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The 1 : 1 Complexes between Benzo-18-crown-6, 18-crown-6 and Aminosulfuric Acid

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Abstract. The title compounds were prepared by treating a methanol solution of the corresponding crown ether with an aqueous solution of aminosulfuric acid.

Crystals of [benzo-18-crown-6·H_2NSO_2OH] suitable for X-ray crystallography were obtained by recrystallization from methanol. The crystals are orthorhombic, space group $P2_12_12_1$, $a = 14.310(7)$, $b = 12.516(4)$, $c = 10.890(4)$ Å. Refinement led to a final conventional R value of 0.051 for 909 reflections.

Crystals of [18-crown-6·H_2NSO_2OH] suitable for X-ray crystallography were obtained by recrystallization from acetone. They are orthorhombic, space group $P2_12_12_1$, $a = 17.027(6)$, $b = 14.866(5)$, $c = 8.345(4)$ Å. The structure was solved by a heavy atom method and refined to an agreement value of 0.067.

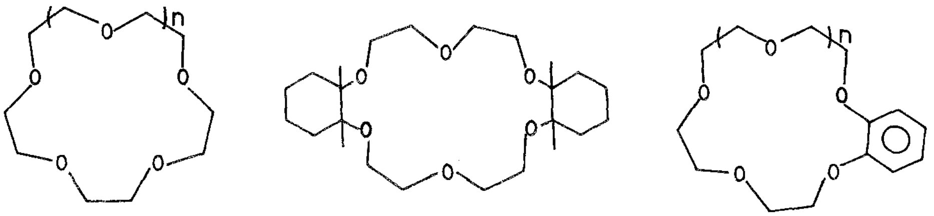
Key words. Crystal structure, crown ether, aminosulfuric acid, host–guest complex, H-bond.

Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82108 (6 pages).

1. Introduction

Among the synthetic macrocycles, crown ethers are of particular interest because they bind metal cations [1], charged species (protonated amines, hydroxonium ion) [2–4] and neutral molecules [5–6] with great selectivity and affinity. Selectivity in separation processes can be achieved when a synthetic macrocyclic receptor is used which has the ability to complex a specific guest selectively [7, 8].

Using X-ray techniques we have investigated [9, 10] the complexation in the crown-ether–aminosulfuric acid system.



Scheme 1. Structures of crown ethers. **1**, $n = 1$: 15C5 [10]; **2**, $n = 2$: 18C6 [11]; **3**, *cis-syn-cis*-DCH18C6 [9]; **4**, *cis-anti-cis*-DCH18C6 [9]; **5**, $n = 1$: B15C5 [10]; **6**, $n = 2$: B18C6 [present work]. The following code is used in the abbreviated names: C = crown, B = benzo, D = di, DCH = dicyclohexano.

These complexes have many features in common with the complexes of protonated amines. The existence of the guest in the form of the zwitterion $H_3^+NSO_3^-$ in all the described species (practically equal S—O distances and the localization of three protons at the nitrogen atom of the guest) explains the similarity of the guest binding in these two types of complexes.

The aminoacid zwitterion ideally matches the 18-membered crown ether cavity with the formation of oxygen–hydrogen bridges. The complexes are similar to those of primary ammonium ions [2, 12]. In both cases they are perching complexes [13, 14] where the guest is anchored by three linear NH···O hydrogen bonds with three oxygen atoms pointing up towards the substrate. The average N···O distance changes in the order **4** > **3** > **2**.

If the host is a 15-membered ring, all the protons of the NH_3^+ group cannot be placed above its cavity. In the complexes with **1** and **5** the guest exists in the form of $(H_3^+NSO_3^-)_2$ dimers united by a strong $H(NH_3^+)\cdots O(SO_3^-)$ hydrogen bond (N···O distance 2.94 Å for complex **1** · $(H_3NSO_3)_2$ and 2.93 Å for complex **5** · $(H_3NSO_3)_2$) and only two of the guest protons take part in the host–guest interactions by bifurcated H-bonds. It would be very interesting to study the interaction in the system with 12-membered crown ethers, where there is no correspondence between the host form and size and the geometry of the tetrahedral guest NH_3^+ group. It would complete the investigation of the crown ether complexing ability with regard to aminosulfuric acid. Unfortunately we have failed in our attempts to synthesize the proper complex of 12-crown-4.

In continuation of our previous work [9, 10] the present paper is devoted to a detailed study of aminoacid complexation by benzo-18-crown-6 (**6**) and 18-crown-6 (**2**). In contrast to the previously described complex of 18-crown-6 with aminosulfuric acid [**2**·H_3NSO_3·1/2 C_2H_5OH] [11] complex **2**·H_3NSO_3 has been solved in another space group and with different cell constants.

