Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **16:** 315–327, 1993.
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An X-Ray Study of a 12-Crown-4 Host-Guest Complex. Crystal Structure of the 4 : 6 Complex between 12-Crown-4 and Aminosulfuric Acid

YURII A. SIMONOV,* MARINA S. FONARI,
ALEXANDER A. DVORKIN and TADEUSH I. MALINOVSKI
Institute of Applied Physics of the Academy of Sciences of Moldova, Kishinev, 277028 Moldova.

JANUSZ LIPKOWSKI
Instytut Chemii Fizycznej PAN, 01-244 Warszawa, Poland.

and

EDWARD V. GANIN
Odessa State University of I.I. Mechnikov, 270100, Odessa, Ukraine.

(Received: 21 July 1993; in final form: 12 November 1993)

Abstract. The title compound was prepared by treating a methanolic solution of 12-crown-4 with an aqueous solution of aminosulfuric acid. The crystal for X-ray analysis was obtained by recrystallization from acetone. The compound [(12-crown-4)$_4$ · [NH_3SO_3)$_6$] (**1**) is monoclinic, space group $P2_1/a$, $a = 21.900(8)$, $b = 15.499(5)$, $c = 18.079(5)$ Å, $\gamma = 67.85(2)°$. Refinement led to a final conventional R value of 0.0788 for 3280 reflections.

Key words: 12-Crown-4, aminosulfuric acid, host-guest complex structure, symmetric disparity, H-bonds.

Supplementary Data relating to this publication have been deposited with British Library as Supplementary Publication No. 82160 (22 pages) and include: the list of F_{obs}, F_{calc}; tables of bond distances, bond angles and selected least square planes, as well as a figure of 12-crown-4 in C_4-conformation.

1. Introduction

Crown ether host-guest complexes with guests containing amine-coordinating entities are well known and have been described in [1], for instance. In the isolated units of 1 : 2 complexes two guest molecules approach the ether moiety from both sides, each NH_2 group forming N-H...O hydrogen bonds with two or more nucleophilic sites of the ring. The remaining ring oxygen atoms are also attracted to the polar guests by dipole-dipole interactions.

In the neutral complexes with ammonia salts (and related guests such as the zwitterion of aminosulfuric acid, $NH_3^+SO_3^-$) the positive charge is associated with the nitrogen atom. The corresponding NH_3^+ function ideally matches the 18-membered

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* Author for correspondence.

crown ether cavity. Aminosulfuric acid [2–4] was found to form 1 : 1 complexes with 18-membered crown ethers: 18-crown-6 [2–3], benzo-18-crown-6 [3] and the A and B isomers of dicyclohexano-18-crown-6 [4]. The crown exhibits D_{3d} symmetry, the intermolecular N-H...O hydrogen bonding interaction between the host and the guest moieties occurred only on one face of the macrocycle, involving the NH_3^+ center and the upper triangle of the ether oxygen atoms. Presumably, cation repulsion prevents the arrangement of a second guest molecule on the opposite face of the crown. In all the observed structures the nitrogen atom is displaced by approximately 1 Å from the mean plane of the macrocycle. The guest is bound to the crown by two different types of interactions: hydrogen bonding to a triangle of alternate oxygen atoms located on one face of the crown and ion-dipole attractions involving oxygen atoms located on the opposite side of the ring.

In the case of 15-membered crown-ethers (15-crown-5 [5] and benzo-15-crown-5 [5]) there is a symmetric discrepancy between the crown ether framework and the tripod of the aminoacid NH_3^+ group. It causes a change in the character of the host-guest interaction from the individual 1 : 1 complex to centrosymmetric dimers with N...O_{crown} distances increased to 2.76–2.86 Å, together with deviation of the N-S bond from the normal to the mean plane of the macrocyclic heteroatoms.

In the literature there are only a few reports concerning host-guest complexes of 12-crown-4 with cyclodextrins [6–7], where 12-crown-4 behaves as a guest. We have now succeeded in preparing and describing a new host-guest complex of 12-crown-4. The preparation of a crystalline complex of 12-crown-4 with aminosulfuric acid affords an opportunity to extend our knowledge of the structural properties of this ligand and to explore the change in the host-guest interaction when topological and symmetric disparity between aminosulfuric acid and a small crown ether occurs.

