[17]

2. Results and discussion

In continuation of our previous studies devoted to the conditions of mutagenesis of the biologically important molecules to their carcinogenic *N*-nitroso-derivatives[18] and the stereochemistry of *N*-nitroso-compounds,[19] the nitrosation of 4-hydroxy-L-proline (**Hyp**) by butylnitrite[20] in the acidic medium has been fulfilled and the crystal structure of *N*-nitroso-derivative, 4-hydroxy-1-nitrosopyrrolidine-2-carboxylic acid **1**, was studied by X-ray crystallography (Fig. 1). The aim of this article is to study the product of **Hyp** nitrosation analyzing the structural peculiarities of *N*-nitrosooxyproline in the crystalline, liquid, and gaseous phases.

X-ray structural analysis was carried out at 100 K that permits the unambiguous localization of all the hydrogen atoms and to state that the molecule exists in the crystal in its neutral form. In the neutral molecule **1**, the hydroxyl and carboxyl groups are in the trans configuration relative to the ring, as found earlier for the zwitterions of L-Hyp,[9,11] 4-hydroxy-*N*-methylproline[13] and its hydrochloride salt[14] and differs from *cis*-zwitterion of Hyp in its dihydrate.[12] Molecular bond distances and bond angles as well as torsion angles, labeled according to the IUPAC conventions,[21] are given in Tables 1 and 2, respectively. The average C–C length of 1.530(2) Å is in agreement with 1.533(8) Å in Hyp dihydrate. The carboxylic group is in a *syn*-orientation and practically planar with the asymmetrical C(1)–O(2) 1.204(2) and C(1)–O(1) 1.328(2) Å distances which are consistent with the double and single C–O bonds. C(4)–O(3) length of 1.433(2) Å is consistent with 1.435(7) Å obtained by Shamala et al.[12] The *N*-nitroso-group has an ordinal geometry[19] with the equalized O(4)–N(2) 1.266(1) and N(1)–N(2) 1.289(2) Å distances and N–N–O bond angle O(4)–N(2)–N(1) 113.3(1)°. The dihedral angles formed by the carboxyl [O(1)/C(1)/O(2)] and nitroso [N(1)/N(2)/O(4)] groups with the pyrrolidine ring are equal 65.4(1)° and 11.4(1)°, respectively.

Two approaches could be applied to describe the puckering of the pyrrolidine ring. Generalization by Cremer and Pople[22] requires specification of an appropriate mean plane and uses the displacements of each atom from that plane to define puckering coordinates (q is a puckering amplitude and ψ is a phase angle). Geise et al.[23] use endocyclic torsion angles and thus avoid the need to define a mean plane. We use the advantages of both of these approaches and say that the pyrrolidine ring is in a twisted form with C^γ [C(4)] atom lying 0.608(2) Å [0.516 Å in Hyp[11]] below the plane through N, C^α, C^β, and C^δ, and with the latter four atoms coplanar to within 0.0367 Å [0.037(3) Å in Hyp]. The dihedral angle between the planes N–C^α–C^β–C^δ and C^α–C^β–C^γ–C^δ is 39.6(1)° [33.5° in Hyp]. The pyrrolidine ring conformation corresponds to the C^γ-*endo* or down puckering. The Cremer and Pople puckering ring parameters for **1** are gathered in Table 3 in comparison with those for Hyp and Pro derivatives. The closeness of the conformations for **1**, Hyp, and Pro monohydrates is evident.

To compare the puckering of the pyrrolidine ring in **1** and some derivatives of Hyp we use the data available in the Cambridge Structural Database.[24] Compound **1** and some structurally related molecules were fitted by the same atoms in the pyrrolidine ring skeleton. Figure 2 reveals the overlap

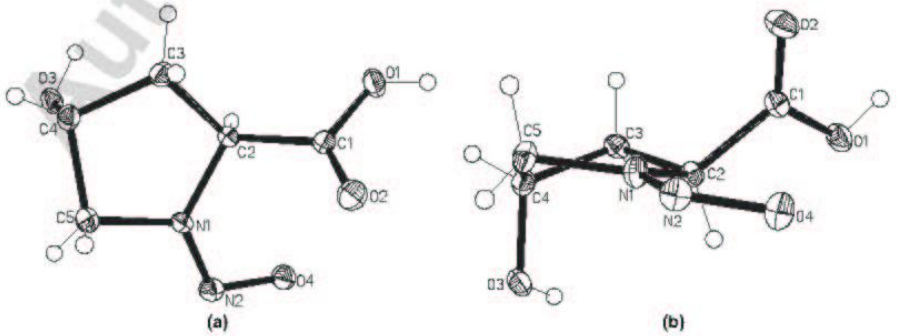

Figure 1. ORTEP (a) top and (b) side view of **1**. Thermal ellipsoids are drawn with the 50% probability level.

Table 1. Bond lengths (Å) and angles (degree) for **1** in crystal, in the gas phase (ε=1), and in solution (ε=78.4)

	Crystal	ε=1	ε=78.4
Bond distances			
O(1)–C(1)	1.328(2)	1.349	1.334
O(1)–H(1)	0.83(3)	0.97	0.99
O(2)–C(1)	1.204(2)	1.203	1.211
O(3)–C(4)	1.433(2)	1.426	1.427
O(3)–H(3O)	0.90(2)	0.96	0.98
O(4)–N(2)	1.266(1)	1.226	1.242
N(1)–N(2)	1.289(2)	1.319	1.299
N(1)–C(2)	1.473(2)	1.466	1.472
N(1)–C(5)	1.477(2)	1.465	1.472
C(1)–C(2)	1.529(2)	1.524	1.523
C(2)–C(3)	1.536(2)	1.547	1.548
C(2)–H(2)	0.97(2)	1.09	1.1
C(3)–C(4)	1.532(2)	1.541	1.541
C(3)–H(31)	0.98(2)	1.09	1.09
C(3)–H(32)	0.96(2)	1.09	1.09
C(4)–C(5)	1.522(2)	1.528	1.526
C(4)–H(4)	0.97(2)	1.1	1.1
C(5)–H(51)	0.91(2)	1.09	1.09
C(5)–H(52)	0.96(2)	1.09	1.09
Bond angles			
C(1)–O(1)–H(1)	109(2)	107	109
C(4)–O(3)–H(3O)	109(2)	109	109
N(2)–N(1)–C(2)	124.4(1)	123.4	124.2
N(2)–N(1)–C(5)	121.7(1)	121.6	121.6
C(2)–N(1)–C(5)	113.5(1)	114.2	113.6
O(4)–N(2)–N(1)	113.3(1)	114.4	115.2
O(2)–C(1)–O(1)	125.6(1)	123.9	124.5
O(2)–C(1)–C(2)	124.5(1)	124.8	124.5
O(1)–C(1)–C(2)	109.8(1)	111.2	111.0
N(1)–C(2)–C(1)	111.9(1)	111.6	111.9
N(1)–C(2)–C(3)	101.7(1)	102.2	102.4
C(1)–C(2)–C(3)	112.4(1)	112.0	112.4
N(1)–C(2)–H(2)	107(1)	109	109
C(1)–C(2)–H(2)	111(1)	109	109
C(3)–C(2)–H(2)	113(1)	113	112
C(4)–C(3)–C(2)	103.7(1)	104.5	104.4
C(4)–C(3)–H(31)	111(1)	109	109
C(2)–C(3)–H(31)	109(1)	113	110
C(4)–C(3)–H(32)	113(1)	110	112
C(2)–C(3)–H(32)	110(1)	113	112
H(31)–C(3)–H(32)	110(2)	108	109
O(3)–C(4)–C(5)	109.0(1)	107.1	107.5
O(3)–C(4)–C(3)	110.5(1)	112.4	112.1
C(5)–C(4)–C(3)	102.8(1)	103.1	102.9
O(3)–C(4)–H(4)	111(1)	111	111
C(5)–C(4)–H(4)	112(1)	112	112
C(3)–C(4)–H(4)	112(1)	113	111
N(1)–C(5)–C(4)	101.6(1)	102.5	102.4
N(1)–C(5)–H(51)	108(1)	111	110
C(4)–C(5)–H(51)	116(1)	110	113
N(1)–C(5)–H(52)	107(1)	112	110
C(4)–C(5)–H(52)	111(1)	111	111
H(51)–C(5)–H(52)	113(2)	110	110

of two molecules. It is evident that the best fitting was found for the zwitterion of Hyp, where the atoms of the pyrrolidine rings of the two molecules fit within 0.06 Å. Figure 2 also reveals an essential difference in an arrangement of the carboxylic and hydroxyl groups that is evident from the corresponding torsion angles. Torsion angles for Hyp in Table 2 are taken from Ref. 11.