2. Experimental

2.1. SYNTHESIS OF THE COMPLEX **2**·H_3NSO_3

18-Crown-6 (1.32 g, 0.005 mol) in 10 mL methanol was mixed with an aqueous solution (3 mL) of aminosulfuric acid (0.49 g, 0.005 mol) at 64°C. The precipitate formed after cooling to 20°C was filtered off, washed with methanol and air dried. Crystals of **2**·H_3NSO_3 suitable for X-ray crystallography were obtained by recrystallization from acetone.

Crystals of the complex are colourless, soluble in methanol, ethanol and water, mp 123–125°C. *Anal. Calcd* for **2**·H_3NSO_3: C, 39.89; N, 3.88; S, 8.88. *Found*: C, 40.02; N, 3.83; S, 9.01.

2.2. SYNTHESIS OF THE COMPLEX **6**·H_3NSO_3

Benzo-18-crown-6 (1.51 g, 0.005 mol) in 10 mL of methanol was mixed with an aqueous solution (3 mL) of aminosulfuric acid (0.49 g, 0.005 mol) at 64°C. The precipitate formed after cooling to 20°C was filtered off, washed with methanol and air dried. Crystals of **6**·H_3NSO_3 suitable for X-ray crystallography, were formed by recrystallization from methanol.

Crystals of the complex are colourless, soluble in methanol, ethanol, water, chloroform, mp 192–193°C; IR (cm^{-1}) 3000–2850 (C—H), 1125 (C—O—C). *Anal. Calc.* for **6**·H_3NSO_3: C, 46.94; H, 6.65; N, 3.42; S, 7.83. *Found*: C, 46.80; H, 6.61; N, 3.56; S, 7.90.

2.3. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

A summary of the data collection parameters for **2**·H_3NSO_3 is given in Table I. The crystal data were collected on a DAR-UMB diffractometer, using CuK_α radiation, by the $\omega - \theta/2\theta$ technique. The intensities were corrected for background and Lp effects but not for absorption. The complex structure was solved by the Patterson method in the SHELXTL complex [15]. Scattering factors were those of SHELX.

Three guest hydrogen atoms were found from a difference Fourier map, the others were placed at calculated positions and the positional parameters of all of them were not varied. Refinements of the non-hydrogen atoms were performed with anisotropic temperature factors. The final agreement factor for **2**·H_3NSO_3 is 0.067. The final values of the positional parameters are given in Table II, bond lengths and angles are given in Tables III and IV.

Intensity data for **6**·H_3NSO_3 were collected on an RED-4 diffractometer equipped with MoK_α radiation and a graphite monochromator by ω scans. Cell dimensions were obtained from a least-squares fit to the setting angles of 15 reflections having $10 < 2\theta < 40°$. Data reduction included corrections for background and Lp effects. Absorption effects were insignificant. Data having $I(hkl) \geqslant 2\sigma(I)$ were considered to be observed and used in the refinement. The

Table I. Crystal data and summary of intensity data collection and structure refinement for **2**·H_3NSO_3 and **6**·H_3NSO_3.

Complex	**2**·H_3NSO_3	**6**·H_3NSO_3
Formula	$C_{12}H_{27}NO_9S$	$C_{16}H_{27}NO_9S$
Mol. wt.	361.5	409.5
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Cell constants		
a, Å	17.027(6)	14.310(7)
b, Å	14.866(5)	12.516(4)
c, Å	8.345(4)	10.890(4)
Cell vol, Å^3	2112(1)	1950(1)
Z	4	4
ρ (calc), g cm^{-3}	1.14	1.39
μ cm^{-1}	16.6	2.2
Radiation	CuK_α ($\lambda = 1.5418$)	MoK_α ($\lambda = 0.71069$)
$F(000)$	776	872
Max. crystal dim, mm	0.2 × 0.15 × 0.2	0.1 × 0.2 × 0.2
Reflections	1909	909
No. of parameters varied	207	243
R	0.067	0.051

Table II. Final fractional coordinates (× 10^4) for complexes **2**·H_2NSO_2OH and **6**·H_2NSO_2OH (with esds in parentheses).

