

Inclusion Compounds of *cis-syn-cis* and *cis-anti-cis* Diastereoisomers of Dicyclohexano-18-crown-6 with Amidosulfuric Acid

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Abstract. Both title complexes were prepared by reacting a methanol solution of the respective isomer of dicyclohexano-18-crown-6 (DCH18C6) with an aqueous solution of amidosulfuric acid. Crystals suitable for X-ray crystallography were obtained by recrystallization from methanol.

Crystals of [*cis-syn-cis*-DCH18C6][NH₂SO₂OH·CH₃OH] (**1**) are monoclinic, space group *P*2₁/*n*, *a* = 21.700(8), *b* = 13.725(5), *c* = 9.118(6) Å, γ = 76.29(2) Å. Refinement led to a final conventional *R* value of 0.065 for 2083 reflections. [*cis-anti-cis*-DCH18C6][NH₂SO₂OH] (**2**) crystallizes in the orthorhombic space group *Pna*2₁ with unit cell dimensions *a* = 17.154(7), *b* = 16.051(7), *c* = 8.630(5) Å. Refinement was terminated at an *R* value of 0.067 for 1936 reflections.

Key words. Crown ethers, amidosulfuric acid, crystal structure.

1. Introduction

Until recently, X-ray crystal studies of complexes formed between crown ethers and uncharged molecules represent a relatively unexplored area, although this type of complexation plays an important role in many biochemical processes [1]. Such complexes are typically formed through R—H···(R = C, N, O) interactions [2]. DCH18C6 as a host occupies to some extent an exceptionally important position in the processes of complexation with neutral molecules. On the one hand, there is the flexibility of the DCH18C6 cavity similar to that of 18-crown-6 [3]; on the other hand, there is the existence of its five non-converted diastereoisomers differing in the cyclohexyl group arrangement about the macrocycle [4]. This brings about an inequality of the two 'sides' of the heterocyclic cavity in these isomers and, in turn, the formation of complexes of different stoichiometry depending on the isomeric composition of DCH18C6 [5].

Purification of the final product of the catalytic hydrogenation of dibenzo-18-crown-6 through column chromatography [3, 6] is essential in preparing commercial DCH18C6, which, according to [3], is a mixture of *cis*-isomers.

We have found that *cis*-isomer isolation from the crude product is easily accomplished by crystalline complex formation of the appropriate DCH18C6 isomer with amidosulfuric acid.

We now report an X-ray investigation of inclusion compounds of the individual

cis-syn-cis and *cis-anti-cis* DCH18C6 isomers with amidosulfuric acid. This study was undertaken to elucidate the peculiarities of the stereochemical conformation of the guest in these complexes, the nature of the host–guest interactions and, in particular, the role of hydrogen-bonding in complexes of this type.

2. Experimental

2.1. ISOLATION OF THE MIXTURE OF DCH18C6 *cis*-ISOMERS

The isopropanol solution (50 mL) of 58.2 g DCH18C6 (formed by catalytic hydrogenation of the dibenzo-analogue [3, 6]) containing 37.2 g (0.1 mol) of *cis*-isomers was mixed at 70–80°C with an aqueous solution (50 mL) of 14.6 g (0.15 mol) of amidosulfuric acid. Crystals of **1** and **2** precipitated after the reaction mixture was cooled to 10–15°C. The crystals were filtered, washed with isopropanol, dissolved in 250 mL 7% aqueous sodium carbonate and extracted with chloroform (50 mL). The organic extract was washed with water (3 × 100 mL), dilute hydrochloric acid and water, dried and evaporated to dryness. The yield of *cis*-isomers is 35.7 g (96%), mp 44–51°C.