A view of the molecular packing and hydrogen-bonding scheme is shown in Figure 3. The hydrogen-bonding geometry is summarized in Table 4. A classical hydrogen bond between the carboxyl hydrogen and the hydroxyl oxygen links the molecules into chains parallel to the [100] direction that can be described by the first level graph set, C(7).[26] Along the [010] direction the hydroxyl group acts as H-donor, being involved in an O–H···O hydrogen bond with the nitroso group oxygen via again C(7) graph set and the second level graph set, $R_4^4(23)$, thus generating the H-bonded sheet. Between the layers only one type of contact C(3)–H(31)···O(4) 3.152(2) Å deserves to be mentioned.

The rather close crystal packing is observed in Hyp itself,[9,11] where the molecules are also combined in the chains via the same C(7) O–H···$^-$OOC synthon, and the chains being further combined in the layer via NH_2^+(ammonium)···$^-$OOC(carboxyl) interactions analogous to those with nitroso group involvement in **1**.

In the analysis of the conformational and intermolecular characteristics of *N*-nitroso-compounds, it is of basic importance to consider environmental effects, so the ab initio calculations at the density functional theory (DFT) level have been thus fulfilled both in gas phase (ε 1) and in an aqueous solution (ε 78.4). To obtain a more definitive estimate of the conformational flexibility and relative stabilities of **1** in different states, geometry optimization was carried out in the solution using the polarizable continuum model (PCM) and in the gas phase. The single-point calculation was performed for the crystal structure. The computed SCF energies and energy differences for **1** in different states are summarized in Table 5.

The criteria of Cremer and Pople[22] have been used to analyze the non-planar character of the five-membered ring. Thus, a 'pure envelope' conformation with apex at 1 would be such that

$$z_2 \quad z_5, z_3 \quad z_4, \quad \psi \quad k \times 36, \tag{1}$$

and a 'pure twist' with axis through 1 would have

$$z_1 \quad z_2 + z_5 \quad z_3 + z_4, \quad \psi \quad k \times 36 + 18, \tag{2}$$

where the values of z_i are the displacements of *i*th atom perpendicular to the least-square plane.

However, it should be noted that for a ring with unequal lengths and angles, the conditions in Eq. 1 do not necessarily imply coplanarity of atoms 2–5. The list of z_i values for **1** in different states is summarized in Table 6.

The most stable conformer of **1** is observed in an aqueous solution. In this state according to the criteria of Cremer and Pople (Tables 3 and 6) the pyrrolidine ring adopts an envelope conformation, which is also maintained in the gas phase. The deviations of the carbon atom C(4) from the best-fit planes [N(1)/C(2)/C(3)/C(5)] in the solution and gas phase are equal to 0.57 and 0.56 Å, respectively. In the crystal structure of **1** the pyrrolidine ring adopts a conformation, which is twisted on C(3)–C(4) bond. Therefore for **1** we performed the conformational search (CS) implemented in Hyperchem 6.03 using the MM+ force field varying the dihedral angles inside the pyrrolidine ring. The envelope conformation of this ring is maintained in the lowest energy

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Table 2. Torsion angles (degree) for **1** and L-Hyp[11]

IUPAC designation[21]	Atoms involved		**1**	L-Hyp[11]
ψ^1	O^1–C–C^α–N^1	O(1)–C(1)–C(2)–N(1)	151.2(1)	3.2(2)
ψ^2	O^2–C–C^α–N	O(2)–C(1)–C(2)–N(1)	31.6(2)	178.7(1)
χ^1	N^1–C^α–C^β–C^γ	N(1)–C(2)–C(3)–C(4)	30.0(1)	18.3(2)
$\chi^1_{2,1}$	C^α–C^β–C^γ–O^δ	C(2)–C(3)–C(4)–O(3)	73.6(1)	87.0(2)
$\chi^1_{2,2}$	C^α–C^β–C^γ–C^δ	C(2)–C(3)–C(4)–C(5)	41.4(1)	32.0(2)
$\chi^1_{3,1,1}$	$H^{\delta1}$–O^δ–C^γ–C^β	H(3O)–O(3)–C(4)–C(3)	30.7(2)	158.8(2)
$\chi^1_{3,1,2}$	$H^{\delta1}$–O^δ–C^γ–C^δ	H(3O)–O(3)–C(4)–C(5)	142.4(2)	87.7(2)
$\chi^1_{3,2,1}$	O^δ–C^γ–C^δ–N	O(3)–C(4)–C(5)–N(1)	81.7(1)	84.0(1)
$\chi^1_{3,2,2}$	C^β–C^γ–C^δ–N^1	C(3)–C(4)–C(5)–N(1)	35.2(1)	33.5(2)
χ^4	C^γ–C^δ–N^1–C^α	C(4)–C(5)–N(1)–C(2)	17.3(1)	23.1(1)
χ^5	C^δ–N^1–C^α–C^β	C(5)–N(1)–C(2)–C(3)	8.0(1)	3.1(1)
	O^4–N^2–N^1–C^α	O(4)–N(2)–N(1)–C(2)	4.6(2)	—
	O^4–N^2–N^1–C^δ	O(4)–N(2)–N(1)–C(5)	176.6(1)	—

Table 3. Computed ring puckering parameters for **1**, L-Hyp,[a] and Pro[b]

Compound	Crystal		Solution (ε=78.4)		Gas phase (ε=1)		Conformers **1a**, **1H**	
	q/Å	ψ/°	q/Å	ψ/°	q/Å	ψ/°	q/Å	ψ/°
1	0.403(1)	276.1(2)	0.373	0.363	279.3	281.9	0.330	280.2
L-Hyp	0.236	309.6	0.376	0.371	270.3	314.1	0.384	336.4
DL-Pro	0.403(2)	57.7(2)						
L-Pro	0.404	89.1						
DL-Pro monohydrate	0.4033(5)	308.63(7)						
L-Pro monohydrate	0.395(4)	309.9(6)						

[a] Atomic coordinates for the computing calculations are taken from Cambridge Structural Database (refcode HOPROL).
[b] All cited puckering parameters for Pro are taken from Ref. 6.

conformer **1a** according to the criteria of Cremer and Pople (Tables 3 and 6). In this molecule the deviation of the C^γ [C(4)] carbon atom from the best-fit plane [N(1)/C(2)/C(3)/C(5)] is equal to 0.51 Å and the values of O(2)–C(1)–C(2)–N(1) (52.0°) and O(3)–N(2)–N(1)–C(2) (11.1°) torsion angles are maximal in comparison with those in other states. For the crystal, gas, and solvent states these values are equal to 31.6(2)°, 4.6(2)°; 41.18°, 6.55°; and 33.67°, 5.86°, respectively. The change of pyrrolidine ring conformation in solution and in gas phase in comparison with the crystal is accompanied by an increase in the dipole moment of the molecule, which is maximal in solution (Table 5).

In order to study the influence of nitrosation on the conformation of pyrrolidine ring, the DFT-based geometry optimizations as well as the CS implemented in Hyperchem 6.03 were carried out for hydroxy-L-proline (Hyp) in solution, gas, and crystal phases. The atomic numbering scheme for hydroxy-L-proline (Hyp) is the same as that of compound **1**. As in the case of **1**, the most stable conformer is observed in solution (Table 5). In the crystal and in solution, the pyrrolidine ring adopts the conformation twisted on the C(4)–C(5) bond. In the gas phase and in the conformer **1H** the pyrrolidine rings are twisted on C(3)–C(4) and N(1)–C(5) bonds, respectively. Thus, the twisted conformation of the pyrrolidine ring is present in all conformers of Hyp and in the crystal structure of **1**. However, due to nitrosation of Hyp, this ring in the crystalline state is twisted on the C(3)–C(4) bond, while in the same state of Hyp the ring is twisted along the C(4)–C(5) bond. In solution and in the gas phase after nitrosation the pyrrolidine ring in **1** adopts an envelope conformation. The optimized geometries of **1** and Hyp in solution and in gas phase as well as bond distances and bond angles in their crystal structures are listed in Table 1.

3. Conclusion

4-Hydroxy-L-proline, an amino acid, an important component of collagen, was transformed into its potentially carcinogenic *N*-nitroso-derivative, 4-hydroxy-1-nitroso-L-pyrrolidine-2-carboxylic acid by butylnitrite in the acidic medium. The X-ray structural analysis and ab initio calculations based on density functional theory at the B3LYP/6-311++G(d, p) level of theory were performed to analyze the influence of the *N*-nitroso-group on conformation of synthesized *N*-nitroso-compound. The most stable conformer of **1** was observed in an aqueous solution. In this state the pyrrolidine ring adopts an envelope conformation, which is maintained in the gas phase. In the crystal structure of **1** this ring adopts a twisted conformation. The change of the five-membered ring conformation in solution and gas phase in comparison with the crystal is accompanied by an increase of the dipole moment of the molecule, which is maximal in solution.