2. Experimental

2.1. SYNTHESIS OF COMPLEX 1

12-Crown-4 (1.76 g, 0.01 mol) in 10 mL methanol was mixed with an aqueous solution (10 mL) of aminosulfuric acid (0.97 g, 0.01 mol). The precipitate formed after cooling to 20°C was filtered, washed with methanol and air dried. Crystals of complex **1** suitable for X-ray crystallography were obtained by recrystallization from acetone. Crystals of the complex are colourless, soluble in methanol, acetone and water, m.p. 212–214°C (decomp.). IR (KBr), ν, cm^{-1}: 2960–2850 (C-H), 1135 (C-O-C). *Anal. Calc.* for **1** (%): C 29.86; H 6.42; N 6.54; S 14.94. *Found*: C 29.72; H 6.40; N 6.61; S 14.90.

2.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

A summary of the data collection parameters for **1** is given in Table I. The intensity data were collected using a RED-4 diffractometer equipped with MoK_{α}-radiation

TABLE I. Crystal data and summary of intensity data collection and structure refinement for complex **1**.

Complex **1**	[(12-crown-4)$_4$ (NH$_3$SO$_3$)$_6$]
Formula	$C_{32}H_{82}N_6O_{34}S_6$
Mol.wt.	1287.4
M.p., °C	212–214
Crystal system	monoclinic
Space group	$P2_1/a$
Cell constants	
a,Å	21.900(8)
b,Å	15.499(5)
c,Å	18.079(5)
γ,°C	67.85(2)
Cell vol., Å^3	5683.7
Z	4
$D_{\text{calc.}}$, g cm^{-3}	1.504
Specimen dimensions, mm	$0.5 \times 0.5 \times 0.4$
Radiation	MoK_α
μ (cm^{-1})	3.247
F (000)	2736
No refl. measured	3280
Condition for obs. refl.	$I > 2\sigma(I)$
R	0.0788
$w = 9.7747/\sigma^2(F)$	
R_w	0.0615
Residual extrema in final difference map (e/Å^3)	0.66 −0.59
Maximum shift/error ration	0.45

by the ω-technique. The intensities were corrected for background and Lp effects but not for absorption. Cell dimensions were obtained by a least-squares refinement of 15 reflections with $10 < 2\vartheta < 40°$. Reflections with $I(hkl) > 2\sigma(I)$ were considered to be observed and used in the refinement. The structure was solved by direct methods using SHELXS-86 [8]. The refinement was carried out using a full-matrix least-squares technique with the SHELX76 [9] system of programs through the CRYSRULER and PARST package [10] (Polish Version) using an IBM 486/487 personal system. It was found in the process of the refinement that one independent molecule of the crown ether was disordered and its two sets of parameters were refined with the site occupation factor of 0.5 in isotropic refinement. The positions of crown ether hydrogen atoms were calculated theoretically. The final R is 0.0788 for 3280 reflections. The final positional parameters are given in Table II, bond lengths and angles are given in the Supplementary Data.

TABLE II. Fractional atomic coordinates ($\times 10^{-4}$) and B(eq) with e.s.d.s. (in parentheses) for non-hydrogen atoms.