2.2. SYNTHESIS OF THE COMPLEXES

The appropriate isomer of DCH18C6 (0.744 g, 0.002 mol) in 5 mL methanol was mixed with an aqueous solution (5 mL) of amidosulfuric acid (0.194 g, 0.002 mol) at 64°C. The precipitates which formed after cooling to 20°C were filtered off, washed with methanol and air dried. Crystals of [*cis-syn-cis* DCH18C6 (isomer A)][NH₂SO₂OH·CH₃OH] **1** and [*cis-anti-cis* DCH18C6][NH₂SO₂OH] **2** suitable for X-ray crystallography were formed by recrystallization from methanol.

Crystals of **1** are colourless, transparent and soluble in chloroform, methanol, ethanol and water; mp 181–182°C; ¹H NMR (CDCl₃) δ, 8.50 (*s*, 3, NH₃), 3.37 (*s*,

Table I. Crystal data and summary of intensity data collection and structure refinement for complexes **1** and **2**

Complex	1	2
Mol. wt.	501.4	469.4
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pna</i> 2 ₁
Cell constants		
<i>a</i> , Å	21.700(8)	17.154(7)
<i>b</i> , Å	13.725(5)	16.051(7)
<i>c</i> , Å	9.118(6)	8.630(5)
γ, Å	76.29(2)	–
Cell vol, Å ³	2638.3	2376.2
Molecules/unit cell	4	4
ρ(calc), g cm ⁻³	1.26	1.31
Radiation	MoK _α	CuK _α
Max. crystal dimension, mm	0.2 × 0.3 × 0.3	0.15 × 0.4 × 0.2
Reflections measured	2083	1936
No. of parameters varied	467	281
<i>R</i>	0.065	0.067

3, CH₃), 3.67 (*m*, 20, OCH), 1.23–1.90 (*m*, 16, CCH₂C). Anal. Calcd. for 1: C, 50.28; H, 8.64; N, 2.79; S, 6.39. Found: C, 50.22; H, 8.48; N, 2.81; S, 6.40.

Crystals of **2** are colourless, transparent and soluble in chloroform, methanol, ethanol and water; mp 182–184°C; ¹H NMR (CDCl₃) δ, 8.50 (*s*, 3, NH₃), 3.70 (*m*, 20, OCH), 1.23–1.90 (*m*, 16, CCH₂C). Anal. Calcd. for 3: C, 51.16; H, 8.37; N, 2.98; S, 6.82. Found: C, 51.08; H, 8.45; N, 3.03; S, 6.85.

2.3. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT FOR COMPLEX 1

Colourless crystals were prepared by recrystallization from methanol. A summary of the data collection parameters is given in Table I. Data were collected on a RED-4M diffractometer by the $\theta - 2\theta$ scan technique. The structure was solved by

Table II. Final fractional coordinates ($\times 10^4$) for **1** and **2** (with esds in parentheses)