4. Experimental

4.1. General

The initial chemicals were used as received without further purification. IR spectra were recorded on a Specord-80 spectrophotometer as KBr disks. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX-250 instrument (300 MHz ^{1}H; 75 MHz ^{13}C) in dimethylsulfoxide using TMS as an internal reference. Mass spectra were recorded on a MX-1321 device. Mass spectrometer operating at 70 eV. Perkin–Elmer 241 MC polarimeter was used for $[\alpha]_D^{20}$ measurements. Crystallographic measurements were carried out on a PX

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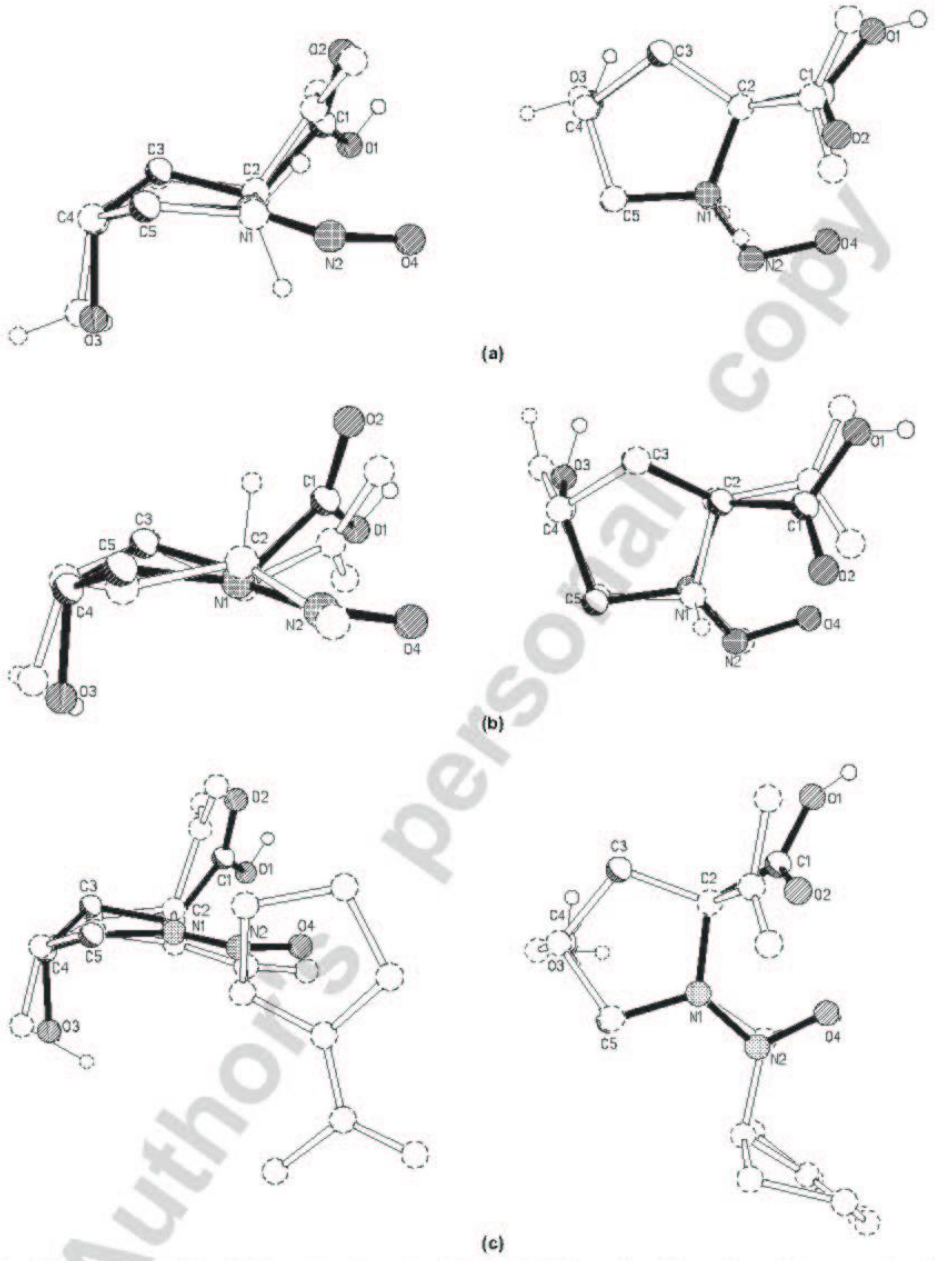

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Figure 2. Fitting of the molecules **1** and Hyp derivatives (side and top views). Molecule of **1** is shown by solid lines. C-bound H-atoms are omitted for clarity. (a) **1** and 4-hydroxy-L-proline[11] (refcode HOPROL12 in CSD). Atoms of the pyrrolidine ring fit within 0.062 Å; (b) **1** and 4-hydroxy-*N*-methylproline[13] (refcode UGUHOT in CSD). Atoms of the pyrrolidine ring fit within 0.172 Å; and (c) **1** and *N*-acetyl-L-prolyl-l-4-hydroxyproline[25] (refcode GLHPRC in CSD). Atoms of the pyrrolidine ring fit within 0.168 Å.

kappa-geometry diffractometer with Onyx CCD camera at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-97 package.[27] All non-hydrogen atoms were refined anisotropically. Locations of all H-atoms were justified by difference Fourier synthesis and refined isotropically. The absolute configuration was not been defined.

Ab initio calculations were carried out using density functional theory with the Gaussian 03 package at the B3LYP/6-311++G(d, p) level of theory.[23] Polarizable continuum model (PCM) was included in the SCF procedure for the description of aqueous solution. The dielectric constant was set at 78.4. All calculations were carried out using the restricted spin formalism (closed-shell). Crystallographic

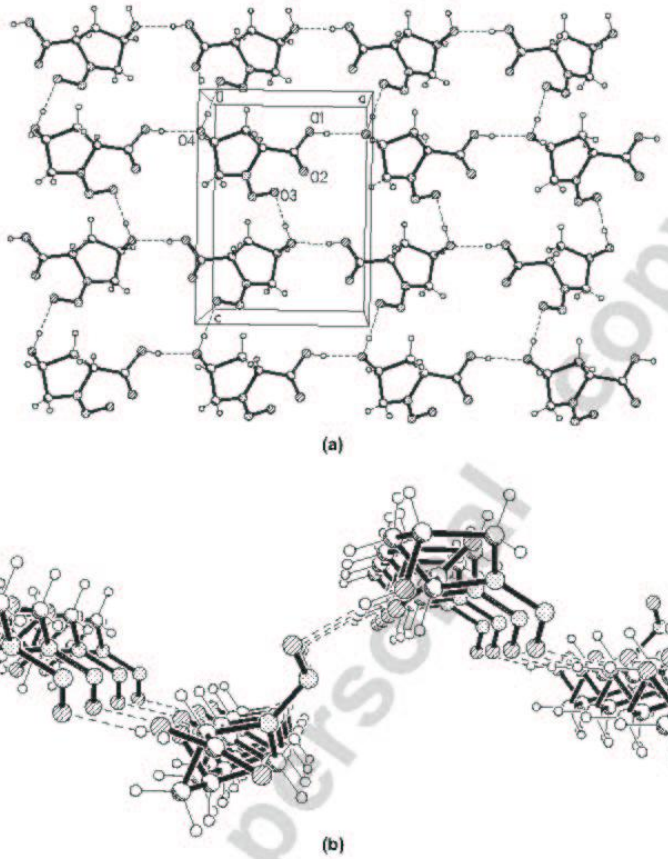

Figure 3. (a) Top and (b) side view of the layer of molecules **1**.

