Stereochemical Role of Lone Pairs in Main-group Elements. Part 3.[1] Structure and Bonding in Trichloro(1,4,7,10,13-pentaoxacyclopentadecane)antimony(III) studied by Means of *X*-Ray Crystallography at 120 K *

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The crystal structure of the complex formed between $SbCl_3$ and 15-crown-5(1,4,7,10,13-pentaoxacyclopentadecane,L) has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ in a unit cell of dimensions $a = 7.575(1)$, $b = 12.734(2)$, and $c = 15.838(3)$ Å. The structure, refined to $R = 0.033$ for 1989 observed reflections, consists of discrete $SbCl_3L$ molecules in which antimony is sandwiched between essentially parallel planes containing five oxygens and three chlorines, respectively.

The complexing properties of macrocyclic polyethers have a number of unusual features.[2] That there is keen interest in these molecules is clearly shown by the three hundred or so structures reported on their complexes with inorganic cations and molecules and neutral organic molecules. Complexes with acceptor molecules containing the heavier *p*-block elements have been relatively little studied, but to date, results show that some interesting features are also evident for these. Tin(II) and tin(IV) complexes with 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane,L) and 18-crown-6(1,4,7,10,13,16-hexaoxacyclo-octadecane) have been studied by means of Mössbauer spectroscopy and *X*-ray diffraction.[3,4] The tin(II) complexes differ from those containing small cyclic ethers such as 1,4-dioxane[5,6] as ligands in that they contain tin in the form of molecular cations. In this respect the 15-crown-5 systems stand out because the tin lone pair is not sterically active. This observation is significant because, with few exceptions, a dominant feature of *p*-block elements in lower valence states is the role played by their lone pairs in producing irregular co-ordinations. Since ideal Sn^{2+} and Sb^{3+} cations are isoelectronic, the antimony(III)–macrocyclic polyether systems are obvious candidates for study. However, the fact that the ionisation energy for the latter is more than twice that of the former[7] (2 119.8 and 4 872.0 kJ mol^{-1}, respectively) gave us cause for anticipating that the antimony(III) systems would depart from the structural pattern shown by tin(II).

We report here the results of the first of our structural studies on antimony(III)–crown ether systems, the crystal structure of $SbCl_3L$.

Experimental

Preparation.—The complex $SbCl_3L$ was obtained as an immediate flocculent precipitate on adding 15-crown-5 to solutions of antimony(III) chloride in organic solvents. In order to produce crystals suitable for *X*-ray diffraction it was necessary to slow the reaction down considerably. Initially, this was achieved by mixing the reactants slowly by diffusing antimony(III) chloride solution through a gel containing the crown ether. The details of the procedure chosen are similar to those described for organic systems by Desiraju *et al.*[8] 15-Crown-5 (0.06 g) in acetone (0.9 cm^3) and toluene (2.9 cm^3) was mixed with Sephadex LH-20 (4.66 g). The gel set almost immediately. Antimony(III) chloride (0.11 g) in acetone (5 cm^3) was poured onto the column of gel and allowed to diffuse for 7 d. Crystals of the complex were found embedded in the gel and were removed singly with the aid of a microscope. Although the crystals were well defined and apparently suitable for diffraction work, the *X*-ray structure solution progressed no better than to an *R* factor of 0.11. However, the single finding of a single large crystal, which had grown out of acetone washings of the gel by slow evaporation in a stoppered flask over several weeks, enabled a new data set to be collected. The crystals used in the two data sets are designated (**A**) and (**B**) respectively.

Crystallography.—*Crystal data.* $C_{10}H_{20}Cl_3O_5Sb$, $M = 448.3$, orthorhombic, crystal (**A**): $a = 7.587(1)$, $b = 12.751(1)$, $c = 15.860(2)$ Å, $U = 1\,535.1$ Å^3; crystal (**B**) $a = 7.575(1)$, $b = 12.734(2)$, $c = 15.838(3)$ Å, $U = 1\,527.7$ Å^3; $D_m = 1.84$ g cm^{-3} (flotation), $Z = 4$, $D_c = 1.94$ g cm^{-3}, $F(000) = 1\,128$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 23.5$ cm^{-1}. Absent spectra consistent with space group $P2_12_12_1$.