Atom	Complex 1			Complex 2		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
S	936(1)	2097(1)	152(2)	2251(1)	1997(1)	0000(0)
O(1S)	1308(2)	2822(4)	214(6)	2809(4)	2448(4)	-870(9)
O(2S)	371(2)	2297(5)	1037(6)	1915(4)	2430(4)	1297(8)
N	606(2)	2264(4)	-1644(6)	2844(3)	1229(4)	979(8)
O(3S)	1291(2)	1070(4)	123(6)	1740(4)	1484(5)	-822(10)
O(1)	1599(2)	1954(3)	-3852(5)	3801(3)	345(3)	-1315(7)
C(2)	1811(3)	1007(5)	-4566(9)	3543(5)	-436(6)	-1930(11)
C(3)	1650(3)	219(5)	-3621(9)	2738(6)	-571(6)	-1590(11)
O(4)	979(2)	381(3)	-3607(5)	2565(3)	-586(3)	-14(9)
C(5)	783(3)	-313(5)	-2666(9)	1743(5)	-633(5)	319(13)
C(6)	73(4)	-97(5)	-2642(9)	1657(6)	-734(5)	1989(12)
O(7)	181(2)	878(3)	-2034(5)	1786(3)	45(3)	2736(7)
C(8)	-850(3)	1074(5)	-1697(8)	1852(5)	-22(5)	4401(11)
C(9)	-1025(3)	1984(5)	-754(6)	1977(4)	863(5)	5002(12)
O(10)	-899(2)	2802(3)	-1572(5)	2670(3)	1166(3)	4313(7)
C(11)	-1019(3)	3734(5)	-791(9)	2952(4)	1935(5)	5009(12)
C(12)	-784(3)	4474(5)	-1685(9)	3780(5)	2044(5)	4564(10)
O(13)	-110(2)	4257(3)	-1674(5)	3867(3)	2154(3)	2959(7)
C(14)	137(4)	5019(6)	-2373(9)	4643(4)	2378(4)	2503(10)
C(15)	831(4)	4783(5)	-2394(9)	4720(5)	2395(5)	809(10)
O(16)	1074(2)	3955(3)	-3339(5)	4674(3)	1561(3)	214(7)
C(17)	1752(3)	3565(5)	-3214(8)	4636(4)	1538(4)	-1435(8)
C(18)	1915(3)	2720(5)	-4325(8)	4516(4)	620(4)	-1914(9)
C(19)	1755(3)	3091(6)	-5869(8)	5208(4)	99(5)	-1461(11)
C(20)	2120(4)	3878(6)	-6253(9)	5963(4)	421(5)	-2184(11)
C(21)	1981(4)	4749(6)	-5169(9)	6091(4)	1337(5)	-1717(12)
C(22)	2125(4)	4351(6)	-3597(9)	5385(4)	1870(5)	-2186(11)
C(23)	-1265(3)	1176(6)	-3065(9)	1138(4)	-407(5)	5161(13)
C(24)	-1959(4)	1344(7)	-2586(12)	416(5)	131(6)	4904(14)
C(25)	-2146(3)	2261(6)	-1612(11)	567(5)	1006(6)	5527(12)
C(26)	-1719(3)	2153(6)	-269(9)	1267(4)	1412(5)	4782(10)
C(27)	-151(6)	2646(8)	4750(11)			
O	-477(3)	2689(5)	3420(8)			

Table III. Bond lengths (Å) for **1** and **2** (esds in parentheses)

Atoms	Distance, 1	Distance, 2	Atoms	Distance, 1	Distance, 2
O(1)—C(2)	1.43(1)	1.43(1)	C(18)—O(1)	1.45(1)	1.40(1)
C(2)—C(3)	1.48(1)	1.42(1)	C(18)—C(19)	1.51(1)	1.50(1)
C(3)—O(4)	1.42(1)	1.39(1)	C(19)—C(20)	1.52(1)	1.52(1)
O(4)—C(5)	1.42(1)	1.44(1)	C(20)—C(21)	1.52(1)	1.54(1)
C(5)—C(6)	1.49(1)	1.45(2)	C(21)—C(22)	1.54(1)	1.53(1)
C(6)—O(7)	1.43(1)	1.42(1)	C(22)—C(17)	1.53(1)	1.53(1)
O(7)—C(8)	1.45(1)	1.44(1)	C(23)—C(8)	1.52(1)	1.52(1)
C(8)—C(9)	1.49(1)	1.52(1)	C(23)—C(24)	1.53(1)	1.52(1)
C(9)—O(10)	1.43(1)	1.42(1)	C(24)—C(25)	1.51(1)	1.52(1)
O(10)—C(11)	1.43(1)	1.46(1)	C(25)—C(26)	1.52(1)	1.50(1)
C(11)—C(12)	1.48(1)	1.48(1)	C(26)—C(9)	1.53(1)	1.51(1)
C(12)—O(13)	1.42(1)	1.40(1)	C(27)—O	1.39(1)	—
O(13)—C(14)	1.43(1)	1.43(1)	O(1S)—S	1.424(5)	1.415(7)
C(14)—C(15)	1.47(1)	1.46(1)	O(2S)—S	1.438(6)	1.438(7)
C(15)—O(16)	1.42(1)	1.44(1)	O(3S)—S	1.437(5)	1.396(8)
O(16)—C(17)	1.45(1)	1.42(1)	N—S	1.780(6)	1.808(6)
C(17)—C(18)	1.51(1)	1.54(1)			