Atom	Complex **2**·H_2NSO_2OH			Complex **6**·H_2NSO_2OH		
	x	*y*	*z*	*x*	*y*	*z*
S	−247(1)	124(1)	1295(2)	6041(2)	1717(2)	280(2)
O(1A)	−183(3)	887(3)	258(6)	5898(5)	1927(5)	1564(6)
O(2A)	−240(4)	−726(3)	490(6)	6990(4)	1463(5)	−64(6)
O(3A)	−779(3)	214(5)	2586(6)	5544(5)	2413(5)	−533(6)
N	685(3)	131(4)	2283(6)	5446(5)	457(5)	87(6)
O(1)	1783(3)	−290(3)	−200(6)	6723(4)	−1289(5)	−961(5)
C(2)	2252(4)	400(5)	−949(8)	7001(7)	−749(9)	−2102(9)
C(3)	1801(5)	1283(5)	−808(8)	6194(7)	−640(8)	−2934(8)
O(4)	1780(3)	1540(3)	816(5)	5542(4)	86(5)	−2469(5)
C(5)	1342(5)	2360(5)	1024(9)	4809(7)	296(8)	−3299(9)
C(6)	1298(5)	2588(5)	2739(8)	4174(7)	1133(9)	−2728(8)
O(7)	843(3)	1920(3)	3545(5)	3756(4)	674(5)	−1636(5)
C(8)	721(5)	2100(5)	5193(8)	3194(6)	1422(8)	−1002(10)
C(9)	173(6)	1420(5)	5854(8)	2823(6)	873(8)	139(8)
O(10)	572(3)	567(4)	5834(5)	3590(4)	790(5)	997(5)
C(11)	22(6)	−109(6)	6386(9)	3293(6)	266(9)	2105(10)
C(12)	505(6)	−1003(6)	6367(8)	4121(7)	157(8)	2938(9)
O(13)	626(3)	−1256(3)	4731(5)	4779(4)	−537(5)	2388(6)
C(14)	1042(5)	−2087(5)	4577(9)	5536(7)	−706(10)	3169(9)
C(15)	1085(5)	−2322(5)	2862(9)	6150(7)	−1584(9)	2640(8)
O(16)	1565(3)	−1683(3)	2054(6)	6532(4)	−1177(5)	1474(5)
C(17)	1620(5)	−1833(5)	381(9)	7299(6)	−1765(8)	1029(9)
C(18)	2167(5)	−1150(5)	−327(9)	7422(6)	−1772(7)	−283(8)
C(19)				8181(7)	−2270(8)	−745(8)
C(20)				8852(7)	−2767(8)	−31(10)
C(21)				8730(6)	−2757(8)	1231(10)
C(22)				7972(7)	−2270(8)	1742(9)

structure was solved by direct methods using SHELX86 [16] and refined by full-matrix least squares using the XTL package [17]. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms of the NH_3^+ group were located by difference maps, all the others were put in calculated positions. All hydrogen atoms were included as fixed contributions.

The final *R* factor is given in Table I, the final positional parameters are given in Table II, bond lengths and angles are given in Tables III and IV.

3. Discussion

3.1. OVERALL SYSTEM OF INTERACTIONS

3.1.1. *18-Membered Crown Ethers*

2 and **6** extract aminoacid efficiently forming 1 : 1 perching complexes [13–14]. The structure of the complex **2**·H_3NSO_3 is shown in Figure 1. The complex is stabilized by three classic NH···O hydrogen bonds and three ion–dipole interactions via

Table III. Bond lengths (Å) for **2**·H_2NSO_2OH (A) and **6**·H_2NSO_2OH (B) (esds in parentheses)

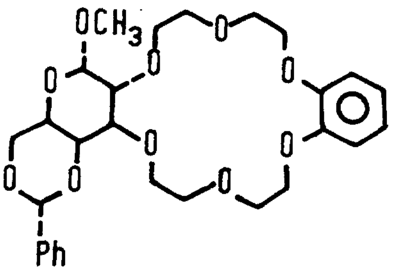
Atoms	Distance (A)	Distance (B)
O(1)—C(2)	1.44(1)	1.47(1)
C(2)—C(3)	1.52(1)	1.47(1)
C(3)—O(4)	1.41(1)	1.39(1)
O(4)—C(5)	1.44(1)	1.41(1)
C(5)—C(6)	1.47(1)	1.52(1)
C(6)—O(7)	1.43(1)	1.44(1)
O(7)—C(8)	1.42(1)	1.41(1)
C(8)—C(9)	1.48(1)	1.51(1)
C(9)—O(10)	1.43(1)	1.44(1)
O(10)—C(11)	1.44(1)	1.43(1)
C(11)—C(12)	1.56(1)	1.49(1)
C(12)—O(13)	1.43(1)	1.41(1)
O(13)—C(14)	1.43(1)	1.39(1)
C(14)—C(15)	1.47(1)	1.52(2)
C(15)—O(16)	1.42(1)	1.47(1)
O(16)—C(17)	1.42(1)	1.40(1)
C(17)—C(18)	1.50(1)	1.43(1)
C(18)—O(1)	1.44(1)	1.38(1)
C(18)—C(19)		1.35(1)
C(19)—C(20)		1.38(1)
C(20)—C(21)		1.38(2)
C(21)—C(22)		1.36(1)
C(17)—C(22)		1.39(1)
S—N	1.788(5)	1.805(7)
S—O(1A)	1.431(5)	1.437(7)
S—O(2A)	1.431(5)	1.444(6)
S—O(3A)	1.413(5)	1.431(7)

oxygen atoms of the crown ether (Table V). The system of H-bonds is similar to that found in the complexes of **2** with the ammonium salts: $[(NH_4)\cdot\mathbf{2}]_2[UCl_6]\cdot 2\ CH_3CN$ [18], $[(NH_4)\cdot\mathbf{2}]_2ClPF_6$ [19], $[(NH_4)\cdot\mathbf{2}]_2[UO_2(NCS)_4]\cdot H_2O$ [20], $[(NH_4)\cdot\mathbf{2}][Br]\cdot 2\ H_2O$ [21].

