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STRUCTURE OF THE MOLECULAR COMPLEXES OF 18-CROWN-6 WITH 1,2,5-OXADIAZOLE DERIVATIVES

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This paper reports on an X-ray diffraction analysis of host–guest type molecular complexes of 18-crown-6 with 1,2,5-oxadiazole derivatives: ethyl 4-amino-1,2,5-oxadiazole-3-carboxylic ether (1:1) (complex I), 4-(2-chloroethylamino)-1,2,5-oxadiazole-3-carboxylic acid hydrazide (1:2) (complex II), and 4-amino-1,2,5-oxadiazole-3-carboxylic acid amide monohydrate (1:1:1) (complex III). Crystals I are monoclinic with cell parameters $a = 8.960(2)$, $b = 18.118(4)$, $c = 14.405(3)$ Å, $\beta = 106.9(3)°$, *space group* $P2_1/n$, $R = 0.054$ *for 4082 reflections. The 18-crown-6 and guest molecules are linked by hydrogen bonds of NH$\cdots$O(crown) and CH$\cdots$O(crown) types based on the ‘‘head-to-tail’’ principle, alternating in infinite chains along the y axis in the crystal. Crystals II are triclinic with cell parameters* $a = 8.615(2)$, $b = 9.249(2)$, $c = 10.987(2)$ Å, $\alpha = 106.86(3)$, $\beta = 95.25(3)$, $\gamma = 97.74(3)°$, *space group* $P\bar{1}$, $R = 0.046$ *for 3006 reflections. The guest molecules are united into dimers by N–H$\cdots$O=C hydrogen bonds. The 18-crown-6 molecules and the dimer associates of the guest form chains along [110] in the crystal. Crystals III are monoclinic with cell dimensions* $a = 13.238(3)$, $b = 19.004(4)$, $c = 8.485(2)$ Å, $\beta = 100.75(3)°$, *space group Cc,* $R = 0.051$ *for 2032 reflections. The crown ether molecule is disordered over two positions. The NH$\cdots$O=C and NH$\cdots$N type hydrogen bonds link the guest molecules into chains. The water molecules serve to bridge the chains with crown ether molecules, forming ribbons whose axis lies along the z direction in the crystal.*

There was extensive literature on crown ether complexes with metals and neutral organic molecules [1, 2]. It was established [2] that a small neutral molecule can form adducts with crown ethers if it has a high dipole moment and proton donors capable of hydrogen bonding with crown ether oxygens provided it leads to structure complementarity. Also, it is known that crown ether complexes with neutral organic molecules exhibit some properties characteristic of biologically controlled processes and enzyme catalysis [3]. Moreover, such complexes are models for understanding the role of weak C–H$\cdots$O interactions in stabilization of supramolecular associates [4].

In this series, complexes of 18-crown-6 (H — host) and some of its analogs with five-membered heterocyclic molecules (G — guest) — di-, tri-, and tetrazole derivatives — were studied [5-7]. In these complexes, interaction with crown ether is mediated by the donor groups NH_2, NH, CH. The presence of two or more proton donor centers in the guest ensures a chain structure with alternating 18-crown-6 and guest molecules. In the complex of 18-crown-6 with 3,4-diamino-1,2,5-oxadiazole [5], both amino groups are coordinated to different 18-crown-6 molecules (in one case, via the bridging water molecule), linking the C_i and D_{3d} 18-crown-ether molecules into a chain. In a complex with the *cis-anti-cis* isomer of dicyclohexano-18-crown-6, the guest molecule is bonded in the same way to two crown ether molecules, and the polymer chain is of the form –H–G–H–. Also, dimerization of guests such as 1,2,4-1H-triazole and 5-amino-1H-tetrazole via the hydrogen bonds CH$\cdots$N [6] or NH$\cdots$N [7] is possible and leads to a chain structure of –H–G–G–H– type. In the

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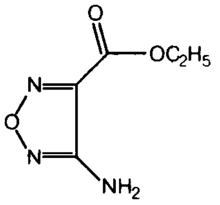
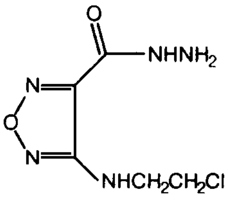
crystal structure of the 18-crown-6 complex with 5-amino-1,2,4-triazole, the –H–G–H–G– and –G–G–G– chains differing in composition are linked into a three-dimensional net via the guest molecules. In most cases, 18-crown-6 forms centrosymmetric complexes with four or six oxygens participating in the interaction with the small molecule. In some cases, however, only one side of the macrocycle is involved [8], or the sides are nonequivalent [9].

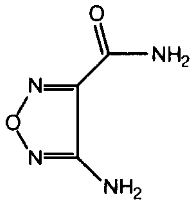
The aim of this publication is to study the crystal structures of three new complexes of 18-crown-6 with 1,2,5-oxadiazoles having substituents in the 3 or 4 position of the oxadiazole ring: amino and ester group (guest 1, complex I); hydrazide and chloroethylamine group (guest 2, complex II); amino and amide groups (guest 3, complex III).



G1



G2



G3

Guest molecules G1-G3 have the amino group, which, according to numerous structural data [10], is complementary to the macrocycle of 18-crown-6 and its analogs and generally coordinates the oxygen atoms of the host molecule separated by the oxyethylene fragment.

EXPERIMENTAL

Ethyl 4-amino-1,2,5-oxadiazole-3-carboxylic ether was prepared by the procedure described in [11].

