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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

EDUARD V. GANIN[1], MARINA S. FONARI[2,*], YURII A. SIMONOV[2], GABRIELE BOCELLI[3], STEPAN S. BASOK[4], VYACHESLAV V. TKACHUK[4], SERGEI A. KOTLYAR[4] and GERBERT L. KAMALOV[4]

[1]*Odessa State Environmental University, Ministry of Education and Science of Ukraine, Lvovskaya st., 15, 65016, Odessa, Ukraine;* [2]*Institute of Applied Physics Academy of Sciences of Moldova, Academy str., 5, MD2028 Chisinau Moldova;* [3]*IMEM-CNR, Parma, Italy;* [4]*A.V. Bogatsky Physico-Chemical Institute, National Academy of Science of Ukraine, Lustdorfskaya doroga 86, 650080, Odessa, Ukraine*

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Abstract

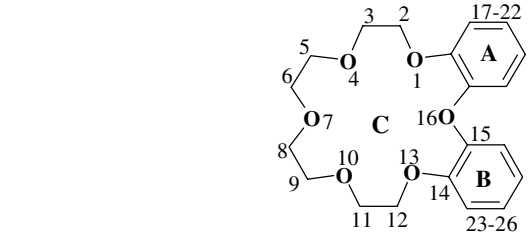
[1.5]Dibenzo-18-crown-6 ([1.5]DB18C6) forms the H-bonded supramolecular complexes with 3-nitro-1*H*-1,2,4-triazole (1:1), 2,4(1*H*,3*H*)-pyrimidinedithione (1:1), 1,2,5-oxadiazole-3,4-diamine monohydrate (1:1:1), ethanedithioamide (1:1) and 1,2-hydrazinedicarbothioamide (2:3). The first two complexes 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

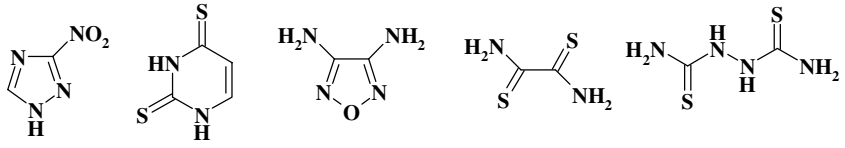
The research of organic molecules complexation *via* weak non-covalent interactions such as H-bonding, π-stacking and electrostatic interactions is a matter of a great concern. In biological systems, many heterocyclic bases such as imidazole, purine, uracil and their derivatives are very important and 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,

* Author for correspondence. E-mail: fonari.xray@phys.asm.md



[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]DB18C**6**·**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)