In **6**·H_3NSO_3 the zwitterion of the aminosulfuric acid binds to the macrocyclic receptor by two strong NH···O hydrogen bonds (distances H···O 2.10, 2.10 Å, Table V, Figure 2) with two oxygen atoms separated by a biethylene oxide fragment. There is also one bifurcated NH···O hydrogen bond with the pyrocatechol oxygen atoms of **6** (distances H···O 2.22, 2.35 Å) and two electrostatic interactions. All the N···O distances are similar. Thus all the oxygen atoms participate in N···O interactions and in complex stabilization. The system of hydrogen bonds in **2**·H_3NSO_3 is analogous to that found in the complex of the benzo-18-crown-6 derivative of glucose (**7**) with NH_3^+—CHPh—$COOCH_3\cdot PF_6^-$ [22]. The salt is fixed on the *β*-face of the crown by four hydrogen bonds between the $\overset{+}{H}$ of NH_3^+ and three oxygen atoms of the macrocycle (the corresponding values of the NH···O interactions in all the complexes described are collected in Table V).

Table IV. Angles (deg) for **2**·H_2NSO_2OH (A) and **6**·H_2NSO_2OH (B) (esds in parentheses)

Atoms	Angle, (a)	Angle, (b)
C(2)—O(1)—C(18)	110.3(5)	117.2(7)
O(1)—C(2)—C(3)	107.4(6)	110.5(8)
C(2)—C(3)—O(4)	108.7(6)	111.1(8)
C(3)—O(4)—C(5)	111.0(5)	112.7(7)
O(4)—C(5)—C(6)	109.7(6)	108.1(8)
C(5)—C(6)—O(7)	108.9(6)	107.9(7)
C(6)—O(7)—C(8)	113.9(6)	111.8(7)
O(7)—C(8)—C(9)	108.9(6)	107.4(7)
C(8)—C(9)—O(10)	107.4(6)	107.2(7)
C(9)—O(10)—C(11)	107.6(6)	110.5(7)
O(10)—C(11)—C(12)	104.2(7)	108.3(8)
C(11)—C(12)—O(13)	108.0(7)	109.0(8)
C(12)—O(13)—C(14)	112.6(6)	110.6(7)
O(13)—C(14)—C(15)	108.4(6)	109.1(8)
C(14)—C(15)—O(16)	109.2(6)	106.9(8)
C(15)—O(16)—C(17)	113.4(6)	113.9(7)
O(16)—C(17)—C(18)	108.8(6)	116.1(8)
C(18)—C(18)—O(1)	106.8(6)	116.0(7)
C(18)—C(17)—C(22)		117.8(8)
C(17)—C(18)—C(19)		118.1(8)
C(18)—C(19)—C(20)		123.8(9)
C(19)—C(20)—C(21)		117.7(9)
C(20)—C(21)—C(22)		120.6(9)
C(21)—C(22)—C(17)		121.7(9)
O(1A)—S—O(2A)	114.5(3)	115.2(4)
O(2A)—S—O(3A)	116.5(3)	116.1(4)
O(1A)—S—O(3A)	115.8(3)	114.8(4)
O(1A)—S—N	101.9(3)	101.8(4)
O(3A)—S—N	102.4(3)	103.0(4)



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In the complexes **2**·H_3NSO_3 and **6**·H_3NSO_3 the deviations of the N atom from the mean plane of the crown ether oxygen atoms (0.97 Å for **2** and 0.98 Å for **6**) are identical to those observed previously [18] (0.99 Å) and [21] (1.00 Å) and in the complex [Naph(OEtOEtO)$_2$Et]·$Me_3CNH_3ClO_4$ (0.99 Å) [12] and somewhat less than in the complexes with DCH18C6 [9]. In amines where R = Me and Et the