S(1)	1510(2)	8582(2)	9002(1)	2.73(9)
O(1S1)	899(4)	8740(5)	9358(5)	4.5(3)
O(2S1)	2084(4)	8198(5)	9448(4)	3.9(2)
O(3S1)	1515(4)	9311(5)	8514(4)	4.0(2)
N(1S1)	1595(4)	7660(5)	8384(4)	2.4(2)
S(2)	2998(2)	9632(2)	7942(1)	3.2(1)
O(1S2)	2567(5)	9914(6)	7347(5)	6.2(4)
O(2S2)	3467(4)	10074(5)	8026(5)	5.1(3)
O(3S2)	3273(4)	8658(5)	8104(4)	4.6(2)
N(1S2)	2467(4)	10092(6)	8712(5)	3.3(3)
S(3)	1542(2)	8065(2)	4183(1)	2.80(9)
O(1S3)	2080(4)	8349(5)	4354(4)	3.7(2)
O(2S3)	1669(4)	7106(5)	4314(4)	4.4(3)
O(3S3)	916(4)	8712(5)	4395(5)	4.5(3)
N(1S3)	1527(4)	8111(5)	3203(4)	2.4(3)
S(4)	2072(2)	5232(2)	9560(2)	3.3(1)
O(1S4)	2520(5)	5001(6)	10141(5)	6.2(3)
O(2S4)	1766(4)	6189(5)	9394(4)	4.5(3)
O(3S4)	1635(5)	4742(5)	9530(5)	5.8(3)
N(1S4)	2608(4)	4771(6)	8784(5)	3.4(3)
S(5)	1569(2)	2930(2)	8277(1)	2.9(1)
O(1S5)	2109(4)	3215(5)	8098(4)	3.9(2)
O(2S5)	927(4)	3564(6)	8073(5)	4.7(3)
O(3S5)	1695(4)	1968(5)	8154(4)	4.8(2)
N(1S5)	1557(5)	2985(5)	9268(5)	3.0(3)
S(6)	1412(2)	3768(2)	3513(2)	2.8(1)
O(1S6)	804(4)	3925(5)	3145(5)	4.7(3)
O(2S6)	1996(4)	3382(5)	3070(4)	4.5(2)
O(3S6)	1416(4)	4490(5)	4004(4)	4.3(2)
N(1S6)	1486(4)	2829(5)	4113(4)	2.7(2)
O(1A)	372(5)	7519(7)	2951(5)	5.9(3)
C(2A)	−115(10)	7906(20)	2504(9)	9.8(1.2)
C(3A)	−228(7)	8959(10)	2597(10)	5.6(5)
O(4A)	384(6)	9139(6)	2314(6)	6.7(4)
C(5A)	456(12)	9136(12)	1573(11)	8.9(9)
C(6A)	1120(10)	9002(12)	1381(9)	6.5(7)
C(7A)	1611(5)	8076(7)	1650(5)	6.3(4)
C(8A)	1675(10)	7340(17)	1225(9)	9.1(9)
C(9A)	1940(10)	6493(11)	1616(8)	8.7(7)
O(10A)	1589(5)	6428(6)	2325(5)	6.0(3)
C(11A)	1101(11)	6190(11)	2161(10)	8.3(7)
C(12A)	665(9)	6442(9)	2763(9)	6.6(6)
O(1B)	1808(4)	2556(7)	768(4)	5.2(3)
C(2B)	1429(11)	2982(18)	1322(9)	10.1(1.1)
C(3B)	1054(10)	3970(10)	1067(7)	6.9(6)

3. Discussion

3.1. THE OVERALL SYSTEM OF INTERACTIONS

12-Crown-4 is known to exhibit binding properties toward metal entities. Two main types of complexes are formed. The first [11–29] is a complex with a metal : crown stoichiometry of 1 : 1, the coordination sphere of the metal being filled by four oxygen atoms of the crown ether and anions. The second type [20–26] is a sandwich-like complex with a metal : crown stoichiometry of 1 : 2 and the coordination sphere of the metal being filled by eight oxygen atoms of two molecules of crown ether. As stressed above, there are no molecular complexes based on 12-crown-4.

The complex of 12-crown-4 with aminosulfuric acid has a host-guest stoichiometry of 4 : 6. The structural formula for **1** is $[(12\text{-crown-4}) \cdot NH_3SO_3]_4 \cdot 2\,NH_3SO_3$. The projection of the crystal packing on the ab plane is shown in Figure 1. Out of the four independent host molecules (labelled A, B, C and D) one (D) is disordered, and it was possible to distinguish its two positions (Figure 2). Four out of the six molecules of aminosulfuric acid take part in the host-guest interactions (the corresponding guest indexes are $n = 1$–6). The two molecules of aminosulfuric acid ($n = 2, 4$) do not participate in the host : guest interactions. They act like solvents and fill the empty cavities in the crystal packing, as the sulfaguanidine molecule does in the complex with isomer A of dicyclohexano-18-crown-6 [30]. We consider that in the described system, as in the complexes of aminosulfuric acid with 18- and 15-membered crown-ethers [2–5] the guest molecules are present in the form of zwitterions, $NH_3^+SO_3^-$ (within the limits of $2\sigma(R)$ all S-O distances were found to be similar and their average value for all six guest molecules is 1.42 Å). In the independent part of the crystal cell six NH_3^+ groups serve as donors of protons. Table III illustrates all the contacts of these groups which are shorter than the sum of the van der Waals radii of an NH_3^+ group and an oxygen atom [31].