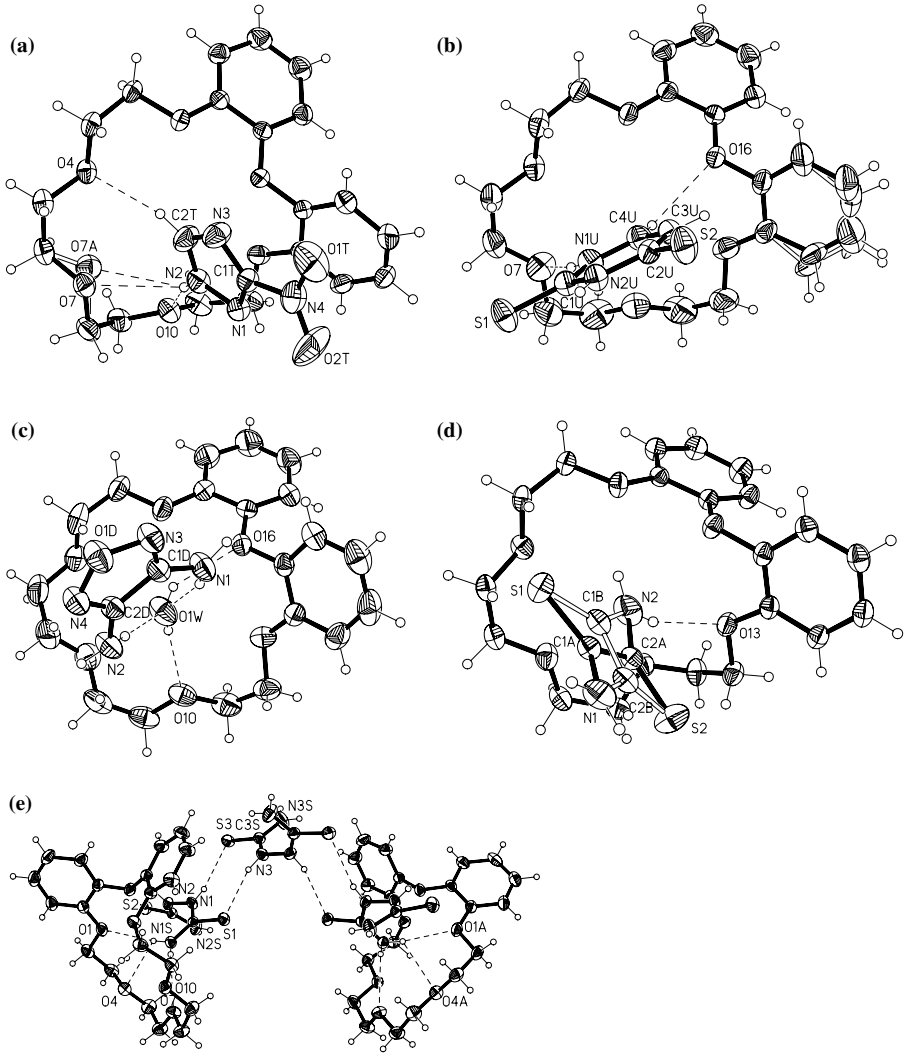


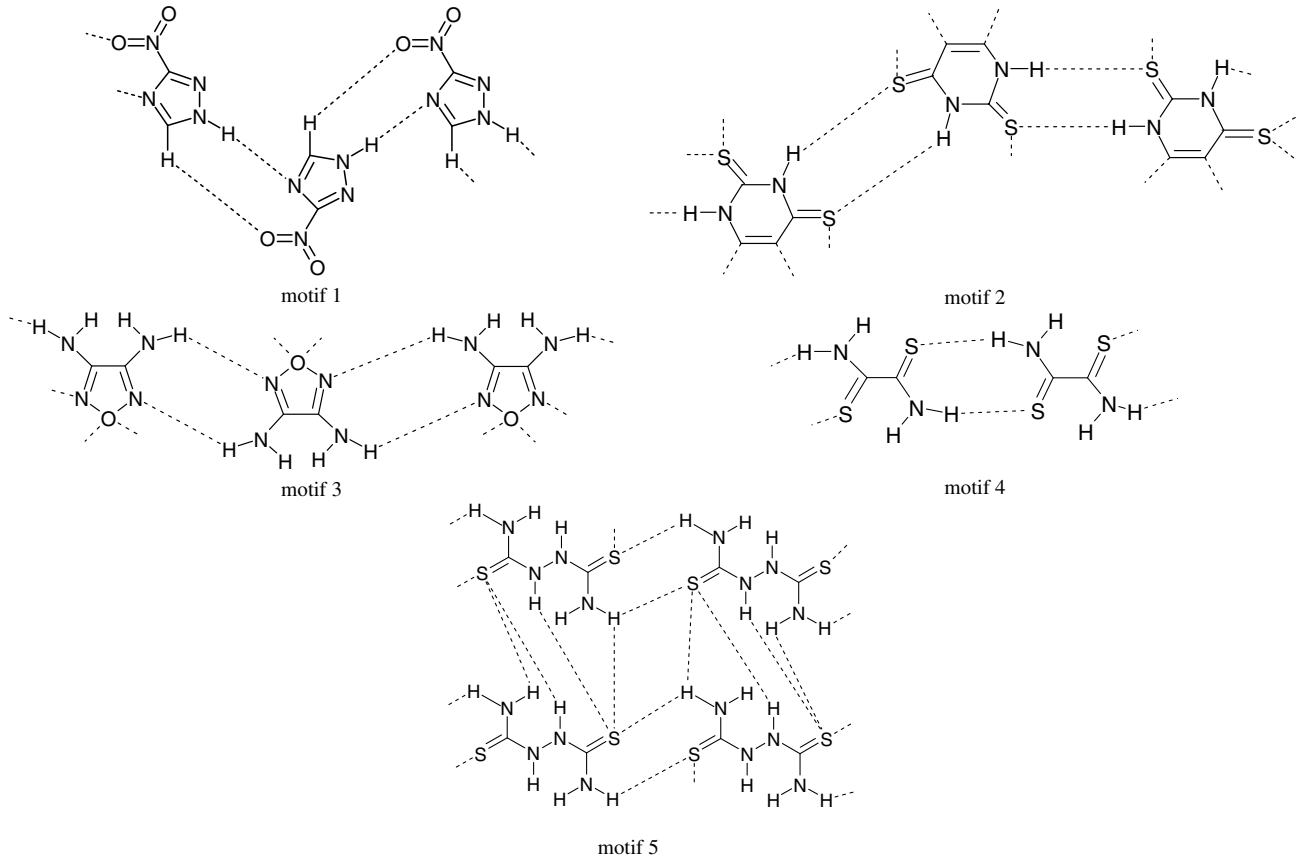
Figure 1. (a–e) ORTEP view of [1.5]DB18C6·**1**, [1.5]DB18C6·**2**, [1.5]DB18C6·**3**·H_2O, [1.5]DB18C6·**4** and [1.5]DB18C6·**5**. Ellipsoids for non-hydrogen atoms are drawn at the 30% probability level.