Table IV. Angles (deg) for **1** and **2** (esds in parentheses)

Atoms	Angle, 1	Angle, 2	Atoms	Angle, 1	Angle, 2
C(2)—O(1)—C(18)	114.7(5)	114.1(6)	C(17)—C(18)—O(1)	106.9(6)	108.5(6)
O(1)—C(2)—C(3)	108.5(6)	110.8(8)	C(18)—C(17)—C(22)	108.6(6)	109.2(6)
C(2)—C(3)—O(4)	107.5(6)	114.1(8)	C(17)—C(18)—C(19)	111.8(6)	110.8(6)
C(3)—O(4)—C(5)	111.0(5)	113.8(7)	C(18)—C(19)—C(20)	109.7(6)	112.0(7)
O(4)—C(5)—C(6)	109.4(6)	107.5(7)	C(19)—C(20)—C(21)	111.5(7)	109.7(7)
C(5)—C(6)—O(7)	109.8(6)	109.5(8)	C(20)—C(21)—C(22)	109.8(7)	110.4(7)
C(6)—O(7)—C(8)	113.7(5)	113.3(6)	C(21)—C(22)—C(17)	111.3(6)	110.7(7)
O(7)—C(8)—C(9)	108.9(6)	106.2(6)	C(8)—C(23)—C(24)	108.5(6)	111.2(7)
C(8)—C(9)—C(23)	111.5(6)	110.1(7)	C(23)—C(24)—C(25)	110.6(7)	109.3(8)
C(8)—C(9)—O(10)	107.4(6)	107.1(6)	C(24)—C(25)—C(26)	110.7(7)	112.4(8)
C(9)—O(10)—C(11)	114.5(5)	113.4(6)	C(25)—C(26)—C(9)	109.7(7)	109.5(7)
O(10)—C(11)—C(12)	108.6(6)	108.1(7)	C(8)—C(9)—C(26)	109.8(6)	112.7(7)
C(11)—C(12)—O(13)	110.8(6)	111.8(7)	O(1S)—S—O(2S)	116.2(3)	115.9(4)
C(12)—O(13)—C(14)	112.5(5)	113.6(6)	O(2S)—S—O(3S)	115.6(3)	115.3(4)
O(13)—C(14)—C(15)	112.5(6)	111.1(6)	O(1S)—S—O(3S)	115.1(3)	117.1(4)
C(14)—C(15)—O(16)	110.6(6)	109.4(7)	O(1S)—S—N	102.8(3)	102.5(4)
C(15)—O(16)—C(17)	113.6(5)	112.5(6)	O(2S)—S—N	101.1(3)	101.0(4)
O(16)—C(17)—C(18)	105.2(6)	107.3(6)	O(3S)—S—N	102.4(3)	100.8(4)

the Patterson method using the SHELXTL package [7]. All non-hydrogen atoms were found and refined with anisotropic temperature factors; all hydrogen atoms were found and refined isotropically except for the hydrogen atom of the methanol hydroxy group. The final *R*-factor is given in Table I. The final values of the positional parameters are given in Table II, bond lengths and angles are given in Tables III and IV.

2.4. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT FOR COMPLEX 2

The crystals of **2** were prepared in the same manner as **1**. Intensity data were recorded on a DAR-UMB diffractometer by the $\omega-\theta/2\theta$ scan technique. The structure solution was accomplished by means of the direct methods program MULTAN [8] and the subsequent calculation of a difference Fourier map allowed the location of all non-hydrogen atoms. The hydrogen atoms were placed at calculated positions and their parameters were not varied. Anisotropic refinement of nonhydrogen atoms converged at $R = 0.067$. A summary of the data collection parameters is also presented in Table I. Final positional parameters are listed in Table II, bond lengths and angles are given in Tables III and IV [9].