Each of the guest molecules ($n = 1, 3, 5, 6$) interacting with 12-crown-4 has four shortened contacts lying within the limits of 2.979–3.130 Å. Besides, pairs 3–5 and 1–6 of these molecules are united in dimers by hydrogen bonds of the N-H...O type (the corresponding N...O distances are 2.811–2.960 Å). A similar dimerization of the zwitterion of aminosulfuric acid has been observed in its complexes with 15-crown-5 and benzo-15-crown-5 [5]. Thus, in the crystal host (H) : guest(G) 1 : 1 units are tied in the dimeric associates of the following type: Ha $\Leftarrow$ G3 = G5 $\Rightarrow$ Hb and Hc $\Leftarrow$ G6 = G1 $\Rightarrow$ Hd (arrows show H-bonds) (Figure 3). An analysis of the system of interactions of the coordinated guest molecules with the solvated ones permits us to select some more guest-guest H-bonds (Table III): G1 $\Leftrightarrow$ G4 = 2.835, G3 $\Leftrightarrow$ G2 = 2.835, G5 $\Leftrightarrow$ G4 = 2.832 and G6 $\Leftrightarrow$ G2 = 2.831 Å. Thus, every molecule taking part in host : guest interactions with the formation of 1 : 1 entities, participates as a hydrogen donor in two intermolecular hydrogen bonds of the guest-guest type. Such participation requires two protons from each NH_3^+ group for these bonds. There remains only one proton from each NH_3^+ group for the

TABLE II. Continued.

O(4B)	656(5)	4007(6)	375(5)	5.7(3)
C(5B)	91(11)	3935(10)	522(11)	8.8(7)
C(6B)	−148(6)	3664(9)	9842(9)	5.0(5)
O(7B)	324(4)	2680(7)	9577(4)	5.4(4)
C(8B)	287(8)	1959(12)	9951(10)	6.6(6)
C(9B)	812(8)	1145(9)	9751(8)	4.7(5)
O(10B)	1494(6)	1203(6)	9987(5)	6.3(3)
C(11B)	1586(11)	1088(12)	698(10)	8.8(8)
C(12B)	2097(6)	1501(9)	887(7)	4.5(5)
O(1C)	370(4)	2198(7)	4517(4)	4.7(3)
C(2C)	615(11)	1186(14)	4711(8)	8.0(8)
C(3C)	1093(10)	885(11)	5217(12)	8.4(7)
O(4C)	1642(4)	1077(5)	5072(4)	4.6(2)
C(5C)	2041(10)	1200(13)	5741(7)	8.6(7)
C(6C)	1770(12)	2021(19)	6090(9)	9.7(12)
O(7C)	1709(4)	2754(7)	5677(4)	4.9(3)
C(8C)	1239(10)	3718(16	5932(10)	8.7(8)
C(9C)	581(12)	3876(11)	5842(9)	8.9(8)
O(10C)	469(5)	3824(5)	5102(5)	5.1(3)
C(11C)	−164(7)	3655(9)	4918(9)	7.0(5)
C(12C)	−103(9)	2743(14)	4991(11)	8.8(8)
O(1D)	487(3)	7023(4)	7972(3)	4.5(1)
C(2D)	13(3)	7515(4)	7480(3)	4.5(1)
C(3D)	−66(3)	8513(4)	7610(3)	4.5(1)
O(4D)	579(3)	8651(4)	7405(3)	4.5(1)
C(5D)	690(3)	8659(4)	6668(3)	4.5(1)
C(6D)	1381(3)	8499(4)	6549(3)	4.5(1)
O(7D)	1829(3)	7548(4)	6858(3)	4.5(1)
C(8D)	1916(3)	6844(4)	6383(3)	4.5(1)
C(9D)	2176(3)	6007(4)	6815(3)	4.5(1)
O(10D)	1724(3)	5938(4)	7473(3)	4.5(1)
C(11D)	1237(3)	5749(4)	7214(3)	4.5(1)
C(12D)	750(3)	5975(4)	7820(3)	4.5(1)
O(1D′)	1474(6)	7760(7)	6378(6)	4.3(2)
C(2D′)	2017(6)	7296(7)	6796(6)	4.3(2)
C(3D′)	2205(6)	6291(7)	6571(6)	4.3(2)
O(4D′)	1653(6)	5939(7)	6797(6)	4.3(2)
C(5D′)	1624(6)	5787(7)	7531(6)	4.3(2)
C(6D′)	984(6)	5751(7)	7700(6)	4.3(2)
O(7D′)	425(6)	6675(7)	7505(6)	4.3(2)
C(8D′)	300(6)	7315(7)	8044(6)	4.3(2)
C(9D′)	−83(6)	8191(7)	7706(6)	4.3(2)
O(10D′)	254(6)	8485(7)	7038(6)	4.3(2)
C(11D′)	701(6)	8774(7)	7286(6)	4.3(2)
C(12D′)	1115(6)	8763(7)	6639(6)	4.3(2)