Synthesis of 4-(2-chloroethylamino)-1,2,5-oxadiazole-3-carboxylic acid hydrazide. 4-(2-oxyethylamino)-1,2,5-oxadiazole-3-carboxylic acid (1.73 g, 0.01 mol) [11] was dissolved in anhydrous tetrahydrofuran (100 ml) with a catalytic amount of dimethylformamide. Thionyl chloride (2.8 ml) was added to the solution for 1 h, while the temperature of the mixture was kept below 60°C. The solvents and excess thionyl chloride were distilled off. The residue was dissolved in ethanol, and the mixture was filtered. To the filtrate was added 50 ml of 30% aqueous hydrazine. The precipitate was filtered off, washed with water, and dried in air. Yield 1.74 g (85%).

Synthesis of 4-amino-1,2,5-oxadiazole-3-carboxylic acid amide. Gaseous ammonia was bubbled through a saturated alcohol solution of ethyl 4-amino-1,2,5-oxadiazolo-3-carboxylic ether (1.57 g, 0.01 mol) until the solution was saturated. The reaction mixture was stored at room temperature until a crystalline precipitate settled. The precipitate was filtered off and recrystallized from alcohol. Yield 1.28 g (90%).

Syntheses of complexes I-III. Complexes I-III were prepared by analogous procedures. An appropriate guest (0.1 mmol) and 18-crown-6 (26 mg, 0.1 mmol) were dissolved at 64°C in methanol (2 ml), then benzene (5 ml) was added, and the mixture was allowed to stay until the solvents spontaneously evaporated. The crystals suitable for an X-ray analysis were obtained by recrystallization of the resulting crystalline mass from a mixture of ethyl acetate (5 ml) and heptane (3 ml). T_m is 81-82°C for I, 108-109°C for II, and 157-158°C for III.

Element analysis data:

Analysis	C	H	N	Cl
Found (%)	48.42	7.50	10.04	–
Calculated for $C_{17}H_{31}N_3O_9$ (I)	48.45	7.41	9.97	–
Found (%)	39.23	6.05	20.70	10.56
Calculated for $C_{22}H_{40}Cl_2N_{10}O_{10}$ (II)	39.12	5.97	20.73	10.50
Found (%)	44.53	7.35	13.57	–
Calculated for $C_{15}H_{30}N_4O_9$ (III)	43.90	7.37	13.65	–

Crystal and refinement data and experimental conditions are listed in Table 1. The least-squares refinement used 31 reflections (2θ 13.74-37.79°) for I, 25 reflections (2θ 13.29-32.50°) for II, and 32 reflections (2θ 18.20-43.47°) for III (KUMA KM-4 diffractometer, CuK_α radiation). The structures were solved by direct methods. The calculations used the

TABLE 1. Crystal Data, Data Collection Details, and Refinement Parameters for I-III

Complex	I	II	III
Molecular formula	$C_{17}H_{31}N_3O_9$	$C_{22}H_{40}Cl_2N_{10}O_{10}$	$C_{15}H_{30}N_4O_9$
M	421.45	675.54	410.43
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	Cc
Lattice parameters			
a, Å	8.960(2)	8.615(2)	13.238(3)
b, Å	18.118(4)	9.249(2)	19.004(4)
c, Å	14.405(3)	10.987(2)	8.485(2)
α, deg	90	106.86(3)	90
β, deg	106.90(3)	95.25(3)	100.75(3)
γ, deg	90	97.74(3)	90
V, Å^3	2237.5(3)	822.3(3)	2097.2(8)
Z	4	1	4
d_{calc}, g/cm^3	1.251	1.364	1.300
μ, mm^{-1}	0.859	2.342	0.915
F (000)	904	356	880
Crystal size, mm	0.25×0.80×1.50	0.20×0.30×0.30	0.25×0.35×2.30
θ range from data collected, deg	4.03-70.15	4.24-68.62	4.12-69.13
Index ranges from data collected	$-10 < h < 0$, $-22 < k < 0$, $-16 < l < 17$	$-10 < h < 10$, $-10 < k < 11$, $-13 < l < 0$	$-10 < h < 15$, $0 < k < 23$, $0 < l < 10$
Scan mode	$\omega / 2\theta$	$\omega / 2\theta$	$\omega / 2\theta$
Reflections collected	4367	3177	2034
Unique reflections, [R_{int}]	4082 [0.0116]	3006 [0.0263]	2032 [0.0660]
GooF S (on F^2)	1.051	0.921	1.051
Refinement method	Full-matrix on F^2		
Final R indices from reflections with [$I > 2\sigma(I)$]	$R_1 = 0.0540$ $wR_2 = 0.1641$	$R_1 = 0.0463$ $wR_2 = 0.1096$	$R_1 = 0.0505$ $wR_2 = 0.1343$
Final R indices (all data)	$R_1 = 0.0739$ $wR_2 = 0.1799$	$R_1 = 0.1478$ $wR_2 = 0.1388$	$R_1 = 0.0548$ $wR_2 = 0.1396$
$w = I/[\sigma^2 (Fo^2) + (ap)^2 + bp]$, $p = (\mathrm{Max}\ (Fo^2, 0) + 2F_c^2)/3$			
	$a = 0.1215$ $b = 0.1592$	$a = 0.0659$ $b = 0$	$a = 0.1155$ $b = 0.2934$
Residual peaks $\Delta\rho_{max}$, $\Delta\rho_{min}$, eÅ^{-3}	0.355, –0.218	0.315, –0.237	0.222, –0.280

SHELXL-97 program [12]. All hydrogen atoms in the structure were localized on difference electron density maps. For refinement, the methyl and methylene hydrogens were placed at the calculated ideal positions and refined as atoms tightly bonded to the corresponding carbon atom. The NH and NH_2 hydrogens localized on the difference maps were also refined in a rigid group approximation. The positions refined individually were the positions of the hydrogen atoms of the terminal amino group (complex II) and of the water hydrogens (complex III). The isotropic thermal parameters of the CH_3 and water hydrogen atoms were taken to be equal in magnitude: 1.5 U_{eq} of the nonhydrogen atoms bonded to the H atoms and 1.2 U_{eq} for the rest of the hydrogen atoms, respectively. The full-matrix least-squares refinement on F^2 used the weighting schemes given in Table 1. The final coordinates of the basic nonhydrogen atoms, anisotropic thermal parameters, and full geometry of the complexes were deposited at the Cambridge Crystallographic Data Center as CCDC Ref. Nos. 143357-143359. The geometrical parameters of the complexes are listed in Table 2; the hydrogen bond parameters are given in Table 3.