3. Discussion

Both *cis*-isomers of DCH18C6 form 1:1 complexes with amidosulfuric acid. By X-ray investigation it has been unequivocally found that the guest molecules exist in the form of the $^+\text{H}_3\text{NSO}_3^-$ zwitterion, which probably conforms with the greatest complex stability.

3.1. [*Cis-syn-cis*-DCH18C6(ISOMER A)][$\text{NH}_2\text{SO}_2\text{OH}\cdot\text{CH}_3\text{OH}$] (**1**)

The structure of molecular complex **1** is shown in Figure 1. In contrast to the complex with lead nitrate, which has the composition [*cis-syn-cis*-DCH18C6][$\text{Pb}(\text{NO}_3)_2\text{CCl}_4$] (**3**) [10], where the cation enters the macrocyclic cavity on the side that is proximal to the *syn*-cyclohexyl groups, the zwitterion of amidosulfuric acid in **1** approaches the crown ether from the distal side. Previously it has been shown that isomer A in DCH18C6 forms proximal complexes not only with electrically charged species (metal ions [10] or the hydroxonium ion [11]) but also with neutral molecules such as malononitrile [5]. The methanol molecule does not interact with the crown ether to form a 2:1 mixed guest–host complex. It simply forms a hydrogen bond with the guest zwitterion ($\text{O}(\text{CH}_3\text{OH})\cdots\text{O}(2)\text{S}(\text{H}_3\text{NSO}_3)$) distance is 2.816 Å). Unlike in **3** where the cation is at a distance from the mean plane of the crown ether of 0.084 Å, the nitrogen atom of the zwitterion in **1** is at a distance of 1.03 Å from the mean plane of the crown ether. This could be the result of a weakening of ion–dipole interactions in **1** with respect to **3**. It may also be seen in the difference between the $\text{N}\cdots\text{O}$ DCH18C6 distances (**1**, minimum is 2.81 Å) and the $\text{Pb}\text{—}\text{O}$ DCH18C6 distances (**3**, minimum is 2.72 Å). Complex **1** is stabilized by hydrogen bonds (Table V) between the protonated amine-group and the crown–

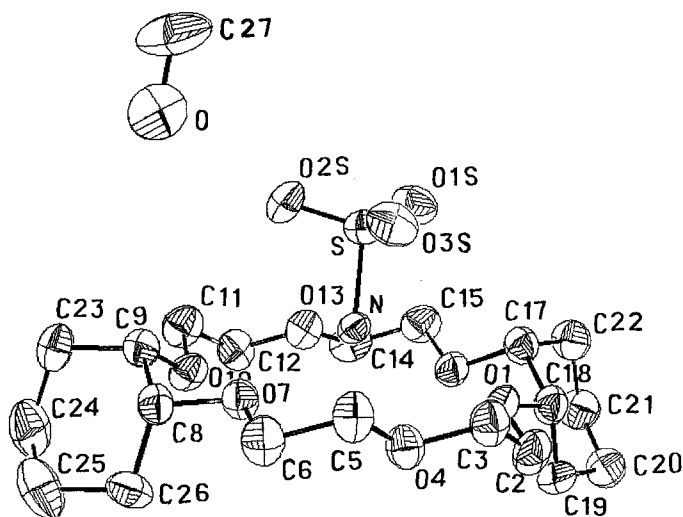


Fig. 1. ORTEP plot of **1**. Hydrogen atoms omitted for clarity.

ether oxygens, every other oxygen atom (O(1), O(7), O(13)) of the ligand is associated with one of the hydrogen atoms of the NH_3^+ -group.