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

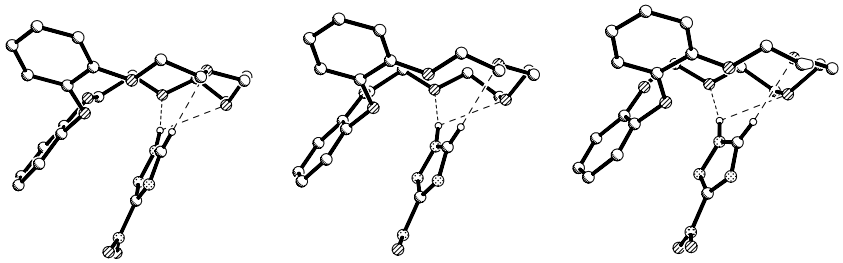


Figure 2. Arrangement of translated [1.5]DB18C6·**1** units in the crystal.

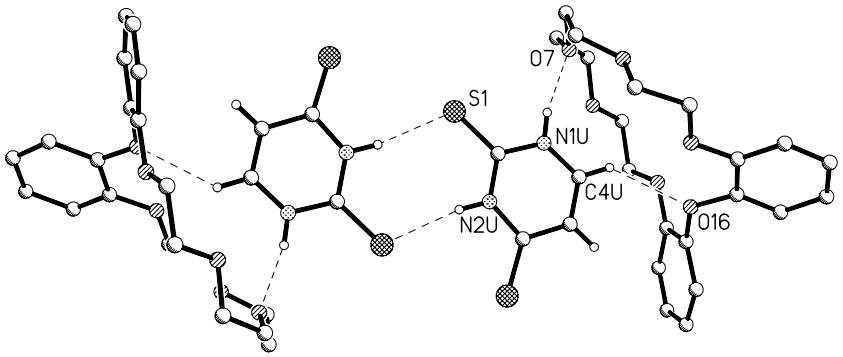


Figure 3. The centrosymmetric molecular capsule in [1.5]DB18C6·**2**.

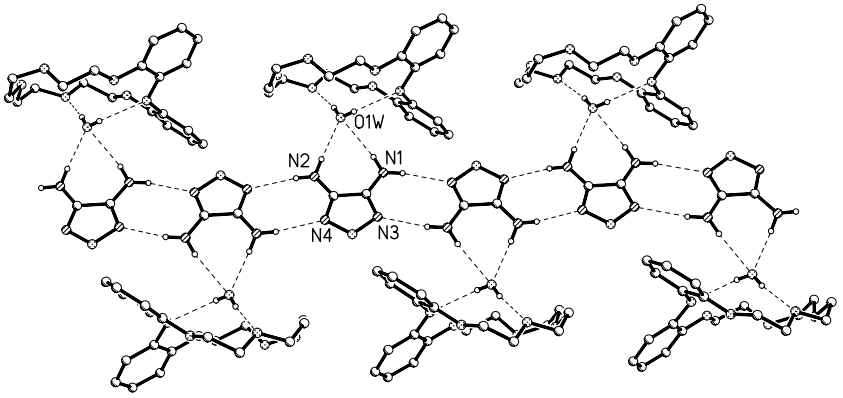


Figure 4. The fragment of the infinite chain in [1.5]DB18C6·**3**.