Intensity data collection and structure refinement. Crystals (**A**) and (**B**) with approximate dimensions (the latter being trimmed from the large crystal) 0.40 × 0.40 × 0.10 and 0.55 × 0.30 × 0.15 mm respectively were mounted in general orientations and intensity data collected at 120 K in the ω—2θ scan mode on a Nonius CAD4 automatic four-circle diffractometer out to $\theta = 30°$ using monochromatised Mo-K_α radiation. Cell dimensions were determined from the refined setting angles of 25 reflections located by a search routine. The space group was determined from the systematic absences. The data were transferred to a VAX 11/750 computer, Lorentz and polarisation corrections applied, systematic absences rejected, and equivalent reflections merged. The crystals were stable under data collection. Of the 2 118 reflections measured, 1 989 reflections were classified as observed, *i.e.* $I_{net} > 3.0\sigma(I)$. Scattering factors and dispersion corrections were taken from ref. 9. Antimony values were used for antimony(III). Calculations were performed by means of the CRYSTALS Issue 8 package[10] and plots were drawn by the program ORTEP.[11] The structure was solved by Patterson and Fourier techniques. For crystal (**A**) full-matrix least-squares refinement of the non-hydrogen atoms only converged to an *R* factor of 0.11 with anisotropic thermal parameters. That the model was not fully satisfactory for this data set was also manifest from the

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates ($\times 10^5$ for Sb and Cl, $\times 10^4$ for other atoms) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb	−24 251(5)	230(3)	−37 726(2)
Cl(1)	−48 510(2)	−280(1)	−47 785(8)
Cl(2)	−41 100(2)	12 490(1)	−29 371(9)
Cl(3)	−36 160(2)	−14 820(1)	−30 520(1)
O(1)	−791(6)	−1 354(3)	−4 991(2)
C(2)	179(4)	−861(4)	−5 661(3)
C(3)	−848(4)	78(4)	−5 976(2)
O(4)	−1 001(6)	877(3)	−5 346(3)
C(5)	542(6)	1 513(4)	−5 268(2)
C(6)	203(4)	2 327(3)	−4 597(4)
O(7)	−140(6)	1 868(3)	−3 781(3)
C(8)	1 494(4)	1 464(2)	−3 382(4)
C(9)	940(5)	1 293(4)	−2 427(3)
O(10)	−225(6)	378(3)	−2 392(3)
C(11)	595(6)	−542(4)	−2 021(2)
C(12)	1 757(5)	−1 100(3)	−2 676(4)
O(13)	651(6)	−1 369(3)	−3 367(2)
C(14)	1 516(5)	−1 945(3)	−4 016(3)
C(15)	109(6)	−2 245(3)	−4 647(3)

Table 2. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Antimony co-ordination		(*b*) 15-Crown-5 molecule	
Sb–Cl(3)	2.405(1)	O(1)–C(15)	1.432(7)
Sb–Cl(2)	2.412(1)	O(1)–C(2)	1.435(6)
Sb–Cl(1)	2.433(1)	C(2)–C(3)	1.511(7)
Sb–O(10)	2.787(5)	C(3)–O(4)	1.429(7)
Sb–O(1)	2.886(4)	O(4)–C(5)	1.427(7)
Sb–O(7)	2.918(4)	C(5)–C(6)	1.507(7)
Sb–O(4)	2.925(4)	C(6)–O(7)	1.442(6)
Sb–O(13)	2.997(4)	O(7)–C(8)	1.482(6)
		C(8)–C(9)	1.585(8)
Cl(2)–Sb–Cl(3)	93.25(5)	C(9)–O(10)	1.462(7)
Cl(1)–Sb–Cl(3)	90.36(5)	O(10)–C(11)	1.450(7)
Cl(1)–Sb–Cl(2)	88.67(5)	C(11)–C(12)	1.534(7)
O(10)–Sb–Cl(3)	88.9(1)	C(12)–C(13)	1.585(7)
O(10)–Sb–Cl(2)	77.3(1)	O(13)–C(14)	1.423(7)
O(10)–Sb–Cl(1)	165.9(1)	C(14)–C(15)	1.510(7)
O(1)–Sb–Cl(3)	89.67(9)		
O(1)–Sb–Cl(2)	170.74(9)	C(2)–O(1)–C(15)	112.6(4)
O(1)–Sb–Cl(1)	82.52(9)	C(3)–C(2)–O(1)	109.1(3)
O(1)–Sb–O(10)	111.5(1)	C(2)–C(3)–O(4)	112.0(3)
O(7)–Sb–Cl(3)	149.99(9)	C(3)–O(4)–C(5)	113.4(4)
O(7)–Sb–Cl(2)	78.21(9)	C(6)–C(5)–O(4)	108.2(3)
O(7)–Sb–Cl(1)	117.79(9)	C(5)–C(6)–O(7)	112.5(3)
O(7)–Sb–O(10)	61.2(1)	C(8)–O(7)–C(6)	111.9(4)
O(7)–Sb–O(1)	103.4(1)	C(9)–C(8)–O(7)	103.5(3)
O(4)–Sb–Cl(3)	146.97(9)	C(8)–C(9)–O(10)	107.8(3)
O(4)–Sb–Cl(2)	114.97(9)	C(9)–O(10)–C(11)	113.6(4)
O(4)–Sb–Cl(1)	74.4(1)	C(12)–C(11)–O(10)	110.3(3)
O(4)–Sb–O(10)	112.8(1)	C(11)–C(12)–O(13)	107.1(3)
O(4)–Sb–O(1)	59.9(1)	C(14)–O(13)–C(12)	114.1(4)
O(4)–Sb–O(7)	58.5(1)	C(15)–C(14)–O(13)	106.5(3)
O(13)–Sb–Cl(3)	73.66(9)	C(14)–C(15)–O(1)	112.8(3)
O(13)–Sb–Cl(2)	132.57(8)		
O(13)–Sb–Cl(1)	135.38(9)		
O(13)–Sb–O(10)	57.5(1)		
O(13)–Sb–O(1)	56.7(1)		
O(13)–Sb–O(7)	90.9(1)		
O(13)–Sb–O(4)	96.7(1)		