When going from isomer A [12, 13] to the complex with lead nitrate **3** [10] and further to the complex with amidosulfuric acid **1**, one can observe the macrocyclic cavity changing from the elliptical shape (uncomplexed isomer A) to almost circular in **1**. The O(1)⋯O(10), O(4)⋯O(13), O(7)⋯O(16) distances are 6.17, 6.55, 5.66 Å, respectively in **1**. Moreover, there is, in the same order, a flattening of the crown ether framework, which may be demonstrated as an increasing coplanarity of the oxygen atoms; the extreme deviations from coplanarity being: uncomplexed isomer A ± 0.666 Å; **3** ± 0.547 Å; **1** ± 0.221 Å.

Conformational peculiarities depend on the nature of the guest: in contrast to **3**, where the crown ether is characterized by six *gauche*-OCCO torsion angles and 10

Table V. Hydrogen bonds in **1** and **2**

Compound	D ^b ⋯A, Å	D—H, Å	A⋯H, Å	angle D—H⋯A, deg	
[18C6][NH ₂ SO ₂ OH] ^a	O(1)	2.884			
	O(7)	2.834			
	O(13)	2.875			
1	O(1)	2.905	1.14	2.01	175.5
	O(7)	2.864	1.02	1.74	167.1
	O(13)	2.808	0.89	1.79	174.8
2	O(1)	2.936	0.85	2.16	173.5
	O(7)	3.036	0.84	2.20	167.8
	O(13)	2.865	0.78	2.08	156.6

^a Ref. 15.

^b D = proton donor (amidosulfuric acid); A = crown ether.

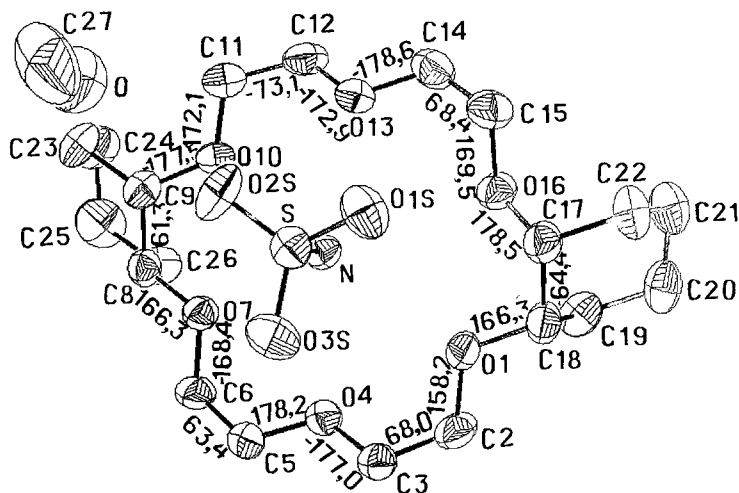


Fig. 2. ORTEP plot of **1** as projected onto the macrocyclic plane. Torsion angles within the macrocyclic ring are given. Hydrogen atoms omitted.

trans- and 2-*gauche*-COCC torsion angles, the framework of the crown ether in **1** adopts a D_{3d} conformation, described by six *trans-gauche-trans* COCC—OCCO—CCOC fragments. (The values of the corresponding torsion angles are in Figure 2.)

3.2. [*Cis-anti-cis*-DCH18C6][NH₂SO₂OH] (**2**)

The structure of the 1:1 molecular complex of *cis-anti-cis*-DCH18C6 with amidosulfuric acid is presented in Figures 3 and 4. As in **1**, the zwitterion in **2** does not enter the macrocyclic cavity, the distance of 1.35 Å between the guest's nitrogen atom and the mean plane of the crown ether molecule being slightly greater than in **1**. It seems interesting to note that in the [*cis-anti-cis*-DCH18C6][Pb(NO₃)₂·CHCl₃] (**4**) complex [14] the Pb(II) cation is situated in the mean plane of the crown ether's oxygens. The difference between **1** and **4** is probably connected with the guest