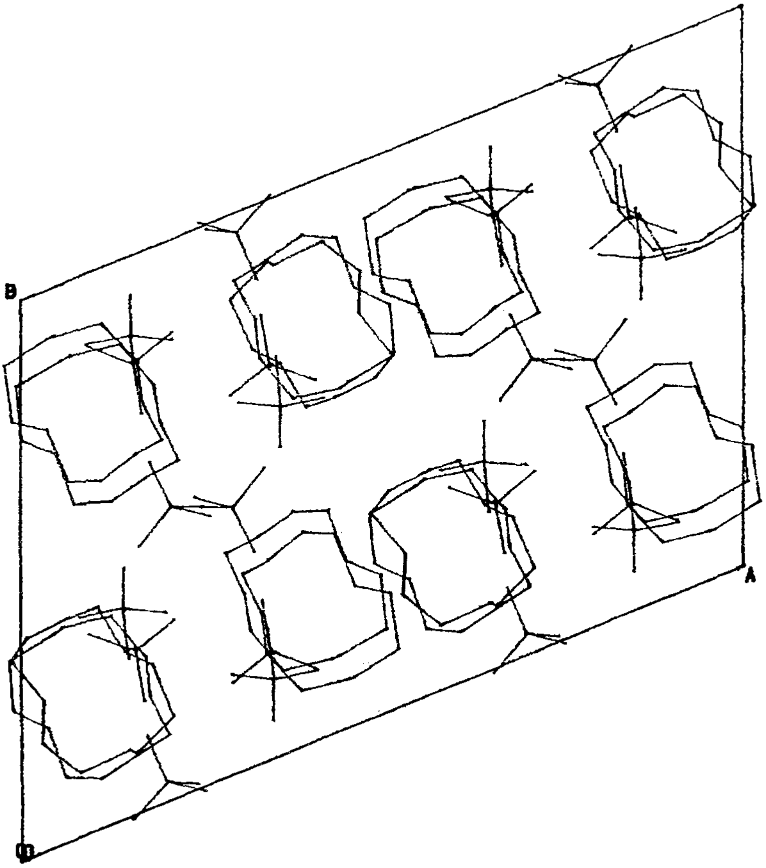

Fig. 1. Crystal packing of complex **1**.

interactions with the crown ether. Apparently, a collective system (six-centered N, H and four O atoms of crown ether) of electrostatic host-guest interactions is formed. This is responsible for the conformational change of 12-crown-4 in the complex.

3.1.1. *The Overall System: Remarks*

1. In the complexes of aminosulfuric acid with 18-membered crown ethers (18-crown-6, dicyclohexano-18-crown-6 (isomers *A* and *B*)) described previously three classic N-H...O hydrogen bonds are formed [2–4].

2. In the corresponding complex with benzo-18-crown-6 we observed the tendency of one of these bonds to bifurcate which was suggested by the rigidity of the pyrocatechol fragment entering the crown ether ring [3].