Table 4. Hydrogen-bonding geometry in **1**

D–H···A	*d*(H···A)/Å	*d*(D···A)/Å	∠DHA/°	Symmetry code for acceptor
O(1)–H(1)···O(3)	1.81(3)	2.625(1)	167(3)	*x*+1, *y*, *z*
O(3)–H(3O)···O(4)	1.79(2)	2.681(2)	171(2)	*x*+1/2, *y*+1, *z* 1/2
O(3)–H(3O)···N(2)	2.47(2)	3.254(2)	146(2)	*x*+1/2, *y*+1, *z* 1/2
C(3)–H(31)···O(4)	2.50(2)	3.152(2)	124(1)	*x*+1, *y*+1/2, *z*+1/2

data available for **1** and Hyp provided the initial geometries. The search of conformers was performed using the module conformational search implemented in Hyperchem 6.03[29] for finding low energy conformations of molecular systems by varying user-specified dihedral angles. The method involves random variation of dihedral angles to generate new structures and then energy minimizing of these angles using the MM+ force field. The dihedral angles in a ring are rotated by the 'torsion flexing' motion of Kolossvary and Guida,[30] which effectively leads to new ring conformations while avoiding large atomic displacements that can decrease the efficiency of optimization. The analysis of conformations has been carried out using the PLATON program package.[31]

Table 5. Computed SCF energies, energy differences, and dipole moments for **1** and Hyp compounds in the crystal, gas phase, and in solution and conformers **1a** and **1H**[a]

	1			Hyp		
	E/au	Δ*E*/au	*μ*/D	*E*/au	Δ*E*/au	*μ*/D
Crystal	605.7354	0	6.3821	476.3587	0	2.1041
Gas phase	605.864	0.1286	6.0627	476.5233	0.1646	1.87
Solution	605.902	0.1666	9.1683	476.5532	0.1945	2.4104
1a, **1H**	605.7952	0.0598	6.0367	476.4664	0.1077	5.7367

[a] Conformers found by the conformational search implemented in Hyperchem 6.03 for **1** (**1a**) and **Hyp** (**1H**).

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Table 6. Displacements of pyrrolidine ring atoms from the least-square plane

	z_1	z_2	z_3	z_4	z_5
I					
Atoms of the pyrrolidine ring	N(1)	C(2)	C(3)	C(4)	C(5)
Crystal	0.027(1)	0.129(1)	0.2324(14)	0.249(1)	0.1707(14)
Gas phase	0.037	0.1032	0.204	0.2269	0.1631
Solution	0.0485	0.0963	0.2044	0.2344	0.1748
1a	0.0385	0.0894	0.1831	0.2069	0.1516
Hyp					
Crystal	0.0951	0.0093	0.0801	0.1389	0.1446
Gas phase	0.0014	0.1369	0.2229	0.2237	0.1391
Solution	0.1657	0.0337	0.1112	0.2136	0.2344
1H	0.223	0.123	0.0237	0.1613	0.2374

4.1.1. 4-Hydroxy-1-nitroso-L-pyrrolidine-2-carboxylic acid, 1. 4-Hydroxy-L-proline (0.2 g) was stirred with the solution of butylnitrite (0.3 ml) and glacial acetic acid (0.2 ml) at 25 °C for 7 days. The colorless precipitate of 4-hydroxy-1-nitrosopyrrolidine-2-carboxylic acid was filtered off and recrystallized from a 1:1 mixture of *n*-butanol (5 ml) and methanol (5 ml). The yield of 4-hydroxy-1-nitrosopyrrolidine-2-carboxylic acid was 82%, mp 138–140 °C (dec). Anal. Calcd for $C_5H_8N_2O_4$: C, 37.50; H, 5.04; N, 17.49. Found: C, 37.47; H, 5.09; N, 17.53. IR (cm^{-1}, peaks of strong absorption only, Vaseline oil): 3500–3200, 3170, 3150, 3125, 3120, 3110, 3090, 3080, 3050, 3040, 3030, 3020, 3000–2800, 2780–2570, 1730, 1430, 1365, 1310, 1290, 1280, 1260, 1250, 1190, 1130, 1060. ^1H NMR δ (ppm) (DMSO-d_6, 300 MHz): 1.61 m (2H, CH_2), 2.78 m (2H, CH_2), 3.35 m (1H, CH). ^{13}C NMR δ (ppm) (DMSO-d_6, 300 MHz): 34.62 (C–CH_2–C), 54.15 (C–CH_2–N), 56.18 (C–CH–COOH), 67.54 (C–CH_2–OH), 172.94 (COOH). MS: *m/z* 160(22) (calcd for $C_5H_8N_2O_4$, 160.128) 130(5), 115(46), 88(20), 86(24), 85(16), 84(22), 68(15), 56(100); $[\alpha]_D^{20}$ 1.47.

Crystal data for (**1**), orthorhombic, $P2_12_12_1$, *a* 7.644(2), *b* 8.849(3), *c* 10.303(3) Å, *V* 696.9(4) Å^3, *Z* 4, D_x 1.526 g cm^{-3}, *T* 100 K, λ(Mo Kα) 0.71073 Å, μ 1.33 cm^{-1}, *F*(000) 336, GooF 1.097, *R* indices (all data) *R*1 0.0337, *wR*2 0.0836 for 1369 reflections and 132 parameters and *R* indices *R*1 0.0309, *wR*2 0.0821 for 1261 reflections obeying $I>2\sigma(I)$ criterion of observability.

Crystallographic data for the structural analysis of compound **1** have been deposited at the Cambridge Crystallographic Data Center, CCDC no. 602946. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.06.097.

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Копія статті Hexafluorosilicates of 2-Substituted Anilinium Derivatives

УДК 541.49:546.284.161-32:547.551

КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА ГЕКСАФТОРОСИЛИКАТА *ОРТО*-ТОЛУИДИНИЯ

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Методом РСА определено строение комплекса (o-$CH_3C_6H_4NH_3)_2SiF_6$. В ионной структуре гексафторосиликата анионы SiF_6^{2-} (Si–F 1.595(9) – 1.683(17) Å) и катионы o-$CH_3C_6H_4NH_3^+$ объединены Н-связями NH···F (расстояния N···F 2.757(10) – 3.25(2) Å). Компоненты структуры объединены в слой, центральную часть которого формируют анионы SiF_6^{2-}, а наружные гидрофобные поверхности – ароматические циклы катионов.

Известно [1-3], что реализующиеся в структурах «ониевых» гексафторосиликатов межионные Н-связи в заметной степени определяют особенности геометрии анионов SiF_6^{2-} и физико-химическое поведение солей. Настоящая работа продолжает начатые ранее исследования [4-6] влияния эффекта Н-связей на строение и свойства гексафторосиликатов ариламмония и посвящена изучению кристаллической структуры гексафторосиликата *орто*-толуидиния.

ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

Синтез. Монокристаллы соединения (o-$CH_3C_6H_4NH_3)_2SiF_6$ **(I)** были получены по методике [4].

РСА. Параметры элементарной ячейки и трехмерный набор интенсивностей отражений для монокристалла **I** размером 0.24 x 0.14 x 0.01 мм получены на дифрактометре Nonius Kappa CCD (MoKα-излучение, графитовый монохроматор, ω-сканирование, $2\theta_{max}$ = 51.0 º) при 293 К. Всего зарегистрировано 5483 отражений ($-16 \le h \le 16$, $-6 \le k \le 6$, $-11 \le l \le 12$), из них 1452 независимых.

Кристаллы **I** (**$C_{14}H_{20}F_6N_2Si$**, M = 358.41) моноклинные: a = 14.582(3), b = 5.892(1), c = 10.184(2) Å, β = 105.83(3) º, V = 841.8(3) Å^3, $\rho_{выч}$ = 1.414 г/см^3, μ = 0.198 мм$^{-1}$, $F(000)$ = 372, Z = 2, пр. гр. $P2_1/c$.

Структура расшифрована прямым методом (SHELXS-97 [7]) и уточнена полноматричным анизотропным методом наименьших квадратов (SHELXL-97 [7]).

Окончательные результаты уточнения: R_1 = 0.0525, wR_2 = 0.1167 по отражениям с $I > 2\sigma(I)$, R_1 = 0.1380, wR_2 = 0.1376 по всем отражениям. Значения $\Delta\rho_{max}$, $\Delta\rho_{min}$ составляют 0.212 и –0.145 eÅ^{-3} соответственно.

Гексафторосиликат-анион занимает частное положение в центре инверсии и его атомы фтора разупорядочены по двум позициям с заселенностями 0.602 и 0.398; обе позиции уточняли в анизотропном приближении. Положение атомов водорода при атомах углерода рассчитано геометрически и уточнено по модели «наездника». Атомы водорода аммонийной группы локализованы из разностных синтезов Фурье и уточнялись изотропно с применением мягких ограничений (инструкция SADI для расстояний N–H и H···H). Длины некоторых связей и валентные углы приведены в табл. 1, параметры водородных связей – в табл. 2. Cif файл депонирован в Кэмбриджском банке структурных данных, номер регистрации CCDC 614304.