TABLE 2. Interatomic Distances *d* (Å) and Bond and Torsion Angles (deg) for I-III

Bond	I	II	III	Bond	I	II	III
O(1)–C(2)	1.416(3)	1.409(4)	1.379(14)	C(9)–O(10)	1.414(3)	—	1.424(6)
C(2)–C(3)	1.480(4)	1.492(6)	1.422(9)	O(10)–C(11)	1.414(3)	—	1.448(9)
C(3)–O(4)	1.417(3)	1.425(4)	1.477(17)	C(11)–C(12)	1.479(3)	—	1.486(12)
O(4)–C(5)	1.423(3)	1.408(4)	1.412(9)	C(12)–O(13)	1.419(3)	—	1.407(7)
C(5)–C(6)	1.482(4)	1.485(6)	1.418(9)	O(13)–C(14)	1.407(3)	—	1.360(11)
C(6)–O(7)	1.407(3)	1.421(4)	1.462(11)	C(14)–C(15)	1.486(4)	—	1.517(13)
O(7)–C(8)	1.409(3)	1.407(4)	1.389(10)	C(15)–O(16)	1.422(3)	—	1.406(7)
C(8)–C(9)#1	—	1.483(6)	—	O(16)–C(17)	1.413(3)	—	1.408(12)
O(1)–C(9)	—	1.421(4)	—	C(17)–C(18)	1.481(4)	—	1.518(14)
C(8)–C(9)	1.468(3)	—	1.499(11)	O(1)–C(18)	1.410(3)	—	1.422(9)

Angle	I	II	III
1	2	3	4
C(18)–O(1)–C(2)	113.3(2)	—	113.6(8)
O(1)–C(2)–C(3)	109.1(2)	109.1(3)	111.9(8)
O(4)–C(3)–C(2)	109.8(2)	108.8(3)	112.8(7)
C(3)–O(4)–C(5)	112.9(2)	112.3(3)	114.1(5)
O(4)–C(5)–C(6)	109.9(2)	109.3(3)	109.5(5)
O(7)–C(6)–C(5)	108.7(2)	109.8(3)	110.2(5)
C(6)–O(7)–C(8)	112.9(2)	113.6(3)	112.3(6)
O(7)–C(8)–C(9)#1	—	109.7(3)	—
O(1)–C(9)–C(8)#1	—	109.2(3)	—
C(2)–O(1)–C(9)	—	112.5(3)	—
O(7)–C(8)–C(9)	109.6(2)	—	111.0(5)
O(10)–C(9)–C(8)	110.1(2)	—	109.0(5)
C(9)–O(10)–C(11)	112.4(2)	—	112.0(5)
O(10)–C(11)–C(12)	109.5(2)	—	109(5)
O(13)–C(12)–C(11)	109.7(2)	—	108.4(5)
C(14)–O(13)–C(12)	112.7(2)	—	112.6(7)
O(13)–C(14)–C(15)	108.4(2)	—	111.9(8)
O(16)–C(15)–C(14)	109.3(2)	—	108.3(6)
C(17)–O(16)–C(15)	112.9(2)	—	113.3(7)
O(16)–C(17)–C(18)	110.0(2)	—	108.4(7)
O(1)–C(18)–C(17)	109.1(2)	—	107.8(6)
C(18)–O(1)–C(2)–C(3)	–175.2(2)	—	–177.2(7)
C(9)–O(1)–C(2)–C(3)	—	180.0(3)	—
O(1)–C(2)–C(3)–O(4)	71.4(3)	–67.4(4)	–62.8(1)
C(2)–C(3)–O(4)–C(5)	177.9(2)	178.3(3)	169.1(7)
C(3)–O(4)–C(5)–C(6)	–178.3(2)	175.4(3)	175.0(5)
O(4)–C(5)–C(6)–O(7)	–68.4(3)	63.5(2)	63.0(6)
C(5)–C(6)–O(7)–C(8)	176.6(2)	–178.4(3)	–173.8(5)
C(6)–O(7)–C(8)–C(9)#1	—	–173.7(3)	—
O(7)–C(8)–C(9)#1–O(1)#1	—	–69.5(5)	—
C(8)–C(9)#1–O(1)#1–C(2)#1	—	175.6(3)	—
C(6)–O(7)–C(8)–C(9)	–178.6(2)	—	–179.9(5)
O(7)–C(8)–C(9)–O(10)	69.6(2)	—	–66.0(6)
C(8)–C(9)–O(10)–C(11)	–176.4(2)	—	–173.3(5)
C(9)–O(10)–C(11)–C(12)	178.2(2)	—	–170.2(5)

TABLE 2 (Continued)

1	2	3	4
O(10)–C(11)–C(12)–O(13)	–68.6(2)	—	63.5(7)
O(11)–C(12)–O(13)–C(14)	–174.3(2)	—	169.3(6)
C(12)–O(13)–C(14)–C(15)	–178.7(2)	—	169.0(6)
O(13)–C(14)–C(15)–O(16)	67.3(2)	—	–63.8(10)
C(14)–C(15)–O(16)–C(17)	177.4(2)	—	–176.8(7)
C(15)–O(16)–C(17)–C(18)	173.1(2)	—	180.0(6)
O(16)–C(17)–C(18)–O(1)	–71.5(2)	—	69.2(8)
C(17)–C(18)–O(1)–C(2)	178.3(2)	—	–179.8(9)