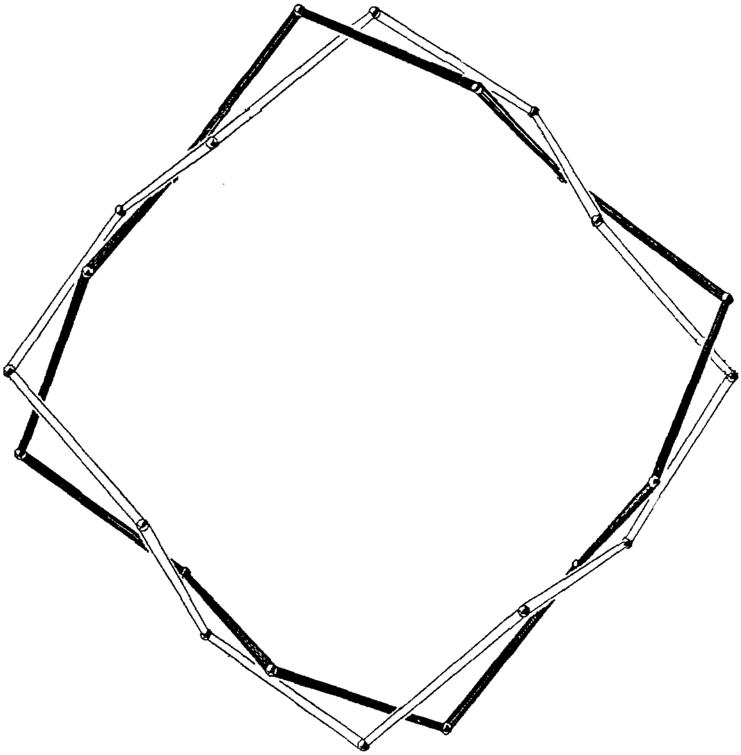

Fig. 2. Disordered molecule (D) of 12-crown-4 in complex **1**.

3. In the complexes with 15-crown-5 and benzo-15-crown-5 we noted collective interactions of two out of the three NH_3^+ protons with five (or four in the case of benzo-15-crown-5) oxygen atoms of the ring [5].

4. In the complex with 12-crown-4 only one proton of the guest zwitterion interacts with the system of the oxygen atoms of the ring. A similar influence and collective ring interaction with the less acidic proton was observed in the benzene complex with phosphorylated dibenzo-18-crown-6 [32].

Apparently, two factors are essential for the understanding of the peculiarities of the interaction:

(a) a geometric one – symmetric and size correspondence (inconsistency) of the NH_3^+ tripod with the crown ether ring;

(b) an electrostatic one – the formation of the positive charge on the nitrogen atom of the aminosulfuric acid zwitterion.

Pairs of solvated molecules of NH_3SO_3 ($n = 2, 4$) acting as H-donors form H-bonds of the N-H...O type (Table III), uniting dimers in the layers which are parallel

TABLE III. The shortest intermolecular N...O distances in **1**.

H-donor	H-acceptor	Distance, N...O, Å	Symmetry code for acceptor
N(1S1)	O(1D)	3.038	
	O(4D)	2.802	
	O(7D)	2.798	
	O(10D)	2.038	
	O(2S4)	2.835	$x,-1+y,z$
	O(1S6)	2.947	$0.5-x,2-y,-0.5+z$
N(1S2)	O(3S1)	2.801	
	O(3S5)	2.936	
N(1S3)	O(1A)	3.033	
	O(4A)	2.895	
	O(7A)	2.815	
	O(10A)	3.012	
	O(1S5)	2.923	$0.5-x,2-y,-0.5+z$
	O(2S2)	2.835	$0.5-x,2-y,0.5+z$
N(1S4)	O(2S3)	2.900	$0.5-x,2-y,0.5+z$
	O(2S6)	2.804	$0.5-x,3-y,-0.5+z$
N(1S5)	O(1B)	2.797	
	O(4B)	2.839	
	O(7B)	2.968	
	O(10B)	3.102	
	O(1S3)	2.924	$0.5-x,2-y,-0.5+z$
	O(3S4)	2.832	
N(1S6)	O(1C)	3.044	
	O(4C)	2.818	
	O(7C)	2.866	
	O(10C)	3.130	
	O(3S2)	2.831	$0.5-x,2-y,0.5+z$
	O(2S1)	2.988	$0.5-x,2-y,-0.5+z$

to the *bc* crystal plane (Figure 1). As H-bond donors, only pairs of these groups form H-bonds. The packing conditions suggest that the third proton is probably blocked and it does not take part in H-bonding. The structure can be described as a flaky one, where the guests are arranged between the sides formed by the crown ethers. Between themselves the crown ethers interact by the hydrophobic parts of the ring and these interactions are of a van der Waals character.