РЕЗУЛЬТАТЫ И ИХ ОБСУЖДЕНИЕ

Структурными единицами комплекса **I** являются гексафторосиликат-анион, занимающий позицию в центре инверсии, и два симметрически связанных катиона *о*-толуидиния, объединенные водородными связями NH···F (рис. 1). Обе позиции разупорядоченных атомов фтора принимают участие в разветвленной системе H-связей. В табл. 2 приведены параметры H-связей для обоих положений разупорядоченного аниона SiF_6^{2-}, однако обсуждение структуры базируется только на позиции с большей заселенностью, поскольку общий мотив упаковки остается неизменным. Все атомы водорода аммонийной группы и все атомы фтора аниона SiF_6^{2-} вовлечены в систему H-связей. Ближайшее окружение катиона формируют три аниона SiF_6^{2-}, занимающие частные позиции и находящиеся в вершинах практически равностороннего треугольника со сторонами 5.892, 5.883 и 5.883 Å. Атом азота аммонийной группы отстоит от этой плоскости на 1.75 Å. В свою очередь, каждый анион SiF_6^{2-} занимает позицию в центре гексагона, образующегося в результате сочленения шести ближайших треугольников таким образом, что катионы ориентированы по обе стороны от плоскости анионов. Компоненты структуры объединены в слой, развивающийся перпендикулярно направлению *a* в кристалле. Центральную часть слоя формируют анионы SiF_6^{2-}, обе наружные гидрофобные поверхности слоя создаются ароматическими циклами катионов.

В заключение отметим, что фиксируемая неэквивалентность длин связей Si–F аниона SiF_6^{2-} (интервал значений 1.595(9) – 1.683(17) Å) согласуется с мультиплетным (дублетным) характером поглощения колебаний ν(SiF) и δ(SiF_2) в ИК-спектре **I** [5], указывающим на понижение симметрии аниона относительно октаэдрической O_h. В структуре **I** отсутствует антибатная корреляция между прочностями H-связей NH···F и соответствующих связей Si–F, обнаруженная в структурах многих «ониевых» гексафторосиликатов [1, 2, 6].

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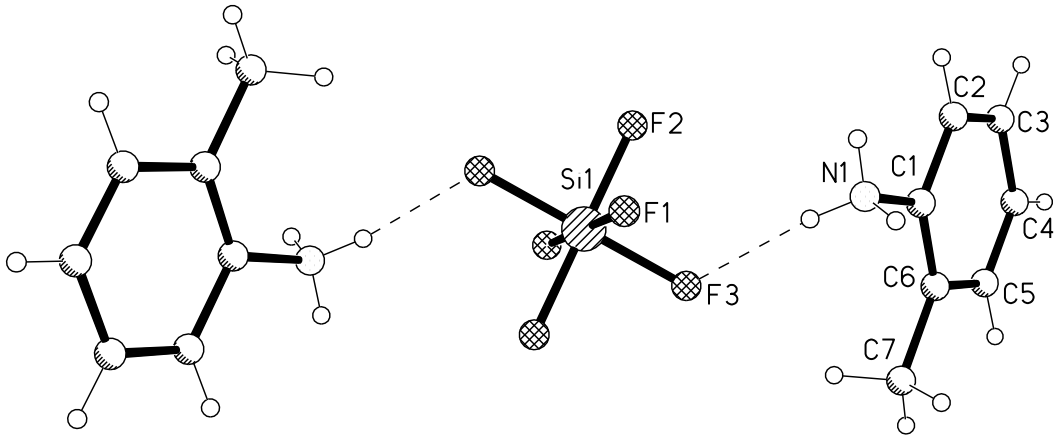

Рис. 1

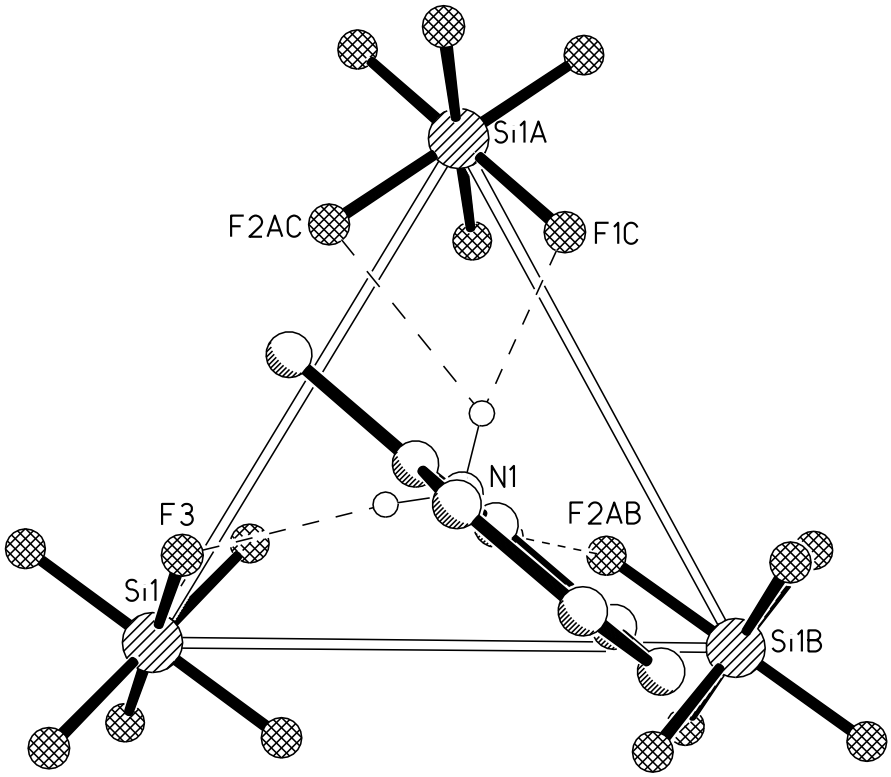

Рис. 2

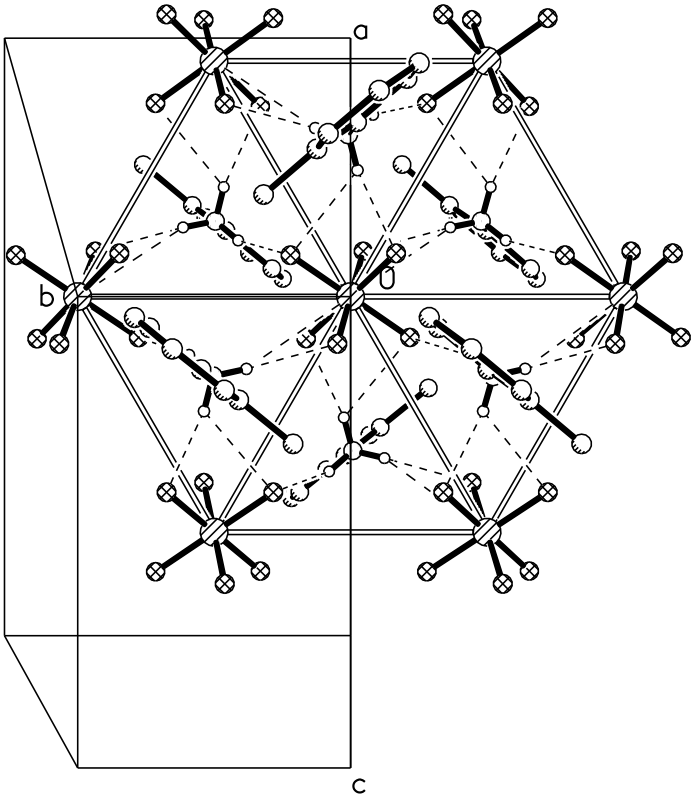

Рис. 3

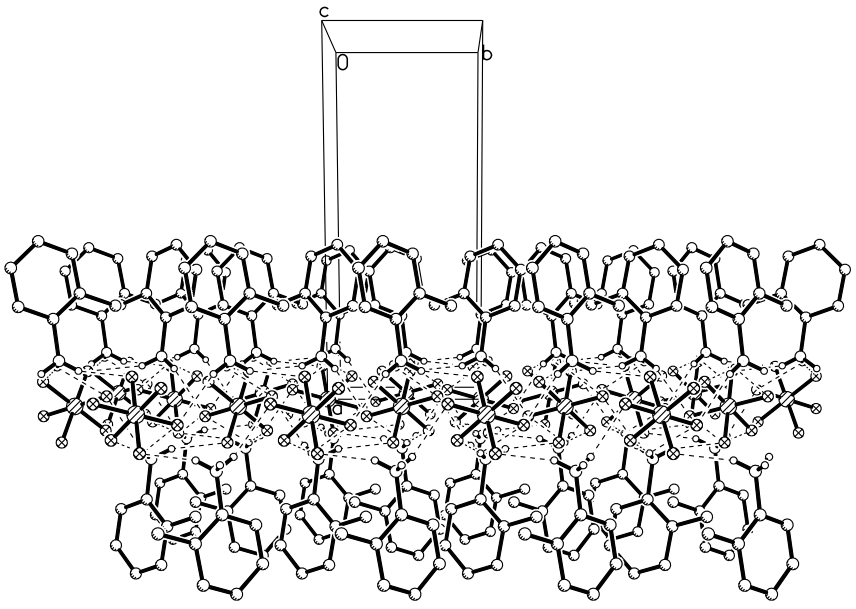

Рис. 4

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Копія статті Crystal Structure of p-Nitroanilinium Hexafluorosilicate

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COORDINATION COMPOUNDS

Crystal Structure of *p*-Nitroanilinium Hexafluorosilicate

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Abstract—Complex $(p\text{-}O_2NC_6H_4NH_3)_2SiF_6$ (I) is prepared by reacting fluorosilicic acid with p-nitroaniline in methanol and structurally studied using single-crystal X-ray diffraction. In the ionic structure of this complex, SiF_6^{2-} centrosymmetrical anions (avg. Si–F, 1.671(3) Å) and $O_2NC_6H_4NH_3^+$ cations are linked through NH···F interionic H-bonds (N···F 2.823(5)–3.205(7) Å). The thermochemical features of complex I are discussed in light of the structure data.