Ethyl 4-amino-1,2,5-oxadiazole-3-carboxylic ether (G1)

Bond	*d*, Å	Angle	ω, deg
O(1*g*)–N(1*g*)	1.352(3)	N(1*g*)–O(1*g*)–N(2*g*)	111.9(2)
O(1*g*)–N(2*g*)	1.412(3)	C(1*g*)–O(3*g*)–C(4*g*)	116.7(2)
O(2*g*)–C(1*g*)	1.191(2)	C(3*g*)–N(1*g*)–O(1*g*)	105.4(2)
O(3*g*)–C(1*g*)	1.314(2)	C(2*g*)–N(2*g*)–O(1*g*)	104.4(2)
O(3*g*)–C(4*g*)	1.479(3)	O(2*g*)–C(1*g*)–O(3*g*)	125.9(2)
N(1*g*)–C(3*g*)	1.293(3)	O(2*g*)–C(1*g*)–C(3*g*)	122.1(2)
N(2*g*)–C(2*g*)	1.310(3)	O(3*g*)–C(1*g*)–C(3*g*)	112.0(2)
N(3*g*)–C(2*g*)	1.334(2)	N(2*g*)–C(2*g*)–N(3*g*)	123.5(2)
C(1*g*)–C(3*g*)	1.477(3)	N(2*g*)–C(2*g*)–C(3*g*)	108.0(2)
C(2*g*)–C(3*g*)	1.433(3)	N(3*g*)–C(2*g*)–C(3*g*)	128.4(2)
C(4*g*)–C(5*g*)	1.468(5)	N(1*g*)–C(3*g*)–C(2*g*)	110.4(2)
		N(1*g*)–C(3*g*)–C(1*g*)	122.0(2)
		C(2*g*)–C(3*g*)–C(1*g*)	127.6(2)
		C(5*g*)–C(4*g*)–O(3*g*)	108.8(2)

4-(2-chloroethylamino)-1,2,5-oxadiazole-3-carboxylic acid hydrazide (G2)

1	2	3	4
Cl(1*g*)–C(5*g*)	1.782(4)	N(1*g*)–O(1*g*)–N(2*g*)	110.7(2)
O(1*g*)–N(1*g*)	1.375(3)	C(3*g*)–N(1*g*)–O(1*g*)	106.1(3)
O(1*g*)–N(2*g*)	1.403(4)	C(2*g*)–N(2*g*)–O(1*g*)	104.6(3)
O(2*g*)–C(1*g*)	1.225(4)	C(2*g*)–N(3*g*)–C(4*g*)	123.4(3)
N(1*g*)–C(3*g*)	1.296(4)	C(1*g*)–N(4*g*)–N(5*g*)	119.8(3)
N(2*g*)–C(2*g*)	1.313(4)	O(2*g*)–C(1*g*)–N(4*g*)	126.7(3)
N(3*g*)–C(2*g*)	1.347(4)	O(2*g*)–C(1*g*)–C(3*g*)	117.6(3)
N(3*g*)–C(4*g*)	1.440(4)	N(4*g*)–C(1*g*)–C(3*g*)	115.7(3)
N(4*g*)–C(1*g*)	1.310(4)	N(2*g*)–C(2*g*)–N(3*g*)	124.7(3)
N(4*g*)–N(5*g*)	1.421(4)	N(2*g*)–C(2*g*)–C(3*g*)	109.2(3)
C(1*g*)–C(3*g*)	1.493(4)	N(3*g*)–C(2*g*)–C(3*g*)	126.1(3)
C(2*g*)–C(3*g*)	1.422(4)	N(1*g*)–C(3*g*)–C(2*g*)	109.4(3)
C(4*g*)–C(5*g*)	1.504(5)	N(1*g*)–C(3*g*)–C(1*g*)	124.0(3)
		C(2*g*)–C(3*g*)–C(1*g*)	126.5(3)
		N(3*g*)–C(4*g*)–C(5*g*)	113.6(3)
		C(4*g*)–C(5*g*)–Cl(1*g*)	111.3(2)

4-(2-chloroethylamino)-1,2,5-oxadiazole-3-carboxylic acid amine (G3)

O(1*g*)–N(1*g*)	1.379(4)	N(1*g*)–O(1*g*)–N(2*g*)	110.3(3)
O(1*g*)–N(2*g*)	1.394(4)	C(3*g*)–N(1*g*)–O(1*g*)	106.5(3)
O(2*g*)–C(1*g*)	1.235(4)	C(2*g*)–N(2*g*)–O(1*g*)	104.9(3)

TABLE 2 (Continued)

1	2	3	4
N(1*g*)–C(3*g*)	1.287(4)	N(4*g*)–C(1*g*)–O(2*g*)	127.0(3)
N(2*g*)–C(2*g*)	1.311(5)	N(4*g*)–C(1*g*)–C(3*g*)	118.5(3)
N(3*g*)–C(2*g*)	1.352(5)	O(2*g*)–C(1*g*)–C(3*g*)	114.5(3)
N(4*g*)–C(1*g*)	1.225(4)	N(2*g*)–C(2*g*)–N(3*g*)	124.1(3)
C(1*g*)–C(3*g*)	1.509(4)	N(2*g*)–C(2*g*)–C(3*g*)	109.2(3)
C(2*g*)–C(3*g*)	1.425(4)	N(3*g*)–C(2*g*)–C(3*g*)	126.5(3)
		N(1*g*)–C(3*g*)–C(2*g*)	109.1(3)
		N(1*g*)–C(3*g*)–C(1*g*)	122.1(3)
		C(2*g*)–C(3*g*)–C(1*g*)	128.8(3)

Note. Symmetry operation: #1 –*x*+2, –*y*+1, –*z*.

