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Synthesis and Structure of Antimony(III)chloride–1,4,7,10,13,16-Hexaoxocyclooctadecane-(18-crown-6)–Acetonitrile (1/1/1)

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Abstract

The adduct $SbCl_3 \cdot 18$-crown-6·MeCN has been synthesised and its structure determined by single crystal X-ray diffraction techniques. $[Sb(C_{12}H_{24}O_6)Cl_3 \cdot CH_3CN]$, $M_r = 533.6$, orthorhombic, *Pnma*, $a = 19.473(6)$, $b = 13.946(5)$, $c = 8.032(3)$ Å, $U = 2181.1(1.1)$ Å^3, $Z = 4$, $D_c = 1.625$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 16.7 cm^{-1}, $T = 293$ K, $F(000) = 1072$, $R = 0.0503$ for 1383 unique observed reflections with $I/\sigma(I) \geqslant 2.0$. In this molecular complex the crown ether possesses approximate D_{3d} symmetry and is bonded by all six oxygen atoms to a pyramidal $SbCl_3$ unit resulting in a half-sandwich structure. The solvent (MeCN) molecule is trapped in the lattice and plays no part in the coordination geometry of the central Sb atom.

Introduction

Crown ethers react with a wide range of metal ions or neutral metal species to form molecular complexes of diverse structural types. Briefly the metal can be situated either within the ring cavity being directly bonded to oxygen atoms of the ring or in an outside location where intermediary hydrogen bonding of the type ($O_{\text{ring}} \cdots\cdots H_2O \cdots\cdots$Metal) holds the metal in place [1, 2]. For M(III)–crown ether systems (M = As, Sb, Bi) stereochemical involvement of the lone pair of electrons associated with M(III) represents a further possible adjunct to the structural type. The first example $SbCl_3 \cdot 15$-crown-5 [3] shows an $SbCl_3$ pyramidal unit linked to the five oxygen atoms of the macrocyclic polyether with the lone pair on antimony pointing towards the centre of the ring. As part of a structural-reactivity study of such systems we have recently reported the structures of $BiCl_3 \cdot 12$-crown-4 and $2BiCl_3 \cdot 18$-crown-6 [4]; whereas the 1:1 complex is neutral the 2:1 complex is ionic and contains two $[BiCl_2 \cdot 18\text{-crown-}6]^+$ cations and a $[Bi_2Cl_8]^{2-}$ anion. Lone pair stereochemical activity is evident in each compound. Here we report the synthesis and structure of another such complex, that between antimony(III)chloride and 18-crown-6.

Experimental

Preparation

A solution of $SbCl_3$ (2.025 g, 8.87 mmol) in MeCN was added dropwise to a chilled (0 °C) solution of 18-crown-6 (2.345 g, 17.74 mmol) in MeCN. After allowing to warm to room temperature the solution was stirred for 24 h. Removal of solvent resulted in the deposition of a white semicrystalline solid. The *product* was washed with n-hexane and recrystallised from $MeCN/CH_2Cl_2$ to give small colourless needle crystals which proved suitable for the diffraction measurements. *Anal.* Calc. for $C_{14}H_{27}NO_6SbCl_3$: C, 31.5; H, 5.1; N, 2.6; Cl, 19.9. Found: C, 31.2; H, 5.2; N, 2.3; Cl, 20.0%.

Crystallographic Data

Crystal dimensions were 0.2 × 0.25 × 0.5 mm. Data were collected with a Syntex R3m four circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range +0.6 to −0.5 (2θ) around the Kα_1–Kα_2 angles, scan speed 6–29° min^{-1} depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. *hkl* ranges were $h = 0 \rightarrow 24$, $k = 0 \rightarrow 17$, $l = 0 \rightarrow 10$. Three standard reflections were monitored every 200 reflections and showed slight changes during data collection of ~5%. The data were rescaled to correct for this. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 22°$). Reflections were processed using profile analysis to give 2020 unique reflections; 1383 were considered observed ($I/\sigma(I) \geqslant 2.0$) and used in refinement; they were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method; maximum

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TABLE 1. Some selected bond distances (Å) and bond angles (°) for $SbCl_3 \cdot 18$-crown-6