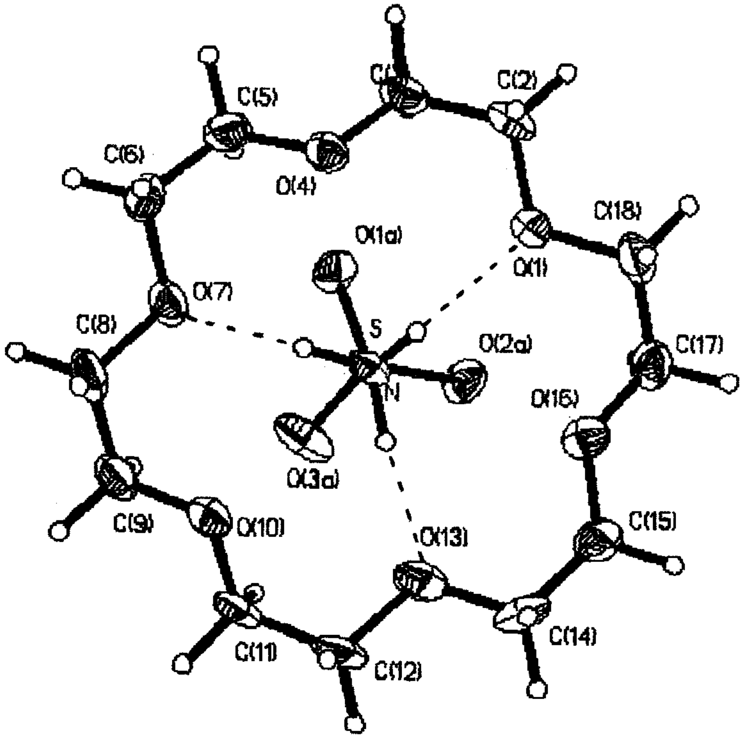

Fig. 1. A view of the molecular structure of $2 \cdot H_3NSO_3$ (with the atomic numbering scheme) as projected onto the macrocyclic plane. Hydrogen bonds are presented by dashed lines.

C—NH_3^+ axis is perpendicular to the mean plane of the ring. In the complex **6**·H_3NSO_3 the S—NH_3^+ axis becomes slightly bent (the deviation from the perpendicular is 2.2°). This is comparable with complexes of **3** and **4** with the aminoacid (2.7°). These results show that the anchoring of the zwitterion to the host, although strong, allows some mobility.

The complex of aminosulfuric acid with DB18C6 has not been described. In contrast there are known to be two types of ammonium salt complexes with DB18C6 [23–25]. In the first of them the NH_4^+ group is on the more hindered side of the crown ether (in the direction of the benzene rings): $[(NH_4)\cdot DB18C6][picrate]$ [23] (average N···O distance 3.064 Å), $[(NH_4)\cdot DB18C6]_2[Co(NCS)_4]\cdot 2\,(CH_3)_2CO$ [24] (average N···O distance 2.93 Å). In the second one the NH_4^+ group is on the less hindered side: $[(NH_4)\cdot DB18C6]_2[UO_2Cl_4]\cdot 2\,CH_3CN$ [25].

3.1.2. *15-Membered Crown Ethers*

Complexes of **1** and **5** with the ammonium ion consist of sandwich $[(NH_4)($**1** or **5**$)_2]^+$ cations. Only two protons of NH_4^+ participate in interactions with every molecule of crown ether (as in complexes of **1** and **5** with aminoacid, Table V [10]).

There is one single and one bifurcated H-bond to each host molecule. The bifurcated hydrogen bond in **5** utilizes one aryl oxygen atom (it is the longest NH···O distance).

Table V. The shortest N···O distances (including H-bonds) and some other parameters in **2**·H_3NSO_3 and **6**·H_3NSO_3 and in related complexes

Oxygen atoms	The parameters of H-bond			N··· ave. plane of cr. eth.°	Ref.	Oxygen atoms	The parameters of H-bond			N··· ave. plane of cr. eth.°	Ref.
	N···O, Å	H···O, Å	NH···O°				N···O, Å	H···O, Å	NH···O°		
2·H_3NSO_3						[**2**·$(NH_4)]_2[UCl_6]\cdot 2\ CH_3CN$					
O(1)(2.875)[a]	2.861	2.05	169.4	0.97	[dc]	O(1)[b]					
O(4)(3.050)	3.060					O(2)	2.887	2.06	167.9	0.99	[18]
O(7)(2.834)	2.873	1.89	177.4								
O(10)(3.039)	3.063										
O(13)(2.904)	2.884	1.90	176.4								
O(16)(3.090)	3.067										
6·H_3NSO_3						**7**·NH_3^+-CHPh-$COOCH_3\cdot PF_6^-$					
O(1)	3.069	2.35	140.5	0.98	[dc]	O(19)	3.15				
O(4)	2.826	2.10	163.2			O(22)	2.96	1.94	156	1.21	[22]
O(7)	3.072					O(25)	3.08				
O(10)	2.865	2.10	155.0			O(32)	2.98	2.16	130		
O(13)	2.955					O(35)	2.91	1.98	143		
O(16)	2.980	2.22	147.7			O(38)	2.90	2.27	115		
DB18C6 does not form the complex with H_3NSO_3						$[(NH_4)(DB18C6)]_2[UO_2Cl_4]\cdot 2\ CH_3CN$					
						O(2)	2.937	1.87	150.3	1.14	[25]
						O(3)	2.920	2.00	165.6		
						O(4)	2.974				

1·$(H_3NSO_3)_2$						$[(NH_4)\cdot$**1**$_2]_2[UO_2Cl_4]\cdot 2\ CH_3CN$					
O(1)	2.79			1.76	[10]	O(2)	3.040	2.30	138.5	1.85	[25]
O(4)	3.03					O(3)	3.019				
O(7)	2.98					O(4)	2.923	2.12	159.6		
O(10)	2.99					O(5)	3.077				
O(13)	2.93					O(6)	2.983	2.22	141.9		
5·$(H_3NSO_3)_2$						$[(NH_4)\cdot$**5**$_2]_2[UO_2Cl_4]\cdot 2\ CH_3CN$					
O(1)	3.056			1.86	[10]	O(1)	3.080	1.99	151.8	1.82	[25]
O(4)	2.738					O(2)	2.90	2.08	123.5		
O(7)	2.909					O(3)	2.91				
O(10)	3.130					O(4)	2.888	2.10	170.6		
O(13)	3.259					O(5)	3.031				

[a] In parentheses are the corresponding N···O distances for the complex **2**·$H_3NSO_3\cdot 1/2C_2H_5OH$ [11].