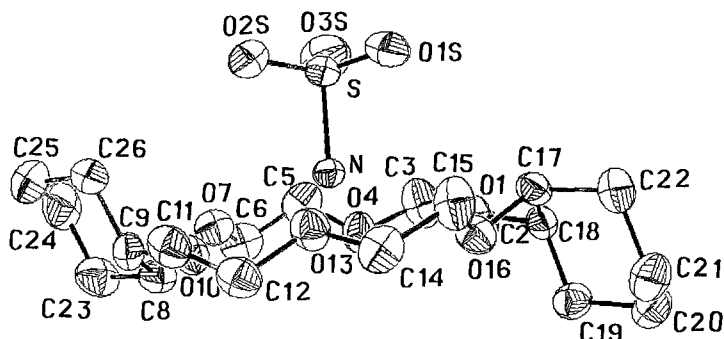


Fig. 3. ORTEP plot of **2**. Hydrogen atoms omitted.

Table VI. Average distances (Å) and angles (deg) in 1-4

Compound	C-C ^a	C-C _b	C-O	N-S	S-O	C-C-C	O-C-C	C-O-C	O-S-O	O-S-N
1	1.52	1.49	1.44	1.780	1.433	110.3	108.8	113.3	115.6	102.1
2	1.52	1.48	1.42	1.808	1.416	110.7	109.3	113.5	116.1	101.4
3^c	1.56	1.55	1.50			111.0	105.0	111.0		
4^d	1.55	1.53	1.43			111.0	107.0	111.0		
[18C6][NH ₂ SO ₂ OH] ^e				1.779	1.434	109.1	112.0	115.5	102.4	
Free NH ₂ SO ₂ OH ^f		1.48	1.42	1.764	1.439				115.1	103.2

^a Bond lengths in cyclohexyl groups.^b Bond lengths in crown ether cycle.^c Ref. 10; ^d Ref. 14; ^e Ref. 15; ^f Ref. 16.

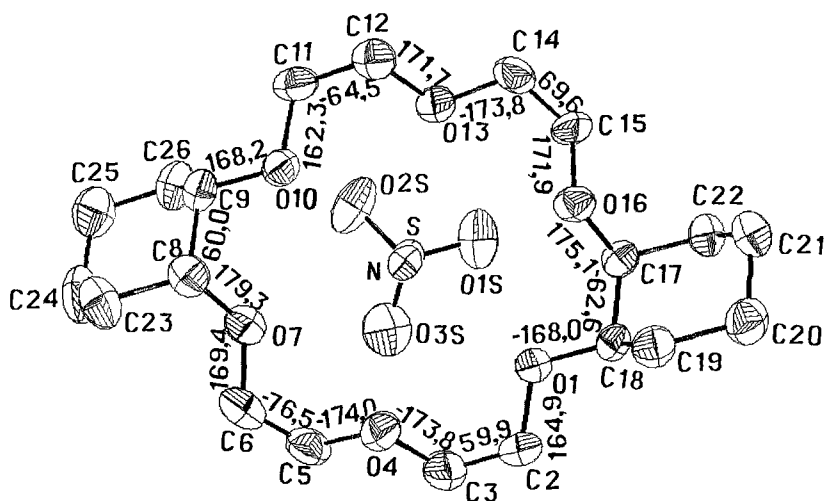


Fig. 4. ORTEP plot of **2** as projected into the macrocyclic plane. Torsion angles within the macrocyclic ring are given. Hydrogen atoms omitted.

dimensions. Such geometric parameters as the transannular oxygen atom distances and their coplanarity are essentially different for **2** and **4**. The difference in O...O distances for **2** is 1.51 Å and for **4** it is 1.18 Å; the maximum deviations of the oxygen atoms from coplanarity are ± 0.205 and ± 0.116 Å for **2** and **4**, respectively. The conformation of the macrocycle is exactly the same in both complexes, and is described by twelve *trans*-COCC and six *gauche*-OCCO angles.