TABLE 3. Geometrical Parameters of Hydrogen Bonds in I-III

Donor–H···Acceptor	*d*(D–H), Å	*d*(H···A), Å	*d*(D···A), Å	∠DHA, deg
Complex I				
N(3*g*)–H(1N3)...O(4)	0.90	2.23	3.087(2)	158
N(3*g*)–H(2N3)...O(16)	0.93	2.46	3.202(2)	137
N(3*g*)–N(2N3)...O(2*g*)	0.93	2.48	3.022(2)	118
C(4*g*)–H(4*g*1)...O(1)#1	0.97	2.43	3.311(3)	150
C(5*g*)–H(5*g*2)...O(7)#1	0.96	2.58	3.537(3)	175
C(6)–H(6*a*)...N(2*g*)	0.97	2.61	3.417(3)	141
C(14)–H(14*b*)...O(2*g*)	0.97	2.46	3.311(3)	147
Complex II				
N(4*g*)–H(4*g*)...O(4)#2	0.86	2.07	2.905(4)	164
N(3*g*)–H(3*g*)...O(2*g*)#3	0.86	2.16	2.873(4)	140
N(3*g*)–H(3*g*)...O(2*g*)	0.86	2.41	2.967(4)	123
N(5*g*)–H(1*g*5)...O(1)	0.95(1)	2.20(2)	3.110(4)	161(3)
N(5*g*)–H(2*g*5)...O(7)	0.95(1)	2.18(2)	3.092(4)	161(3)
Complex III				
N(3*g*)–H(1N3)...O(2*g*)#4	0.86	2.01	2.854(5)	166
N(3*g*)–H(2N3)...O(2*g*)	0.86	2.38	2.928(5)	122
N(3*g*)–H(2N3)...N(2*g*)#5	0.86	2.59	3.077(5)	117
N(4*g*)–H(4*g*2)...O(1*w*)	0.86	1.94	2.783(4)	166
O(1*w*)–H(1*w*)...O(10)	1.12(5)	1.76(5)	2.842(4)	161(4)
O(1*w*)–H(1*w*)...O(10*a*)	1.12(5)	1.97(6)	2.93(2)	142(4)
O(1*w*)–H(2*w*)...O(16)	1.08(6)	1.89(6)	2.959(5)	173(5)
O(1*w*)–H(2*w*)...O(16*a*)	1.08(6)	2.00(6)	2.957(18)	146(4)

Note. Symmetry operations: #1 –*x*+1/2, *y*+1/2, –*z*+3/2, #2 –*x*+2, –*y*+1, –*z*, #3 –*x*+1, –*y*, –*z*, #4 *x*, –*y*+2, *z*–1/2, #5 *x*, –*y*+2, *z*+1/2.

Complex I. Figure 1 presents the structure of molecular complex I. The stoichiometry of the complex is 1:1. The amino group of the guest forms two hydrogen bonds NH···O with 18-crown-6 oxygens; the distances N(3*g*)···O(4) = 3.087(2), N(3*g*)···O(16) = 3.202(2) Å. The amino nitrogen of the guest is 1.797(2) Å away from the mean plane through the heteroatoms of the macrocycle. The ethyl group of the guest interacts with the neighboring 18-crown-6 molecule related to the basic molecule by the twofold screw axis. The short contacts are CH···O(crown) with one hydrogen atom of the