[b] The numbering scheme here and further corresponds to the parent work.

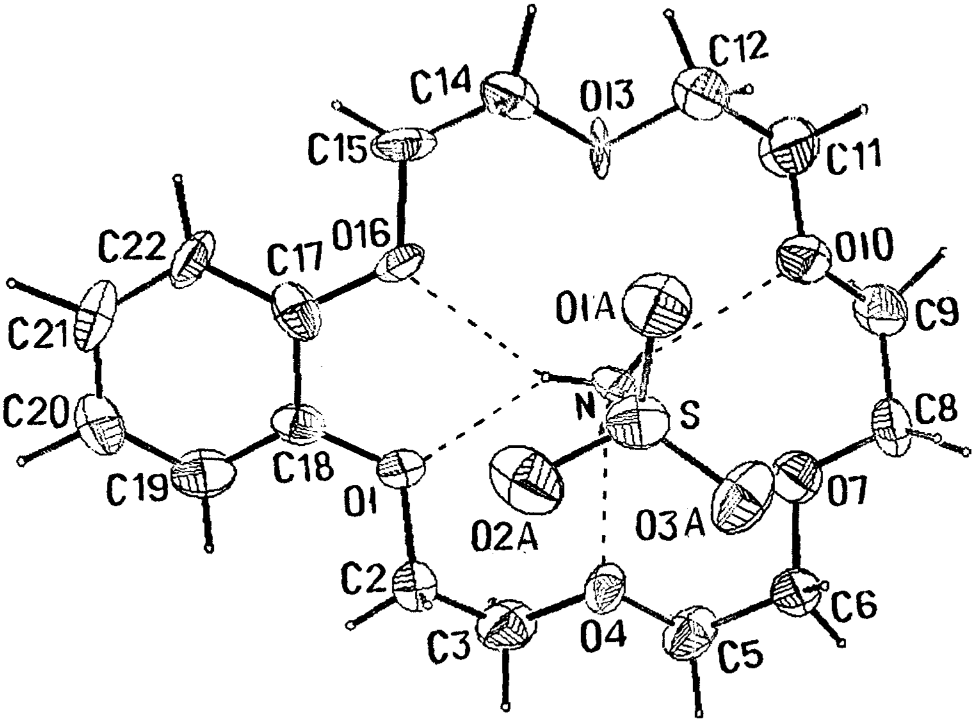

Fig. 2. A view of the molecular structure of $6{\cdot}H_3NSO_3$ as projected onto the macrocyclic plane. Hydrogen bonds are presented by dashed lines.

3.2. CROWN ETHER DESCRIPTION

3.2.1. *18-Crown-6*

The six oxygen atoms are alternately about 0.22 Å above and below their mean plane to form a nearly planar hexagon. The distances between *trans*-annular oxygen atoms of the host are O(1)···O(10) 5.589, O(4)···O(13) 5.640, O(7)···O(16) 5.634 Å. In the crown ether ring the bond distances and angles are ordinal (the corresponding average values are collected in Table VII). The symmetry of the crown ether is close to D_{3d} [26]. The torsion angles about C—C bonds are close to 68°, those about C—O bonds are close to 177° (Table VI). All these data are similar to those in other complexes of **2** [18–21].

3.2.2. *Benzo-18-Crown-6*

Four of the oxygen atoms of **6** O(1), O(4), O(10), and O(13) are coplanar within ±0.006 Å, the remaining two oxygen atoms deviate from that plane by +0.654 Å (O(7)) and −0.568 Å (O(16)). The distances between transannular O atoms of the cavity are O(1)···O(10) 5.606,O(4)···O(13) 5.456, O(7)···O(16) 5.712 Å. The benzene ring of the host is practically flat, the average deviation of its carbon atoms is

Table VI. Torsion angles (deg) in the crown ether framework for **2**·H_2NSO_2OH and **6**·H_2NSO_2OH