Thus, both investigated complexes (**1** and **2**) are inclusion compounds with a 1 : 1 stoichiometry. There are no intermolecular contacts closer than 3.5 Å between individual complexes. The complexes are probably formed by means of $\text{NH}_3^+ \cdots \text{O}$ ion-dipole interactions; the complex stability decreasing in the order: [18-crown-6][$\text{H}_3^+ \text{NSO}_3^-$] > **1** > **2** (Table V). It is assumed that the explanation for this order can be given by the increasing steric hindrances in the crown ether molecules in the same order.

The comparison of the geometric characteristics in the complexes **1**–**4** (Table VI) shows that the C—C and C—O bond lengths in the complexes with lead nitrate are longer than the corresponding values in **1** and **2**, the COC and OCC angles in **1** and **2** are slightly increased. In other words, the bond lengths and angles within the macrocycles in **1** and **2** conform to the values typically found in the literature for the crown ethers, while those in **3** and **4** do not.

The geometry of the amidosulfuric acid molecule is the same in both structures, in the complex with 18-crown-6 [15] and in the free acid [16].

References

1. F. Vögtle, H. Sieger and W. M. Müller: *Host Guest Complex Chemistry I*. In: Top. Curr. Chem., F. L. Boschke, Ed., Vol. 98 Springer-Verlag: New York (1981).
2. A. Elbasyouny, H. J. Brügge, K. von Deuten, M. Dickel, A. Knöchel, K. U. Koch, J. Kopf, D. Melzer and G. Rudolph: *J. Am Chem. Soc.* **105**, 6568 (1983).

3. M. Hiraoka: *Crown Compounds, Their Characteristics and Applications*, Tokyo, Kodansha Ltd., 275 (1982).
4. M. Mercer and M. R. Truter: *J. Chem. Soc. Dalton Trans.* 2215 (1973).
5. J. R. Damewood Jr., J. J. Urban, T. C. Williamson and A. L. Rheinold: *J. Org. Chem.* **53**, 167 (1988).
6. K. B. Yatsimirsky, A. G. Kolchinsky, V. V. Pavlitschuk and G. G. Talanova: *Synthesis of Macrocyclic Compounds*, Kiev, Naukova dumka, 280 (1987).
7. G. M. Sheldrick: *SHELXTL*. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Univ. of Göttingen.
8. P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson: *MULTAN 78* A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univ. of York, England and Louvain, Belgium, 1978.
9. Tables of thermal parameters and structure factors for **1** and **2** are available from the authors.
10. N. F. Krasnova, Yu. A. Simonov, A. A. Dvorkin, M. V. Korshunov, V. V. Yakshin and T. I. Malinowsky: *Izv. Akad. Nauk Mold. SSR, Ser. Fiz.-Tekh. and Mat. Nauk*, **668**, 63 (1984) (Russ.).
11. Yu. A. Simonov, N. F. Krasnova, A. A. Dvorkin, V. V. Yakshin, V. M. Abashkin and B. N. Laskorin: *Dokl. Akad. Nauk SSSR* **272**, 5, 1129 (1983).
12. N. K. Dalley, D. E. Smith and S. B. Larson: *J. Chem. Soc. Chem. Commun.* 43 (1975).
13. Yu. A. Simonov, N. F. Krasnova, N. A. Tsarenko, V. K. Bel'sky, V. V. Yakshin and B. N. Laskorin: *Dokl. Akad. Nauk SSSR* **285**, 892 (1985).
14. N. F. Krasnova, Yu. A. Simonov, M. B. Korshunov and V. V. Yakshin: *Kristallografia*, **32**, 449 (1987).
15. F. Seel, N. Klein, B. Krebs, M. Dartmann and G. Henkel: *Z. Anorg. Allg. Chem.* **524**, 95 (1985).
16. K. Osaki, H. Tadokoro and I. Nitta: *Bull. Chem. Soc. Jpn.* **28**, 524 (1955).