Bond lengths			
Sb(1)–Cl(1)	2.391(2)	O(4)–C(6)	1.422(16)
Sb(1)–Cl(1A)	2.391(2)	C(1)–C(2)	1.413(22)
Sb(1)–Cl(2)	2.361(3)	C(3)–C(4)	1.473(22)
O(1)–C(1)	1.397(17)	C(5)–C(6)	1.391(21)
O(2)–C(2)	1.441(18)	Sb(1)–O(1)	3.025(11)
O(2)–C(3)	1.351(17)	Sb(1)–O(2)	2.989(10)
O(3)–C(4)	1.402(15)	Sb(1)–O(3)	3.401(10)
O(3)–C(5)	1.405(17)	Sb(1)–O(4)	3.290(12)
Bond angles			
Cl(1)–Sb(1)–Cl(2)	90.1(1)	O(1)–C(1)–C(2)	108.5(1.0)
Cl(2)–Sb(1)–Cl(1A)	90.1(1)	C(1)–C(2)–O(2)	114.6(1.3)
Cl(1)–Sb(1)–Cl(1A)	90.3(1)	O(2)–C(3)–C(4)	111.2(1.2)
C(1)–O(1)–C(1A)	115.0(13)	C(3)–C(4)–O(3)	109.1(1.1)
C(2)–O(2)–C(3)	112.1(10)	O(3)–C(5)–C(6)	112.0(1.2)
C(4)–O(3)–C(5)	114.1(10)	C(5)–C(6)–O(4)	109.5(1.0)
C(6)–O(4)–C(6A)	110.5(12)		

and minimum transmission factors were 0.835 and 0.778. The systematic absences $0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$ indicate space groups *Pnma* or $Pn2_1a$. By density considerations *Pnma* was selected and this proved correct by excellent refinement.

Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined. The methyl group was treated as a rigid CH_3 unit, with its initial orientation fixed by the mirror plane and the strongest H atom peaks on a difference Fourier synthesis. Final refinement was on F by least squares methods refining 125 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height $+\frac{1}{2}$ and $-\frac{1}{2}$ el, Å^{-3}. A weighting scheme of the form $W = 1/[\sigma^2(F) + gF^2]$ with $g = 0.000315$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.0503$, $R_w = 0.0475$. Maximum shift/error in final cycle 0.001. Computing with SHELXTL PLUS [5] on a DEC Microvax-II. Scattering factors in the analytical form and anomalous dispersion factors taken from ref. 6.

Results and Discussion

Selected bond distances and angles are given in Table 1. A perspective view of the molecule with atom numbering scheme is shown in Fig. 1. The central Sb atom is bonded to three chlorine atoms and all six oxygen atoms of the 18-crown-6 cyclic ether to give a half sandwich structure (Fig. 1) similar to that of $SbCl_3 \cdot 15$-crown-5. Within the $SbCl_3$ unit the Sb–Cl bonds (2.361(3)–2.391(2) Å) show little variation and the Cl–Sb–Cl bond angles are right

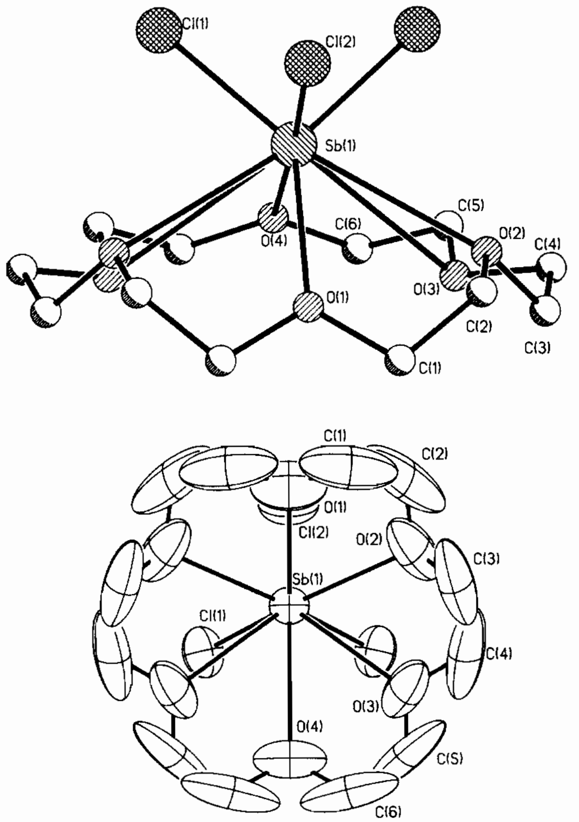

Fig. 1. (a) Structure of the $SbCl_3 \cdot 18$-crown-6 molecule showing the atom numbering scheme used. (b) A perspective view of the complex with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Sb(1)	6571.5(3)	2500	3463.2(8)	54.8(2)
Cl(1)	6348(1)	1284(1)	5491(2)	79(1)
Cl(2)	7743(1)	2500	4218(4)	93(1)
O(1)	7426(6)	2500	319(12)	140(6)
O(2)	6903(5)	4257(5)	1491(10)	132(3)
O(3)	5463(4)	4133(5)	1830(9)	117(3)
O(4)	4889(5)	2500	3103(13)	132(5)
C(1)	7494(7)	3344(13)	−601(13)	185(10)
C(2)	7517(9)	4126(12)	517(19)	207(10)
C(3)	6452(7)	4854(9)	742(20)	175(9)
C(4)	5834(8)	4994(9)	1771(20)	185(10)
C(5)	4908(8)	4145(11)	2947(19)	197(9)
C(6)	4494(5)	3338(12)	2780(16)	186(10)
C(101)	5238(9)	7500	2028(19)	88(6)
C(102)	4602(8)	7500	1198(15)	92(5)
N(101)	5737(8)	7500	2654(22)	148(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