Atoms	Angle, **2**	Angle, **6**
C(18)—O(1)—C(2)—C(3)	178.5	158.6
O(1)—C(2)—C(3)—O(4)	68.3	68.9
C(2)—C(3)—O(4)—C(5)	−178.5	173.7
C(3)—O(4)—C(5)—C(6)	177.3	−177.1
O(4)—C(5)—C(6)—O(7)	−66.1	−64.5
C(5)—C(6)—O(7)—C(8)	−178.3	176.6
C(6)—O(7)—C(8)—C(9)	173.8	−178.1
O(7)—C(8)—C(9)—O(10)	67.5	73.9
C(8)—C(9)—O(10)—C(11)	−176.6	−179.5
C(9)—O(10)—C(11)—C(12)	−178.7	177.5
O(10)—C(11)—C(12)—O(13)	−71.6	−65.2
C(11)—C(12)—O(13)—C(14)	−178.0	−176.5
C(12)—O(13)—C(14)—C(15)	175.8	171.2
O(13)—C(14)—C(15)—O(16)	66.7	64.7
C(14)—C(15)—O(16)—C(17)	−177.9	164.2
C(15)—O(16)—C(17)—C(18)	−177.3	151.4
O(16)—C(17)—C(18)—O(1)	−68.2	−6.2
C(17)—C(18)—O(1)—C(2)	−176.4	146.9

Table VII. Mean bond lengths and angles for **2**·H_3NSO_3 and **6**·H_3NSO_3 (Å, deg)

	C—C_{cr}	C—O_{cr}	C—C_{ar}	C_{al}—O—C_{al}	C—C—O	C—O_{ar}—C_{ar}
2	1.50	1.43		111.5	108.0	
6	1.50	1.42	1.38	111.4	108.5	115.6

±0.003 Å. It makes an angle of 5.5° with the crown ring framework. The average bond lengths and angles are similar to those found in the other complexes of **6** [27, 28].

Two conformations of benzo-18-crown-6 and its derivatives in complexes have been described in the literature. The first one is characterized by five C—C *gauche* bonds (except the pyrocatechol part which is planar), all the C—O bonds are in a *trans* configuration [22, 29, 30]. In the second form one C—O bond turns into a *gauche* configuration [28, 31] with the formation of one angular fragment in the ring. The conformation of **6** in the described complex is of the first type. Apart from the pyrocatechol part (O(1)—C(18)—C(17)—O(16) torsion angle is −6.2°) all C—C subunits from the macrocyclic ring have a *gauche* configuration with the corresponding torsion angles falling within the range 64.5–73.9° (average value is 67.4°) (Table VI). Three of them are $+g$ and the two remaining ones are $-g$. Thus the macrocylic ring is highly asymmetric. The torsion angle C(2)—O(1)—C(18)—C(17) has a maximum deviation from the ideal value (180°) of 33°. The remaining torsion angles around the C—O bonds are in the range 151.4–179.5°.

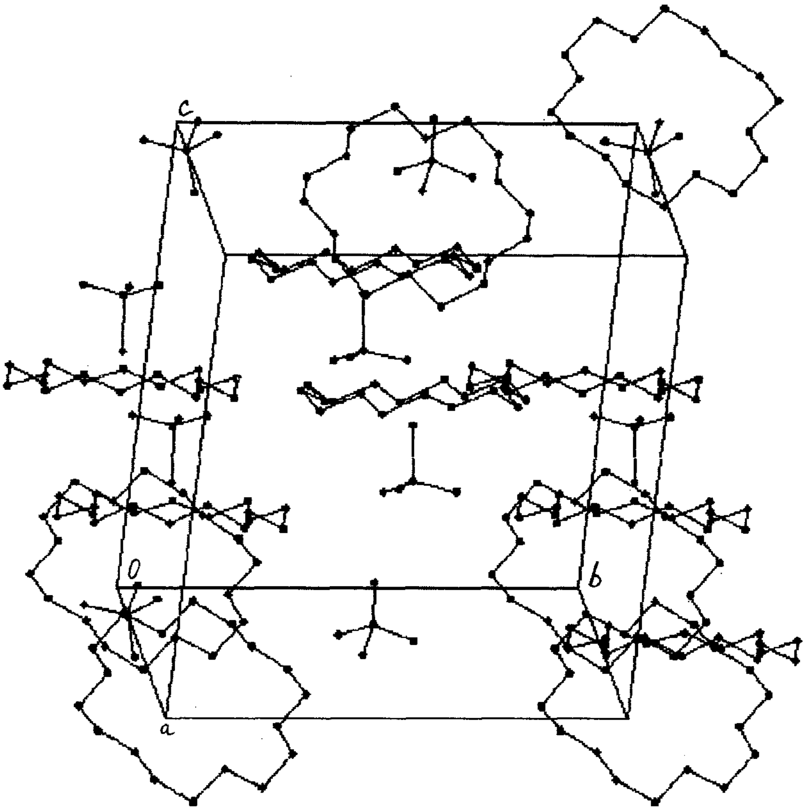

Fig. 3. Representation of the packing of **2**·H_3NSO_3 in the unit cell.

The geometry of the guest molecule is the same in all the complexes investigated [9–11]. The average bond lengths and angles in the molecule are: S—N 1.805(1.788), S—O 1.437(1.425) Å, O—S—O 115.4 (115.6), O—S—N 102.2(102.2)° (the values for H_3NSO_3 in the complex with **2** are given in parentheses).