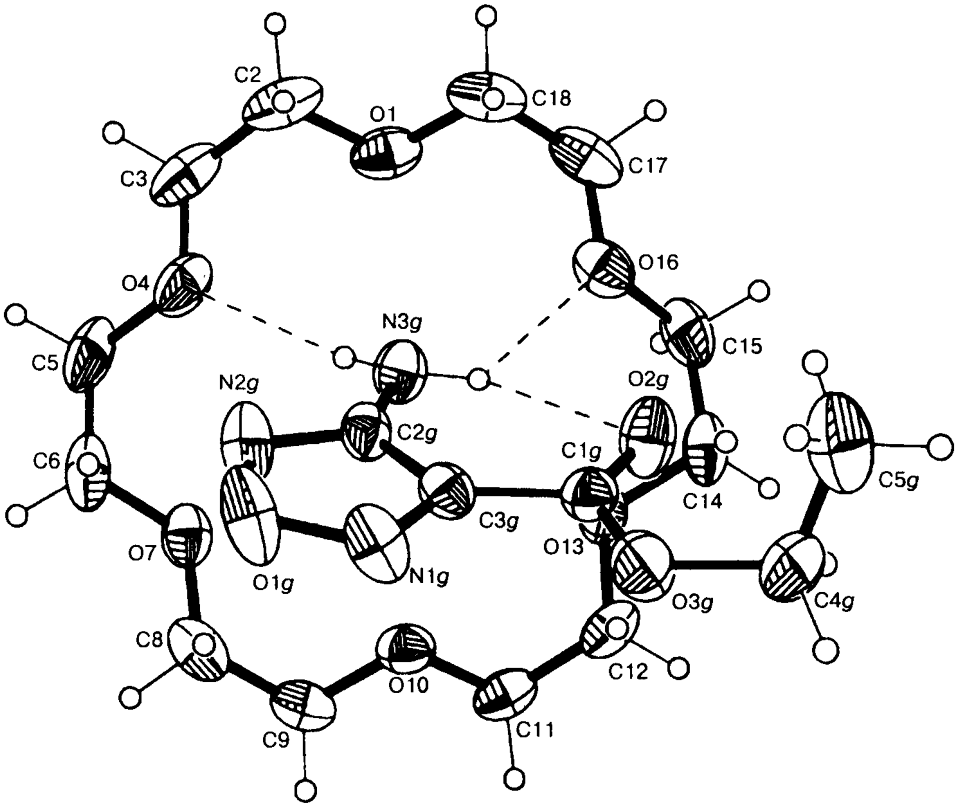


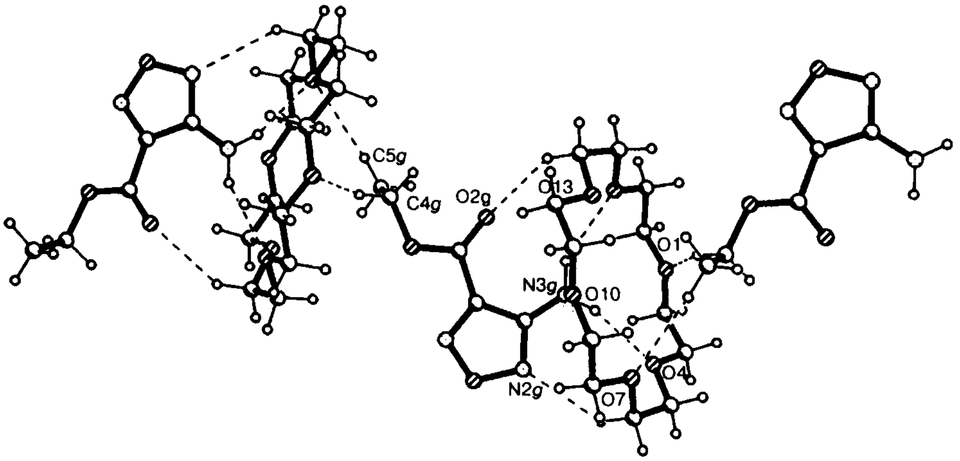
Fig. 1. Structure of complex I with an atomic numbering scheme.

methyl group and one hydrogen atom of the methylene group; C(4*g*)···O(1) $(-x+1/2, y+1/2, -z+3/2)$ = 3.311(3), C(5*g*)···O(7) $(-x+1/2, y+1/2, -z+3/2)$ = 3.537(3) Å. In related complexes, the crown ether–methyl group contacts are C···O = 3.264(7)-3.801(7) Å in the complex with bis-methyl-10-camphorsulfonate [13a] and 3.287(3)-3.598(3) Å in the complex with dimethylsulfoxide [13b]. All of the above-mentioned CH···O distances do not exceed the upper limit adopted in [4]. Thus host–guest interactions involve four of six oxygens of the 18-crown-6 molecule; in each pair [O(4) and O(16), O(1) and O(7)], the oxygen atoms are separated by the oxyethylene fragment.

This arrangement of the complex with the sides of the crown ether molecule coordinating the guest molecule in different ways is a rare occurrence in 18-crown-6 complexes, which was noted, e.g., in a 18-crown-6 complex with 6-chloro-7-sulfamido-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide [11]. The crown ether is most often centrosymmetric in host–guest complexes, with two guest molecules coordinated to the two sides of the macrocycle in the same way [10].

Figure 2 shows a fragment of the –H–G1–H–G1– type polymer chain directed along the *y* axis in a crystal. Two mild interactions, C(6)···N(2*g*) = 3.417(3) and C(14)···O(2*g*) = 3.311(3) Å, stabilize the chain along with the above interactions. The dihedral angle between the planes through the oxygen atoms of the crown ether and the atoms forming the five-membered heterocycle of the guest equals 57.35(8)°.

Complex II. Figure 3 presents the structure of the molecular complex II. Its stoichiometry is 1:2; the crown ether molecule occupies a position around the inversion center at the point (1, 0.5, 0). The two guest molecules flanking the cycle interact with the crown ether molecule in the same way. All hydrogen atoms of the hydrazine group participate in these contacts. The primary amino group forms two hydrogen bonds NH···O with the O(1) and O(7) atoms separated by one oxyethylene fragment. The N···O(crown) distances are N(5*g*)···O(1) 3.110(4) and N(5*g*)···O(7) 3.092(4) Å. The secondary amino group forms an NH···O hydrogen bond with the O(4) atom of the macrocycle; the distance N(4*g*)···O(4) $(-x+2, -y+1, -z)$ = 2.905(4) Å. The same coordination of the hydrazide group was noted for the 18-crown-6 complex with 2,4-dinitrophenylhydrazine [14]. In both cases, the –G–H–G– arrangement is due to the participation of the neighboring nitrogen molecules of the guest molecule in coordination to crown ether. Thus in II, all crown ether oxygens are involved in the complex-forming hydrogen bonds. The amino nitrogen atom of the guest is 1.906(3) Å away from the plane through



Fug. 2. Fragment of a polymer chain in I.