angles (90.1(1)–90.3(1)°). The argument by Nicholson *et al.* [3] for lone pair involvement in the case of $SbCl_3 \cdot 15$-crown-5 (Sb–Cl 2.405(1)–2.433(1) Å, Cl–Sb–Cl 88.67(5)–93.25(5)°) i.e., that the presence of a $SbCl_3$ pyramidal structure in both the parent molecule and the 15-crown-5 complex is synonymous with retention of a stereochemically active lone pair following complexation, is equally applicable in the present instance. A plane of symmetry containing Sb(1), Cl(2), O(4) and O(1) bisects the molecule.

The Sb atom is clearly displaced from a central position over the ring and lies closer to the trio of oxygen atoms O(1) O(2) O(2A); this preference is reflected in the non-uniform Sb–O bond distances which fall into two distinct sets, i.e., those linking O(1) O(2) O(2A), 2.989(10)–3.025(11) Å and those linking O(4) O(3) O(3A), 3.290(12)–3.401(10) Å. When compared with the sum of the covalent radii (~2.2 Å) and, in turn, $SbCl_3 \cdot 15$-crown-5 (Sb–O 2.787(5)–2.997(4) Å, mean 2.902 Å) these Sb–O distances are conspicuously long and suggest extremely weak binding of crown ether ligands to Sb(III) in the relative order 15-crown-5 > 18-crown-6. As shown by bond/angle parameters the ring adopts the 'crown' conformation (D_{3d}) – a situation common to many 18-crown-6 complexes involving both molecular and ionic substrates [7]. Torsion angles about C–C bonds are all close to ±65° whilst those about C–O bonds approach ±180° and the six oxygen atoms lie alternately 0.29–0.31 Å above and below their mean plane. The Sb atom is located 1.65 Å above this mean plane. Evidently the presence of a stereochemically active lone pair and its interactions with the lone pairs on the oxygen atoms of the ring mitigates against direct encapsulation – the estimated value of the 18-crown-6 hole size for a D_{3d} conformation is 2.85 Å [8] as compared with the observed Sb–O (mean) 3.183 Å – and the $SbCl_3$ unit assumes a position on one side of the ring. Presumably the requirement of maximisation of bonding interactions, *ipso facto*, with the crown constrained in the D_{3d} conformation is achieved in the form of a closer attachment of three of the six oxygen atoms. With the smaller crown complex $SbCl_3 \cdot 15$-crown-5, the Sb sits in a central position essentially equidistant from all five oxygen atoms [3].

As observed in previous 18-crown-6 complexes the individual C–C bonds 1.391(21)–1.473(22) Å appear to be abnormally short whereas, apart from C(3)–O(2), 1.351(17) Å, C–O bonds 1.397(17)–1.441(18) Å are much as expected [7, 9]. The ellipsoids of thermal motion are drawn in Fig. 1b. The large amplitude of vibration and the high degree of anisotropy displayed by the carbon and oxygen atoms (C > O) indicate significant internal motions in the ring at room temperature. Bond angles at carbon cover the range 108.5(1.0)–114.6(1.3)°, mean 110.8°, and those at oxygen lie within the range 110.5(1.2)–115.0(1.3)°, mean 112.9°. There is no obvious reason for the anomalous bond length C(3)–O(2); the angle at O(2) 112.1(1.0)° and that at C(3) 111.2(1.2)° are equally acceptable. The solvent (MeCN) molecule is simply trapped in the lattice and plays no part in the coordination geometry of the central Sb atom. Its dimensions are as expected. Our attempts to isolate an As(III)–18-crown-6 complex for comparisons with $SbCl_3 \cdot 18$-crown-6 and $2BiCl_3 \cdot 18$-crown-6 have proved unsuccessful. The product obtained from the $AsCl_3$/18-crown-6/MeCN system is, interestingly, the ligand solvate 18-crown-6·2MeCN [10]. The ability of 18-crown-6 to form complexes with neutral molecules and the nature of the binding between host and guest molecules has attracted recent attention and discussion [11].

Supplementary Material

Tables of observed and calculated structure factors, atomic coordinates, thermal parameters, and full bond angles and bond distances are available from the authors on request.

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