Table 3. Torsion angles (°)

C(15)–O(1)–C(2)–C(3)	−179.0(5)
O(1)–C(2)–C(3)–O(4)	65.0(5)
C(2)–C(3)–O(4)–C(5)	79.9(5)
C(3)–O(4)–C(5)–C(6)	179.2(5)
O(4)–C(5)–C(6)–O(7)	61.4(5)
C(5)–C(6)–O(7)–C(8)	74.9(5)
C(6)–O(7)–C(8)–C(9)	165.0(5)
O(7)–C(8)–C(9)–O(10)	72.2(5)
C(8)–C(9)–O(10)–C(11)	107.4(5)
C(9)–O(10)–C(11)–C(12)	−80.4(5)
O(10)–C(11)–C(12)–O(13)	−58.3(5)
C(11)–C(12)–O(13)–C(14)	−176.9(5)
C(12)–O(13)–C(14)–C(15)	174.7(5)
O(13)–C(14)–C(15)–O(1)	58.4(5)
C(14)–C(15)–O(1)–C(2)	81.1(5)

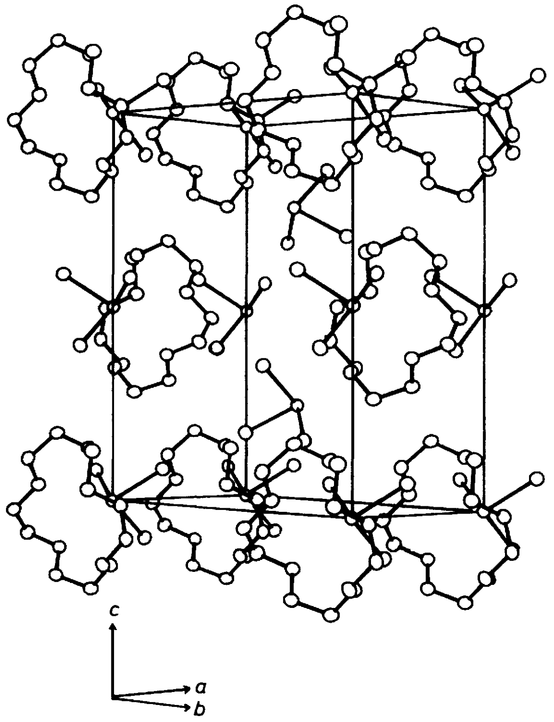

Figure 1. Crystal structure of $SbCl_3L$

significant electron density positioned 0.4 Å on either side of the antimony site along the *b* axis. Therefore, the new data set for crystal (**B**) was collected. The final atomic parameters from the first solution were employed and found acceptable. The absorption corrected data were successfully refined by full-matrix least squares to an *R* value of 0.033 (*R*′ 0.037) (unit weights) together with hydrogen atoms which were placed in calculated positions, restrained to be 0.95 Å from their carbon atoms, and those bonded to the same carbon were given a common isotropic thermal parameter. The final stage of the refinement was to assign each reflection a weight[12] $w = 1/\sum_{r=1}^{n} A_rT_r(X)$, where *n* is the number of coefficients, A_r, for a Chebyshev series, T_r is the polynomial function, and *X* is $F_o/F_o(\max)$. The values of A_r were 5.2, 6.5, and 1.4 and the final *R* value was 0.033 (*R*′ 0.046). The atomic positions are given in Table 1, and Table 2 contains the interatomic distances and valence angles. The torsion angles for the 15-crown-5 ligand are listed in Table 3.