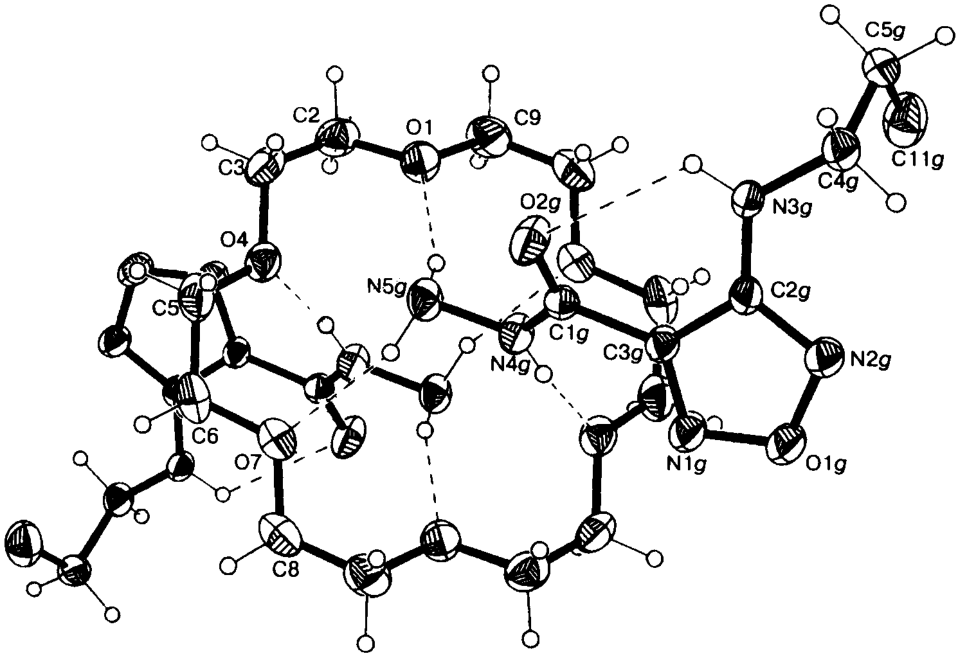


Fig. 3. Structure of complex II with an atomic numbering scheme.

all crown ether oxygens. The dihedral angle between this plane and the plane through the atoms of the five-membered ring of the guest is 46.99(9)°.

Figure 4 presents a fragment of the polymer chain –H–G2–G2–H– formed in the structure of II. The guest molecules are linked into a centrosymmetric dimer by two N–H···O=C hydrogen bonds with the distance N(3*g*)···O(2*g*) (–*x*+1, –*y*, –*z*) = 2.873(4) Å. The chain is of “head-to-head” type and develops along the [110] direction in the crystal.

Complex III. The structure of the molecular complex III is shown in Fig. 5. The crown ether:guest:water ratio in the complex is 1:1:1. All molecules in the complex lie in the general positions. The crown ether molecule is disordered over two positions with an occupancy of 83 and 17%, respectively. The two positions are related to each other by rotation through an angle of 18.6° in the mean plane of the macrocycle. Further discussion concerns only the image of the major component of the crown ether, since an analogous picture of interaction is also preserved for the image with minor occupation. In contrast to I and II, this compound is a monohydrate, in which the water molecule interacts with two crown ether oxygens; O(1*w*)···O(10) 2.842(4) and O(1*w*)···O(16) 2.959(5) Å. For the second position of the crown ether, O(1*w*)···O(10*a*) 2.92(2) and O(1*w*)···O(16*a*) 2.957(18) Å. The oxygen atom of the water molecule is 1.014(3) Å away from the plane

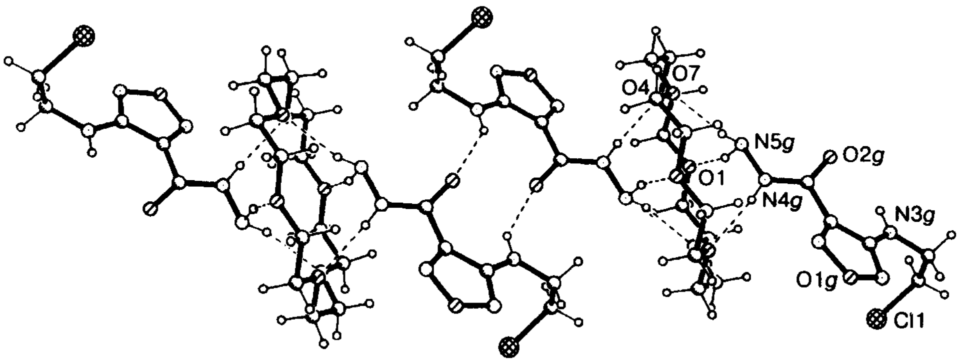


Fig. 4. Fragment of a polymer chain in II.

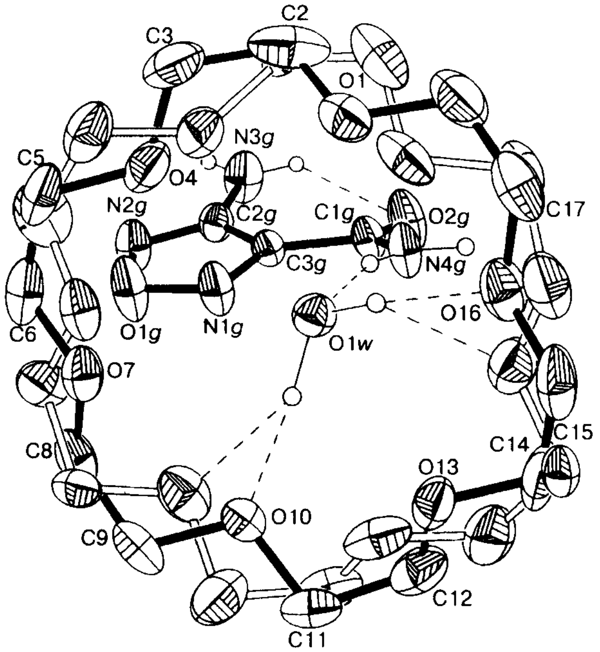


Fig. 5. Structure of complex III with an atomic numbering scheme.

through the heteroatoms of the macrocycle. Thus only two OH···O hydrogen bonds stabilize the 18-crown-6–H_2O fragment. The water molecule bridges the crown ether and the guest with which it interacts by means of the NH···O(1*w*) hydrogen bond, donating a lone electron pair for this purpose; the distance N(4*g*)···O(1*w*) 2.783(4) Å. The bridging function of the water molecule is also observed in some other complexes. e.g., in [18-crown-6·SiF_4·$2H_2O$] [15], [18-crown-6·(BF_3·$2H_2O$)$_2$·$2H_2O$] [16]. The arrangement of the 18-crown-6–water molecule associate is analogous to the arrangement found in the 18-crown-6·H_2O complex with 3,4-diamino-1,2,5-oxadiazole [5], in which the water molecule also forms two OH···O(crown) hydrogen bonds with distances 2.924(4) and 2.878(4) Å, and the electron pair forms a hydrogen bond with the amino group of the guest; the distance N···O(*w*) = 2.905(9) Å.