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Arylammonium hexafluorosilicates are convenient models for studying the effects of interionic hydrogen bonds on the physicochemical properties of salts. Varying the proton–donor parameters of arylammonium cations and their functionality through introducing H-donor/H-acceptor substituents in various positions of the aryl group offers a means for obtaining hexafluorosilicates with various H-bond geometries. Continuing our investigations of the structure and properties of arylammonium hexafluorosilicates [1, 2], here we report the structure solution for *p*-nitroanilinium hexafluorosilicate.

EXPERIMENTAL

Synthesis. Single crystals of the compound formulated as $(p\text{-}O_2NC_6H_4NH_3)_2SiF_6$ (**I**) were prepared by isothermally concentrating the reaction mixture of 45% fluorosilicic acid (analytically pure; hereafter, FSA) and a methanolic solution of *p*-nitroaniline (pure; hereafter, L) taken in the ratio FSA : L = 3 : 1 mol/mol at room temperature.

Mass spectrum of complex I (MX-1321 spectrometer, direct injection, ionizing electron energy of 70 eV): $[ML]^+$ (m/z = 138, I = 96%), $[ML–NO_2]^+$ (m/z = 92, I = 45%), SiF_3^+ (m/z = 85, I = 9%).

X-ray crystallography. Crystals of complex **I** ($C_{12}H_{14}F_6N_4O_4Si$, FW = 420.36) are monoclinic, a = 15.023(2) Å, b = 5.8317(7) Å, c = 10.3061(9) Å, β = 104.69(1)°, V = 873.39(18) Å^3, ρ_{calc} = 1.598 g/cm^3, $\mu(MoK_\alpha)$ = 2.050 mm^{-1}, $F(000)$ = 428, Z = 2, space group $P2_1/c$.

The experimental intensity array was collected from a colorless platy single crystal 0.04 × 0.32 × 0.56 mm in size at 293(2) K on an Enraf-Nonius CAD4 automated four-circle diffractometer (λCuK_α, λ = 1.54178 Å, graphite monochromator, ω scan mode, $2\theta_{max}$ = 59.97°). A total of 1485 reflections were measured with $-16 \le h \le 16$, $-6 \le k \le 0$, and $-1 \le l \le 11$; of them, 1264 reflections were independent (R(int) = 0.1270). Correction for absorption anisotropy was not applied.

The structure was solved using direct methods (SHELXS86 [3]) and refined using the least-squares technique for F^2 (SHELXL97 [4]) in the full-matrix anisotropic approximation for non-hydrogen atoms. The positions of three hydrogen atoms of the LH^+ cation at the nitrogen atoms were determined from difference Fourier synthesis and refined isotropically. The other hydrogen atoms were calculated geometrically and refined as riding.

The final values were $R1$ = 0.0434, $wR2$ = 0.1127, GOOF = 0.993 for 609 reflections with c $I > 2\sigma(I)$; $R1$ = 0.1370, $wR2$ = 0.1492 for all reflections; the number of refined parameters was 137. The extinction coefficient was 0.0004(7); $\Delta\rho_{max}$ and $\Delta\rho_{min}$ were 0.477 and –0.272 eÅ^{-3}, respectively.

The coordinates and temperature factors for the atoms in the structure of complex **I** are listed in Table 1; interatomic distances and bond angles are in Table 2.

RESULTS AND DISCUSSION

The structural units in a crystal of complex **I** are hydrogen-bonded *p*-nitroanilinium cations LH^+ and

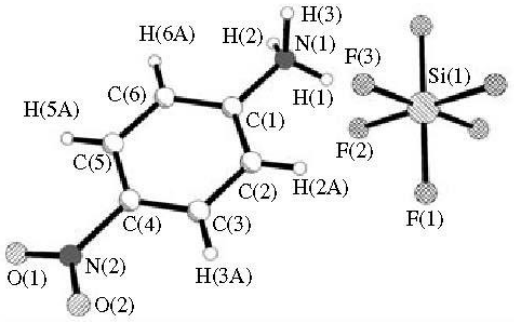

Fig. 1. Structural units of a crystal of complex **I**: a SiF_6^{2-} anion and an LH^+ cation.

centrosymmetrical hexafluorosilicate anions SiF_6^{2-} (Fig. 2) (Table 3).

The Si–F bond lengths in the anion have values ordinary for hexaflurosilicates (avg., 1.671(7) Å) [5]. For example, in the structure of $(L^1H)_2SiF_6$ (where L_1H^+ stands for *o*-$CH_3O(O)CC_6H_4NH_3^+$, an *o*-substituted anilinium cation), the average Si–F distance is 1.679(21) Å.

Three types of layers may be recognized in the H-bonded framework structure of complex **I** (Fig. 2). One type is built of SiF_6^{2-} anions. In each of the other two types of layers formed of *p*-nitroanilinium cations, the latter are linked with one another by plane *c*. Anions from different layers are arranged in the head-to-head

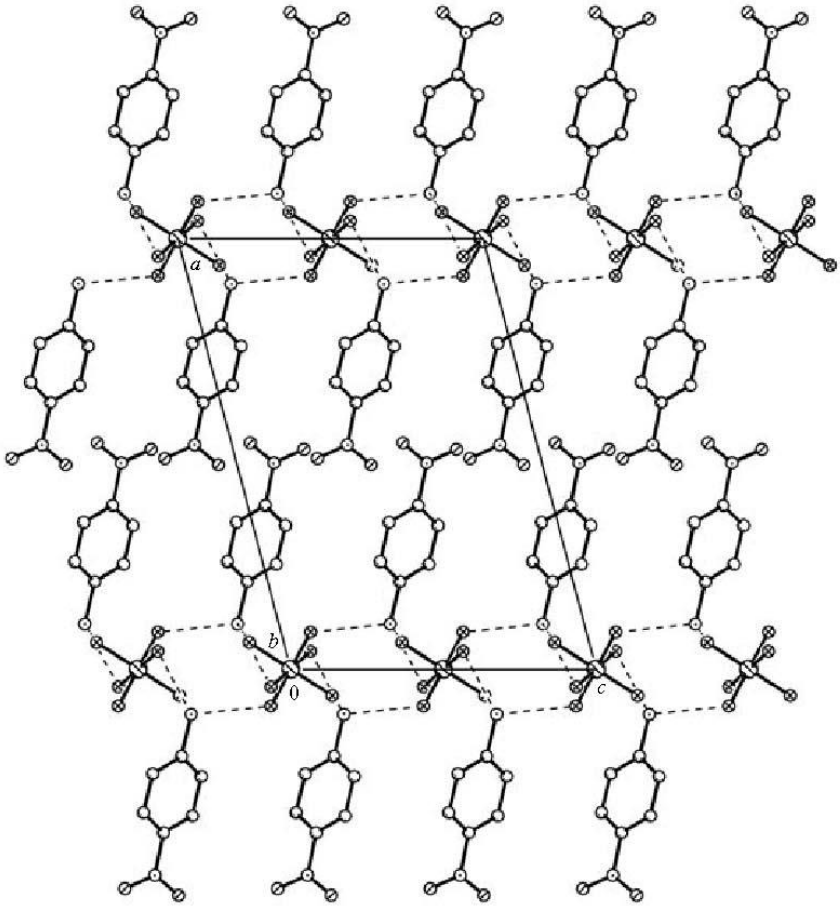

Fig. 2. Packing of structural units in a crystal of complex **I** (projection along axis *b*).