3.2. CONFORMATION AND GEOMETRY OF 12-CROWN-4

12-Crown-4 itself has C_i-symmetry [18] with a set of torsion angles: *gagg–ag–g–ag–gag*. (Here we use the terminology proposed by Dale, J., *Acta Chem. Scand.*,

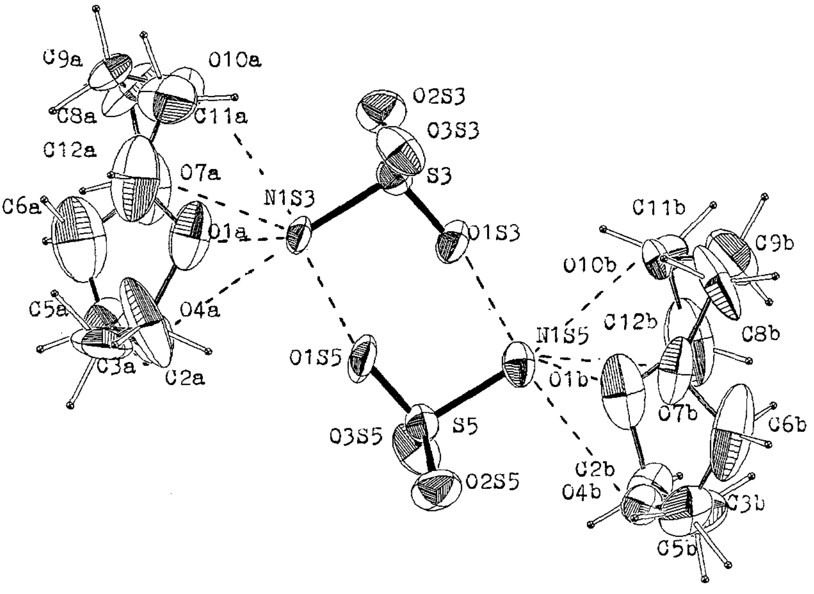

Fig. 3. ORTEP view of the (H-G)$_2$ dimer for complex **1** with the atom numbering scheme (other independent molecules are denoted in a similar way).

27, 1115 (1973), where $g+$,$g-$ *gauche* torsion angles are in the interval $\pm 30 \pm 60°$, while a corresponds to *anti* torsion angle in the range $\pm 120 \pm 180°$.)

Upon complex formation with a variety of metal ions, three other ring conformations have also been found by X-ray crystallography. C_4 symmetry ($ag\pm g\pm ag\pm g\pm ag\pm g\pm ag\pm g\pm$) is the most common one for 12-crown-4 in metal-ion complexes [11, 14, 18, 20, 21]. In these structures the heterocycle acts as a tetradentate ligand. Bonding to the metal occurs through four lone-pair orbitals from the same side of the ring directed toward the metal ion. For the C_s symmetry found for 12-crown-4 in its complex with $CuCl_2$ [12] and described by the set of torsion angles $ggaag{-}g{-}ag{-}aaga$, three lone pairs of oxygen atoms from one side and one from the opposite side of the ring are used. C_i host symmetry ($g{-}gaggg{-}gg{-}ag{-}g{-}g$) is found in its complex with $MgBr_2$ [27], where the metal ion is not connected properly with the crown ether. The oxygen atoms form a rhombic figure. In the complex $[UO_2Cl_2(OH_2)_2(12\text{-crown-}4)] \cdot (12\text{-crown-}4)$ [28] crown ether molecules exhibit neither of the common conformations (C_4 or C_i), although it is close to the normal C_4 symmetry. The conformation of the terminal crown molecule is close to C_i.

As can be seen from the torsion angle values listed in Table IV, the 12-crown-4 ring takes C_4 symmetry in all four independent crown subunits of the complex. Reference [33] reports the calculations of the 12-crown-4 conformation by molecular mechanics calculations. One of the low energy conformations agrees with

TABLE IV. Torsion angles with e.s.d.s. in parentheses (involving non-hydrogen atoms).