A fragment of the structure of III is presented in Fig. 6. The middle of the ribbon is occupied by a chain of guest molecules built according to the ‘‘dendritic parquet’’ motif. The guest molecules in the chain are linked by N–H···O=C and N–H···N type hydrogen bonds; the parameters of these interactions are N(3*g*)···O(2*g*) ($x, -y+2, z-1/2$) = 2.854(5) and N(3*g*)···N(2*g*) ($x, -y+2, z+1/2$) = 3.077(5) Å. A similar guest chain was previously fixed for the 18-crown-6 complex with 5-amino-1,2,4-triazole [7], where the guest molecules are connected by NH···N hydrogen bonds.

Molecular geometries in complexes I, II, and III. In all the complexes, the 18-crown-6 molecule has approximately D_{3d} symmetry. The *gosh*-torsion angles at the C–C bonds are 62.8(12)-71.5(2)°, and the *trans*-torsion angles at the C–O

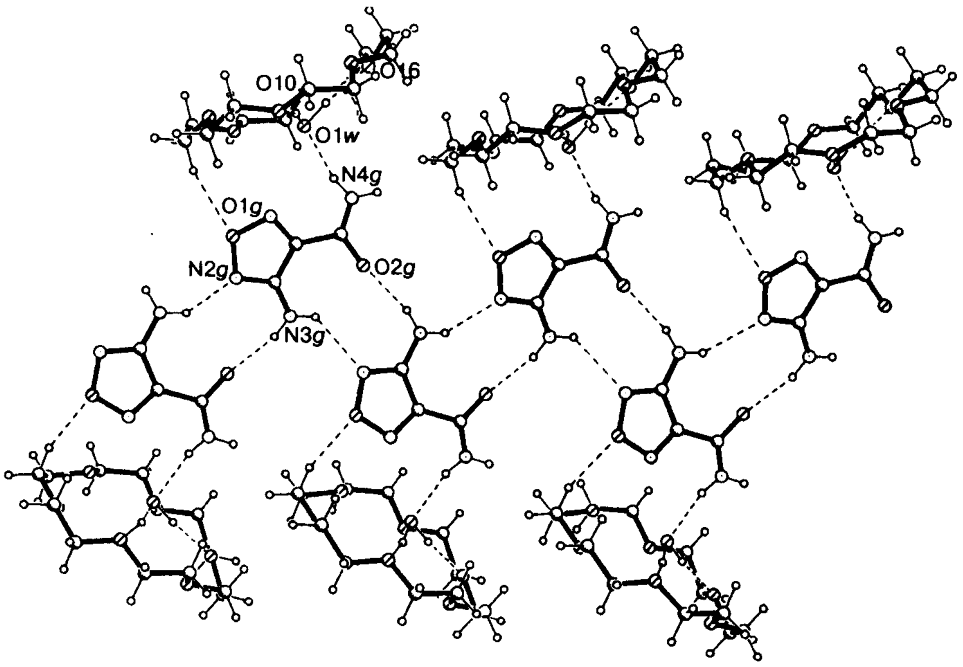


Fig. 6. Fragment of a ribbon in III.

bonds take the values 169.0(6)-179.9(5)°. The O···O transannular distances are from 5.536(5) to 5.716(5) Å. The interatomic distances and the bond angles in the 18-crown-6 molecule in the complexes have values typical in crown ethers.

In the planar five-membered heterocyclic ring of the guest molecules, the nonhydrogen atoms are coplanar to an accuracy of 0.005 (G1), 0.001 (G2), 0.004 Å (G3). In all the three cases, the molecule has an intramolecular hydrogen bond of NH···O=C type (Figs. 1, 3, and 5); the N(3*g*)···O(2*g*) distance is 3.022(2) (I), 2.967(4) (II), and 2.928(5) Å (III). This is a bifurcate bond, since its hydrogen atom is simultaneously involved in an NH···O type hydrogen bond with the crown ether oxygen in I and III, whereas in II it is responsible for the formation of the dimer associate of the guest. The intramolecular hydrogen bond closes the six-membered ring including the atoms ···H(3N3)–N(3*g*)–C(2*g*)–C(3*g*)–C(1)–O(2*g*)···. This ring is also virtually planar, with deviations of its atoms from the mean plane 0.076 (I), 0.145 (II), 0.101 Å (III). Therefore one can say that the heterocyclic framework of the guest involves the five- and six-membered rings fused at the C(2*g*)–C(3*g*) bond to form a nearly planar system. The dihedral angle between the planes of the ring atoms is 3.37(2), 10.09(2), 6.61(3)° in G1-G3 molecules, respectively.

In compounds I-III, the small molecules are coordinated in different ways. The bilateral equivalent coordination mode, often reported in the literature, is met in complex I; in III and II, we have one- and many-sided coordination, respectively. In III, there are no direct host–guest contacts, although the guest has an easily coordinating amino group. The interaction is mediated by the bridging water molecule, and the hydrogen bonds are formed by only two oxygen atoms of the macrocycle. Examples I-III prove that host–guest complexes have diverse topologies depending on changes in the geometry and the nature of the donor groups of the guest.

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