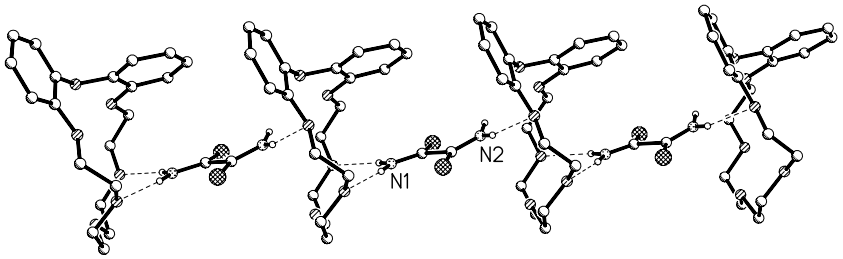


Figure 5. The fragment of the infinite chain in [1.5]DB18C6·**4**.

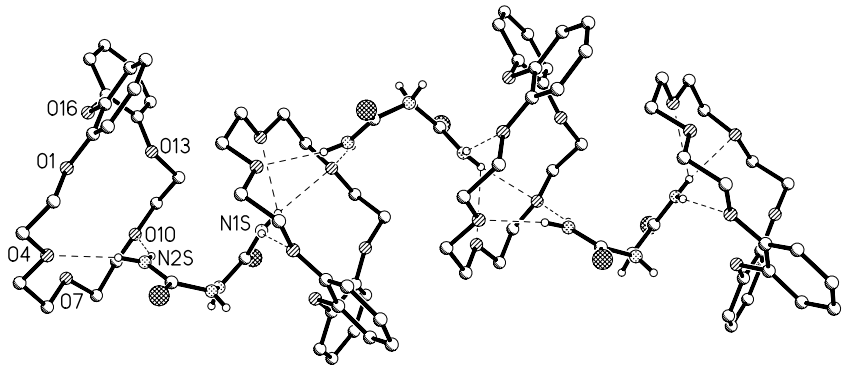


Figure 6. The fragment of the infinite chain in [1.5]DB18C6·**5**.

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.

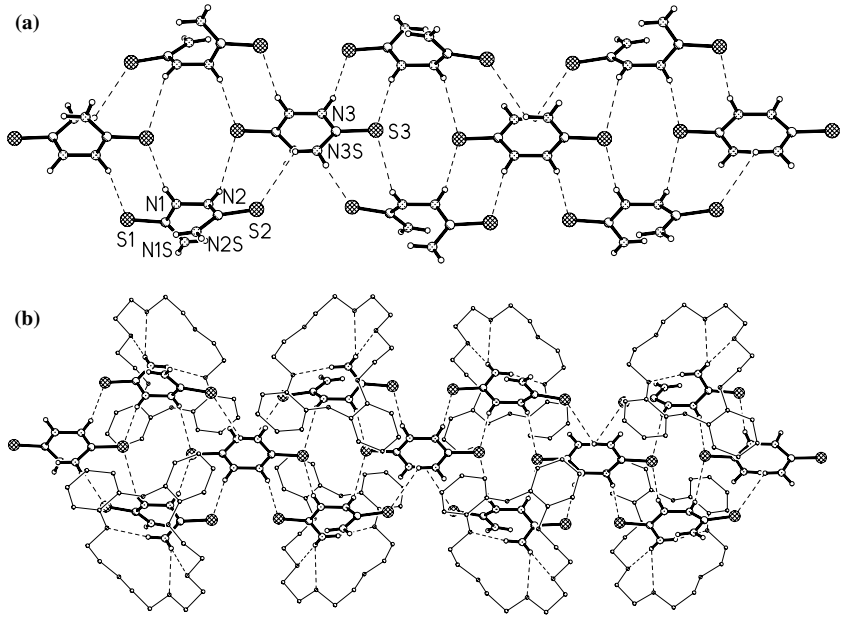


Figure 7. (a) The fragment of the ribbon built on **5** molecules. (b) The fragment of the crystal packing along *a* direction in [1.5]DB18C6·**5**.