C(12A)-O(1A)-C(2A)-C(3A)	−165(1)
C(11A)-C(12A)-O(1A)-C(2A)	82(2)
O(4A)-C(3A)-C(2A)-O(1A)	65(2)
C(5A)-O(4A)-C(3A)-C(2A)	74(2)
C(6A)-C(5A)-O(4A)-C(3A)	−161(2)
O(7A)-C(6A)-C(5A)-O(4A)	62(2)
C(8A)-O(7A)-C(6A)-C(5A)	81(2)
C(9A)-C(8A)-O(7A)-C(6A)	−159(2)
O(10A)-C(9A)-C(8A)-O(7A)	54(2)
O(10A)-C(11A)-C(12A)-O(1A)	61(2)
C(11A)-O(10A)-C(9A)-C(8A)	84(2)
C(12A)-C(11)-O(10A)-C(9a)	−160(1)
C(12B)-O(1B)-C(2B)-C(3B)	−167(1)
C(11B)-C(12B)-O(1B)-C(2B)	79(2)
O(4B)-C(3B)-C(2B)-O(1B)	58(2)
C(5B)-O(4B)-C(3B)-C(2B)	82(2)
C(6B)-C(5B)-O(4B)-C(3B)	−161(2)
O(7B)-C(6B)-C(5B)-O(4B)	64(2)
C(8B)-O(7B)-C(6B)-C(5B)	76(2)
C(9B)-C(8B)-O(7B)-C(6B)	−169(1)
O(10B)-C(9B)-C(8B)-O(7B)	64(2)
C(11B)-O(10B)-C(9B)-C(8B)	75(2)
C(12B)-C(11B)-O(10B)-C(9B)	−160(1)
O(1B)-C(12B)-C(11B)-O(10B)	67(2)
C(12C)-O(1C)-C(2C)-C(3C)	163(1)
C(11C)-C(12C)-O(1C)-C(2C)	−85(2)
O(4C)-C(3C)-C(2C)-O(1C)	−54(2)
C(5C)-O(4C)-C(3C)-C(2C)	151 (2)
C(6C)-C(5C)-O(4C)-C(3C)	−77(2)
O(7C)-C(6C)-C(5C)-O(4C)	−62(2)
C(8C)-O(7C)-C(6C)-C(5C)	163(2)
C(9C)-C(8C)-O(7C)-C(6C)	−74(1)
O(10C)-C(9C)-C(8C)-O(7C)	−62(2)
C(11C)-O(10C)-C(9C)-C(8C)	161(2)
C(12C)-C(11C)-O(10C)-C(9C)	−80(1)
O(1C)-C(12C)-C(11C)-O(10C)	−54(2)

that given in the present work. The averaged values for the torsion angles of the monomer unit are:

	$CCOC_{gauche}$	$COCC_{trans}$	OCCO
Ha	80	161	60
Hb	78	164	63
Hc	79	159	60
Hd		disorder	

As always, the COCC *gauche* angle is much larger than the adjacent OCCO *gauche* angle. Four coplanar ether O atoms form a distorted square with O...O distances lying in the range 2.773–2.847(Ha); 2.766–2.823(Hb); 2.793–2.874(Hc); 2.749–2.820 Å(Hd) (the deviations from coplanarity for oxygen atoms of the rings are presented in Table VI).

The geometry of the hosts in the complex agrees reasonably well with that reported for other 12-crown-4 metal-ion complexes. The average values in each ring of 12-crown-4 are presented below (distances = Å, angles = deg.):

	C-C	C-O	C-O-C	C-C-O
Ha	1.452	1.430	111.8	110.7
Hb	1.472	1.432	112.5	109.1
Hc	1.358	1.443	115.9	113.3
Hd	1.468	1.444	112.3	108.7

3.3. GUEST MOLECULES

The guest molecules are characterized by the bond distances and angles presented below:

	S-N	S-O	O-S-O	O-S-N
G1	1.768	1.426	115.3	102.7
G2	1.782	1.420	115.7	102.1
G3	1.771	1.426	115.3	102.6
G4	1.797	1.409	115.4	102.6
G5	1.792	1.434	115.6	102.3
G6	1.771	1.430	115.3	102.8

Note that for the solvated molecules the S(4)-O(1) and S(2)-O(1) bond distances are somewhat shorter than others. This can be correlated with the fact that these atoms do not take part in the system of H-bonds as acceptors and there is an insignificant redistribution of electron density along these bonds.

Acknowledgements

We wish to thank Dr. N. Udachina for assistance in the preparation of the paper. This work was partly completed in the Institute of Physical Chemistry of PAS and was supported by Project KBN 2 0242 91 01.

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