Table 1. Coordinates of atoms ($\times 10^4$; for H atoms, $\times 10^3$) and their thermal parameters U_{eq}/U_{iso} (Å^2, $\times 10^3$) in the structure of complex **I***

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Si(1)	0	0	0	36(1)
F(1)	864(2)	1492(7)	971(3)	77(1)
F(2)	618(2)	–379(5)	–1130(2)	54(1)
F(3)	414(2)	–2411(5)	800(3)	69(1)
N(1)	1056(3)	–5046(11)	–1358(4)	40(1)
N(2)	4789(3)	–6514(8)	1218(5)	52(1)
O(1)	5256(2)	–7594(7)	616(4)	62(1)
O(2)	5103(3)	–5693(8)	2317(4)	78(1)
C(1)	2024(3)	–5464(9)	–671(4)	40(1)
C(2)	2429(3)	–4184(10)	421(4)	54(2)
C(3)	3333(3)	–4545(10)	1059(4)	51(2)
C(4)	3804(3)	–6176(10)	576(4)	44(1)
C(5)	3411(3)	–7505(10)	–518(5)	59(2)
C(6)	2493(3)	–7140(10)	–1149(5)	56(2)
H(1)	920(40)	–3250(120)	–1270(50)	79(19)
H(2)	960(30)	–5350(70)	–2170(40)	16(10)
H(3)	810(40)	–5800(100)	–970(50)	50(20)

* The coordinates and U_{iso} factors are listed only for the three experimentally determined and refined hydrogen atoms.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the structure of complex **I**

Bond	*d*, Å
Si(1)–F(1)	1.668(3)
Si(1)–F(2)	1.678(2)
Si(1)–F(3)	1.668(3)
N(1)–C(1)	1.468(6)
N(2)–O(2)	1.209(5)
N(2)–O(1)	1.222(5)
N(2)–C(4)	1.474(6)
C(1)–C(6)	1.367(7)
C(1)–C(2)	1.358(6)
C(2)–C(3)	1.367(7)
C(3)–C(4)	1.353(7)
C(4)–C(5)	1.372(7)
C(5)–C(6)	1.384(7)
Angle	**ω, deg**
F(1)Si(1)F(3)	90.41(18)
F(1)Si(1)F(2)	90.11(15)
F(3)Si(1)F(2)	91.69(14)
O(2)N(2)O(1)	122.8(4)
O(2)N(2)C(4)	118.4(4)
O(1)N(2)C(4)	118.7(4)
C(6)C(1)C(2)	121.9(4)
C(6)C(1)N(1)	118.8(4)
C(2)C(1)N(1)	119.3(4)
C(3)C(2)C(1)	119.7(5)
C(4)C(3)C(2)	118.7(4)
C(3)C(4)C(5)	122.9(4)
C(3)C(4)N(2)	119.3(5)
C(5)C(4)N(2)	117.9(4)
C(4)C(5)C(6)	118.0(5)
C(1)C(6)C(5)	118.9(5)

manner. The tails of the cations (protonated NH_3^+ groups) are the H-donors of NH···F interionic H-bonds. The three hydrogen atoms of the NH_3 group are each involved in two or three bifurcated H-bonds; one component of these bonds (H···F 1.75–2.16, N···F 2.823–2.837 Å; angle NHF, 151°–176°) is far stronger than the other one or two components (H···F 2.48–2.60, N···F 3.054–3.205 Å; NHF, 112°–149°).

In closing we may say that the structural features of hexafluorosilicate **I** may be used in interpreting the features of its thermochemical behavior. It is known from [6] that complex **I** is the least stable of the hexafluorosilicates of *p*-substituted anilinium derivatives; the first thermolysis stage of complex **I** is described by the scheme

$$(LH)_2SiF_{6\ (solid)} \longrightarrow SiF_4 \cdot 2L_{(solid)} + 2HF_{(gas)}. \quad (1)$$

Evidently, process (1) may be represented as resulting from the disproportionation of bond lengths in the N–H···F–Si four-center fragments (shortening of the H···F bond and lengthening of the N–H and Si–F bonds until their rupture). In this context, it is relevant that one H···F contact in the structure of complex **I** (N(1)–

Table 3. Geometry of the N–H···F short interionic contacts in the structure of complex I

N–H···F contact	Distances, Å			NHF angle, deg	Coordinates of atom F
	N–H	F···H	N···F		
N(1)–H(1)···F(2)	1.08(7)	1.75(7)	2.824(7)	176(5)	x, y, z
N(1)–H(1)···F(3)	1.08(7)	2.48(6)	3.054(5)	112(4)	x, y, z
N(1)–H(2)···F(1)	0.83(4)	2.00(4)	2.823(5)	171(4)	$x, -y - 0.5, z - 0.5$
N(1)–H(2)···F(2)	0.83(4)	2.57(4)	3.124(5)	125(3)	$-x, y - 0.5, -z - 0.5$
N(1)–H(2)···F(3)	0.83(4)	2.60(4)	3.182(6)	128(3)	$x, -y - 0.5, z - 0.5$
N(1)–H(3)···F(3)	0.75(6)	2.16(6)	2.837(6)	151(5)	$-x, -y - 1, -z$
N(1)–H(3)···F(1)	0.75(6)	2.54(6)	3.205(7)	149(5)	$x, y - 1, z$

H(1)···F(2) 1.75(7) Å) is the shortest of the structurally studied arylammonium hexaflurosilicates [1, 2]. In other words, thanks to a relatively high H-donating ability of LH^+ cations ($pK_a(L) = 1.02$) [7], the structure of complex **I** is adapted to thermal dissociation.

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Додаток 65

Копія статті Взаимодействие краун-эфиров с пятичленными гетероциклами: 1Н-имидазол-4,5-дикарбонитрилом, 3-нитро-1,2,4-триазолом и 1Н-тетразолом

ХИМИЯ ГЕТЕРОЦИКЛИЧЕСКИХ СОЕДИНЕНИЙ. — 2006. — № 9. — С. 1302—1305

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ВЗАИМОДЕЙСТВИЕ КРАУН-ЭФИРОВ С ПЯТИЧЛЕННЫМИ ГЕТЕРОЦИКЛАМИ: 1Н-ИМИДАЗОЛ-4,5-ДИКАРБОНИТРИЛОМ, 3-НИТРО-1,2,4-ТРИАЗОЛОМ И 1Н-ТЕТРАЗОЛОМ

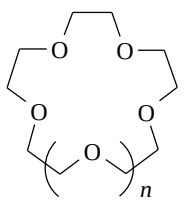
Взаимодействием 1Н-имидазол-4,5-дикарбонитрила, 3-нитро-1,2,4-триазола и 1Н-тетра- зола, содержащих по одному протону при двух соседних протонодонорных атомах, разделенных одной ковалентной связью, с краун-эфирами показана возможность получе-ния незаряженных кристаллических супрамолекулярных соединений за счет протонодо-норных свойств ароматических гетероциклов.

Ключевые слова: 1Н-имидазол-4,5-дикарбонитрил, 3-нитро-1,2,4-триазол, 1Н-тетразол, краун-эфиры , кристаллические супрамолекулярные соединения.

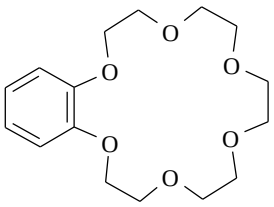
Непременным условием образования кристаллических супрамоле-кулярных соединений [1, 2] краун-эфиров с органическими молекулами является присутствие в последних протонодонорных центров при одном из C, N или O атомов, в частности H_2N–, H_2NSO_2–, H_2NCS–, H_2NHNCO–, H_2C=, H_3C–, H_3CO– и аналогичных групп или молекул воды [1–3], обеспечивающих стабилизацию компонентов супрамолекулярного соеди-нения водородными связями. В связывании, как правило, участвует пара протонов заместителя, причем стабильность соединений падает в ряду: OH > NH_2 > CH_2 [4]. Кристаллические супрамолекулярные соединения краун-эфиров с гетероциклами стабилизированы водородными связями за счет либо одного из перечисленных заместителей при гетероцикле [5–12], либо – циклической аммонийной группы протонированного гетероцикла [13]. Известен единичный пример образования кристаллического супрамо-лекулярного соединения наиболее эффективного [3, 14] краун-эфира (**1b**) с незамещенным триазолом [15].

Целью работы являлось определение возможности синтеза незаря-женных кристаллических супрамолекулярных соединений краун-эфиров различного строения с пятичленными ароматическими гетероциклами, имеющими по одному протону при двух соседних протонодонорных атомах, разделенных одной ковалентной связью и обеспечивающих стабилизацию супрамолекулярного соединения лишь парой протонов ароматического гетероцикла, аналогично данным [15].

Установлено, что при самопроизвольном испарении растворителей из растворов краун-эфиров **1**–**3** с гетероциклами **4**–**6** образуются кристалли- ческие супрамолекулярные соединения – [**1b** · **4**] – **7**, [**2** · **4**] – **8**, [**3** · 2(**4**)] – **9**, [**1a** · **5**] – **10**, [**1b** · 2(**5**)] – **11**, [**2** · 2(**5**)] – **12**, [**3** · 2(**5**)] – **13**, [**3** · 2(**6**)] – **14** соответственно.