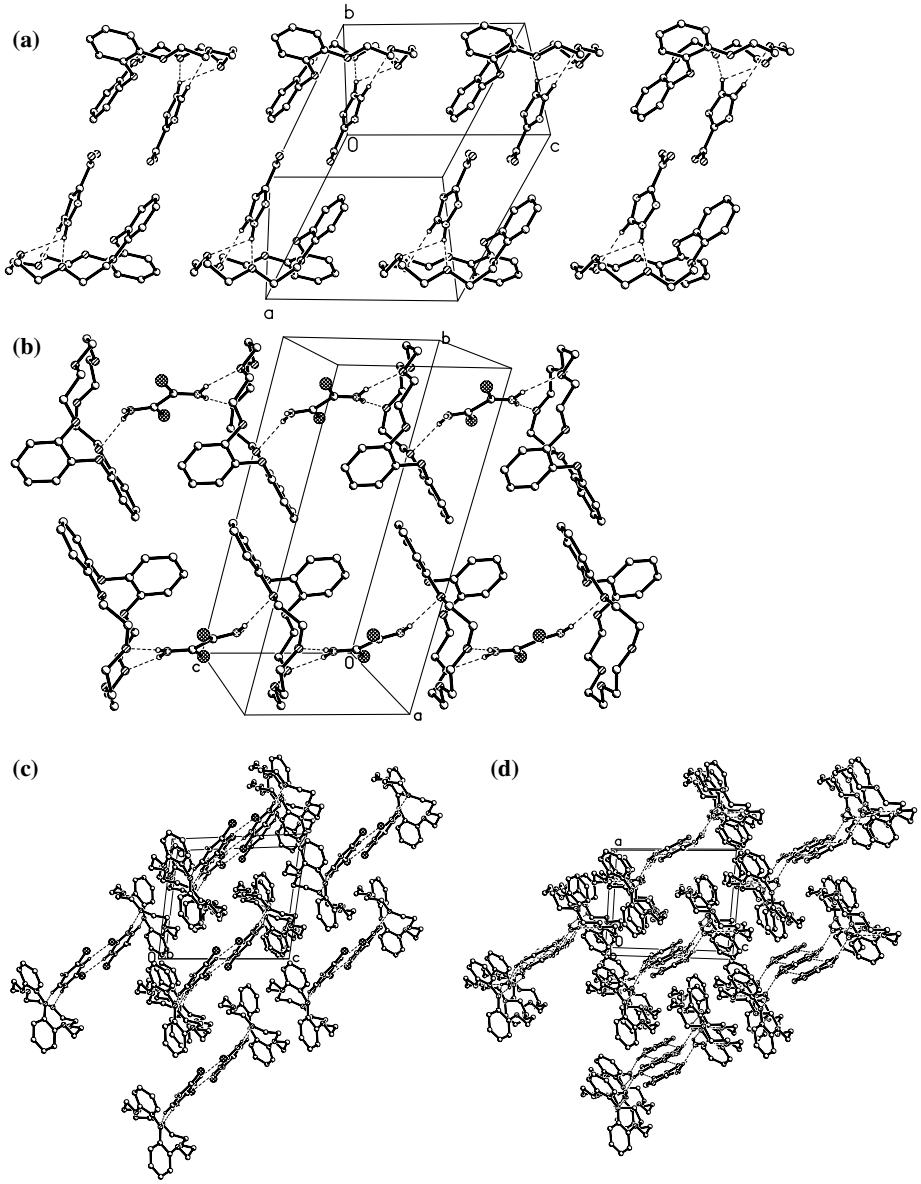


Figure 8. The fragments of crystal packing in (a) [1.5]DB18C6·**1**, (b) [1.5]DB18C6·**4**, (c) [1.5]DB18C6·**2**, (d) [1.5]DB18C6·**3**·H_2O.

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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