The crystal packing of **2**·H_3NSO_3 is shown in Figure 3. The van der Waals distances are shortest between the individual complexes. For **6**·H_3NSO_3 (Figure 4) the short contact distances between the independent complexes are O(1A)···H(C19)$^{\mathrm{i}}$ 2.35, O(1A)···C19$^{\mathrm{i}}$ 3.24 Å; O(2A)···H(C15)$^{\mathrm{ii}}$ 2.70, O(2A)···C(15)$^{\mathrm{ii}}$ 3.65 Å; O(3A)···H(C5)$^{\mathrm{iii}}$ 2.71, O(3A)···C(5)$^{\mathrm{iii}}$ 3.85 Å ($\mathrm{i} = 3/2 - x, -y, 1/2 + z$; $\mathrm{ii} = 3/2 - x, -y, -1/2 + z$; $\mathrm{iii} = 1 - x, 1/2 + y, -1/2 - z$).

It is known [7, 8] that small variations in the host structure can have substantial effects on the hydrogen bonding between the ether and the substrate. In analogy with these results B18C6 and DB18C6 show different complexing ability with aminosulfuric acid (the latter does not form a complex). This can be attributed to an extension of the less basic catechol oxygen atoms and enhancement of the rigidity of the crown ether. It is possible to propose that four catechol and two aliphatic ether oxygen atoms are not enough for the complexation, because the

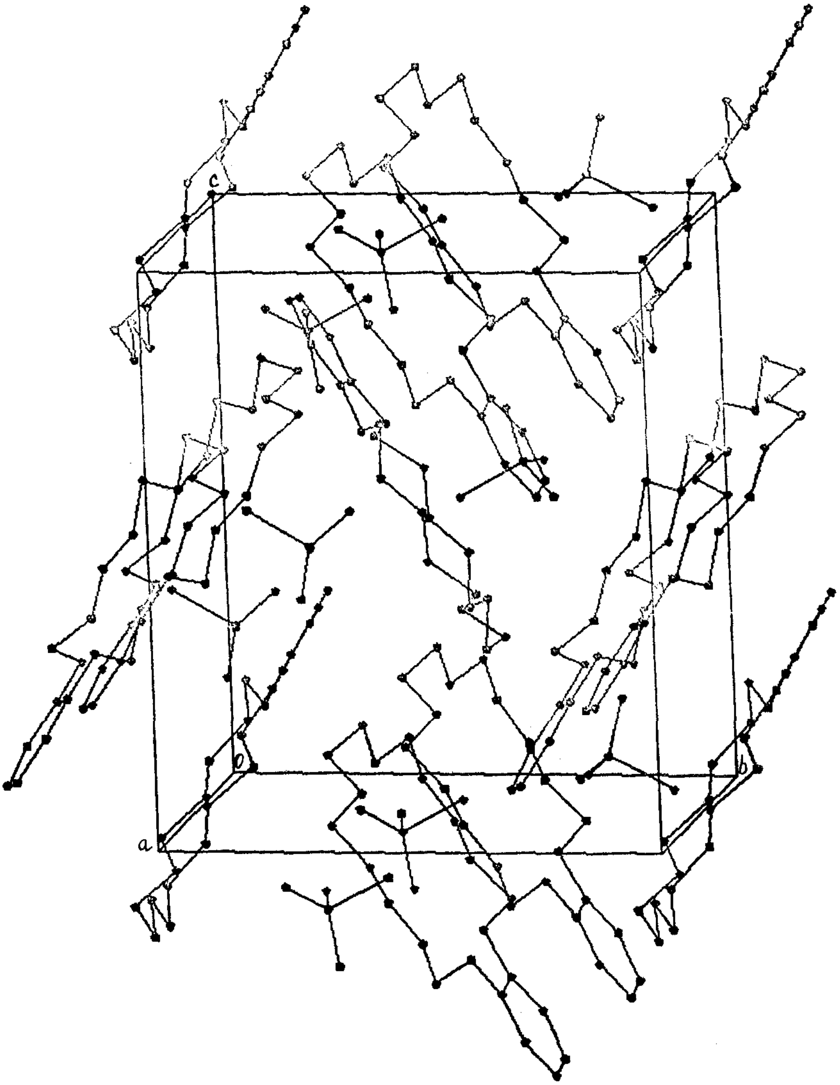

Fig. 4. Representation of the packing diagram for **6**·H_3NSO_3.

catechol oxygen atoms have a lower basicity than the aliphatic ones and, therefore, the correspondent hypothetic hydrogen bonds will have a smaller contribution to the energy of complexation. Because of this and the difference in rigidity B18C6 is a better host for aminosulfuric acid than DB18C6.

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32. Tables of thermal parameters and structure factors for **2**·H_3NSO_3 and **6**·H_3NSO_3 are available from the British Library (see note on the first page of this paper).