1a,b



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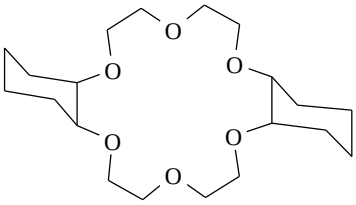

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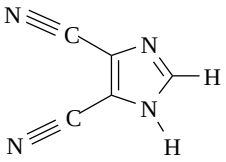

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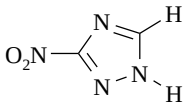

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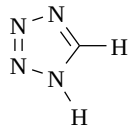

6

1 a – 1,4,7,10,13-пентаоксациклопентадекан, **b** – 1,4,7,10,13,16-гексаоксациклооктадекан; **1 a** *n* = 1, **b** *n* = 2; **2** – 2,3,5,6,8,9,11,12,14,15-декагидро-1,4,7,10,13,16-бензогексаоксацикло-октадецен; **3** – *цис-анти-цис*-эйкосагидродибензо[*b,k*][1,4,7,10,13,16]гексаоксациклоокта-децен; **4** – 1Н-имидазол-4,5-дикарбонитрил; **5** – 3-нитро-1,2,4-триазол; **6** – 1Н-тетразол

Образование устойчивых кристаллических соединений нейтральных гетероциклов **4**–**6** с краун-эфирами, имеющими различный размер макро-циклического кольца (соединения **1a**,**b**), а также различно пространствен-но экранированные стороны макроциклической полости (соединения **2**, **3**), позволяет полагать, что факты связывания краун-эфиров в супрамолеку-лярные соединения парами протонов ароматических гетероциклов носят неслучайный характер. Данные могут быть учтены при анализе и моде-лировании молекулярных взаимодействий незаряженных природных молекул [1, 2, 16], а также направленном синтезе кристаллических супра-молекулярных соединений краун-эфиров с гетероциклами.

Строение всех объектов, описанных в статье, определено также и РСА. Эти данные представляют самостоятельный интерес и будут оформлены как ряд отдельных публикаций.

ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

Спектры ЯМР ^{1}H регистрировали на приборе Bruker AC 300 (300 МГц) в ацетоне-d_6, внутренний стандарт ТМС. ТСХ проводили на пластинах Silufol, элюент метанол–хлороформ, 1:8, с проявлением нингидрином при 200 °С. При ТСХ образцы разрушаются и гетероциклы **4**–**6** проявляются темно-красными, краун-эфиры **1**–**3** – серыми пятнами на розовом фоне. Краун-эфир **3** получали, как описано в работе [17], соединения **1**, **2**, **4**–**6** использовали коммерческие, фирмы Aldrich, без дополнительной очистки.

Супрамолекулярные соединения 7–14. К 0.220 г (1 ммоль) краун-эфира **1a**, 0.264 г (1 ммоль) **1b**, 0.312 г (1 ммоль) **2** или 0.372 г (1 ммоль) **3** добавляют раствор 0.118 г (1 ммоль) гетероцикла **4**, 0.114 г (1 ммоль) **5** или 0.070 г (1 ммоль) **6** в смеси ацетон–гексан, 1:1, и оставляют испаряться при 20 °С. Выделившиеся монокристаллы отделяют, промывают той же смесью растворителей и сушат на воздухе.

Соединение 7 – 1,4,7,10,13,16-гексаоксациклооктадекан (1b) с 1Н-имидазол-4,5-дикарбонитрилом (4), 1:1. Выход 0.35 г (91%). Т. пл. 146–147 °С. Спектр ЯМР ^{1}H, δ, м. д.: 3.58 (24Н, с, CH_2O); 8.29 (1Н, с, СН). Найдено, %: С 53.44; Н 6.89; N 14.63. $C_{12}H_{24}O_6 \cdot C_5H_2N_4$. Вычислено, %: С 53.39; Н 6.85; N 14.65.

Соединение 8 – 2,3,5,6,8,9,11,12,14,15-декагидро-1,4,7,10,13,16-бензогексаоксациклоокта- децен (2) с 1Н-имидазол-4,5-дикарбонитрилом (4), 1:1. Выход 0.4 г (92%). Т. пл. 87–80 °С. Спектр ЯМР ^{1}H, δ, м. д.: 3.58, 3.61, 4.11 (20Н, м, CH_2O); 6.88 (4Н, м, C_6H_4); 8.27 (1Н, с, СН). Найдено, %: С 58.28; Н 6.17; N 12.83. $C_{16}H_{24}O_6 \cdot C_5H_2N_4$. Вычислено, %: С 58.59; Н 6.09; N 13.02.

Соединение 9 – *цис-анти-цис*-эйкосагидродибензо[*b,k*][1,4,7,10,13,16]гексаокса- циклооктадецен (3) с 1Н-имидазол-4,5-дикарбонитрилом (4), 1:2. Выход 0.29 г (96%). Т. пл. 155–156 °С. Спектр ЯМР ^{1}H, δ, м. д.: 1.24–1.81, 3.59 (36Н, м, CH_2O, CH_2, СН); 8.24 (2Н, с, СН). Найдено, %: С 59.24; Н 6.59; N 18.47. $C_{20}H_{36}O_6 \cdot 2C_5H_2N_4$. Вычислено, %: С 59.20; Н 6.62; N 18.41.

Соединение 10 – 1,4,7,10,13-пентаоксациклопентадекан (1a) с 3-нитро-1,2,4-триазо-лом (5), 1:1. Выход 0.3 г (90%). Т. пл. 110–112 °C. Спектр ЯМР ^{1}H, δ, м. д.: 3.53 (20H, с, CH_2O); 8.86 (1H, с, CH). Найдено, %: C 43.15; H 6.61; N 16.84. $C_{10}H_{20}O_5 \cdot C_2H_2N_4O_2$. Вычислено, %: C 43.11; H 6.63; N 16.76.

Соединение 11 – 1,4,7,10,13,16-гексаоксациклооктадекан (1b) с 3-нитро-1,2,4-три-азолом (5), 1:2. Выход 0.215 г (88%). Т. пл. 184–186 °C. Спектр ЯМР ^{1}H, δ, м. д.: 3.50 (24H, с, CH_2O); 8.86 (2H, с, CH). Найдено, %: C 39.11; H 5.76; N 22.84. $C_{12}H_{24}O_6 \cdot 2C_2H_2N_4O_2$. Вычислено, %: C 39.03; H 5.73; N 22.75.

Соединение 12 – 2,3,5,6,8,9,11,12,14,15-декагидро-1,4,7,10,13,16-бензогексаоксацик-лооктадецен (2) с 3-нитро-1,2,4-триазолом (5), 1:2. Выход 0.22 г (81%). Т. пл. 94–96 °C. Спектр ЯМР ^{1}H, δ, м. д.: 3.58, 3.72, 4.05 (20H, м, CH_2O); 6.88 (4H, м, C_6H_4); 8.86 (2H, с, CH). Найдено, %: C 44.41; H 5.28; N 20.77. $C_{16}H_{24}O_6 \cdot 2C_2H_2N_4O_2$. Вычислено, %: C 44.45; H 5.22; N 20.73.

Соединение 13 – *цис-анти-цис*-эйкосагидродибензо[*b,k*][1,4,7,10,13,16]гексаокса- циклооктадецен (3) с 3-нитро-1,2,4-триазолом (5), 1:2. Выход 0.26 г (87%). Т. пл. 178–180 °C. Спектр ЯМР ^{1}H, δ, м. д.: 1.20–1.71, 3.52 (36H, м, CH_2O, CH_2, CH); 8.86 (2H, с, CH). Найдено, %: C 48.08; H 6.76; N 18.73. $C_{20}H_{36}O_6 \cdot 2C_2H_2N_4O_2$. Вычислено, %: C 47.99; H 6.71; N 18.66.

Соединение 14 – *цис-анти-цис*-эйкосагидродибензо[*b,k*][1,4,7,10,13,16]гексаокса- циклооктадецен (3) с 1H-тетразолом (6), 1:2. Выход 0.22 г (86%). Т. пл. 140–142 °C. Спектр ЯМР ^{1}H, δ, м. д.: 1.23–2.05, 3.59 (36H, м, CH_2O, CH_2, CH); 9.19 (2H, с, CH). Найдено, %: C 51.51; H 7.83; N 21.82. $C_{20}H_{36}O_6 \cdot 2CH_2N_4$. Вычислено, %: C 51.54; H 7.87; N 21.87.

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