Results and Discussion

The crystal structure, part of which is shown in Figure 1, consists of pyramidal $SbCl_3$ units with the apex of the pyramid

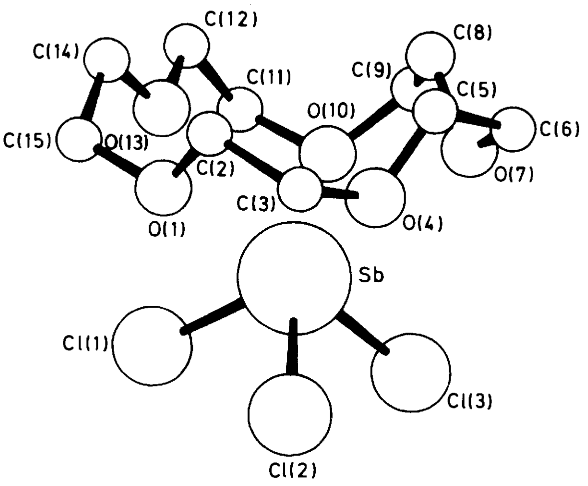

Figure 2. Structure of SbCl$_3$L showing the atom-numbering scheme

approximately directed along the *b* axis towards the centre of a 15-crown-5 (L) molecule (Figure 2). The SbCl$_3$L molecules are linked together *via* van der Waals contacts. When considered alone, the SbCl$_3$ unit is reminiscent of the structure of gas-phase antimony(III) chloride itself[13] [Sb–Cl 2.333(3) Å, Cl–Sb–Cl 97.2(9)°]. The influence of the ligand and crystal-packing forces are expressed by the lengthened Sb–Cl bonds and decreased Cl–Sb–Cl angles (average differences, 0.08 Å and −6.4°, respectively) relative to gas-phase antimony(III) chloride. The stereochemistry of the latter is fully consistent with the pyramidal structure predicted by the valence shell electron pair repulsion model[14] for discrete AX_3E species (A = central atom, X = ligand, and E = lone pair). Since only small structural changes occur on complexing with 15-crown-5 it seems reasonable to infer that the lone pair on antimony points towards the centre of the crown ring (see later). Likewise, pyramidal SbCl$_3$ units are also discernible in 2:1 and 1:1 complexes of antimony(III) chloride with aromatic hydrocarbons such as naphthalene or *p*-xylene,[15] where weak interactions, apparently involving the lone pair and π orbitals, occur. In contradistinction with the present structure, the bond lengths in the SbCl$_3$ unit in the aromatic hydrocarbon complexes are not significantly different [average 2.331(14) Å] from those in gas-phase antimony(III) chloride, although the bond angle has decreased [93.3(5)°]. In the *p*-xylene complex the distance from the antimony atom to the plane of the organic molecule is 3.09 Å and to the nearest C atom 3.18 Å. Both distances are considerably shorter than the van der Waals distance of 3.5 Å. All structural evidence indicates weak antimony–aromatic hydrocarbon interactions.

There are major differences between the acceptor properties of antimony(III) chloride and tin(II) chloride towards 15-crown-5. First, the crown ether is not disordered as is the case for the tin(II) complex.[16] Secondly, the present compound is a molecular adduct whereas reaction between tin(II) acceptors and 15-crown-5 results in detaching the tin atom and incorporating it in a SnL^{2+} complexion. To a large extent this is consistent with the energy associated with the production of Sb^{3+} being more than that released on complexing this hypothetical cation by the ligand as already noted. Thirdly, the antimony lone pair is evidently sterically active and in a position to interact with the relevant lone pairs on the oxygen atoms of the crown ether.

However, in one respect the two complexes are similar, since both tin(II) and antimony(III) exert a similar influence on the conformation of the attached ligands by constraining the five oxygen atoms to be essentially coplanar. The conformation of the ligand is quantified by the torsion angles and is also depicted in Figure 3.

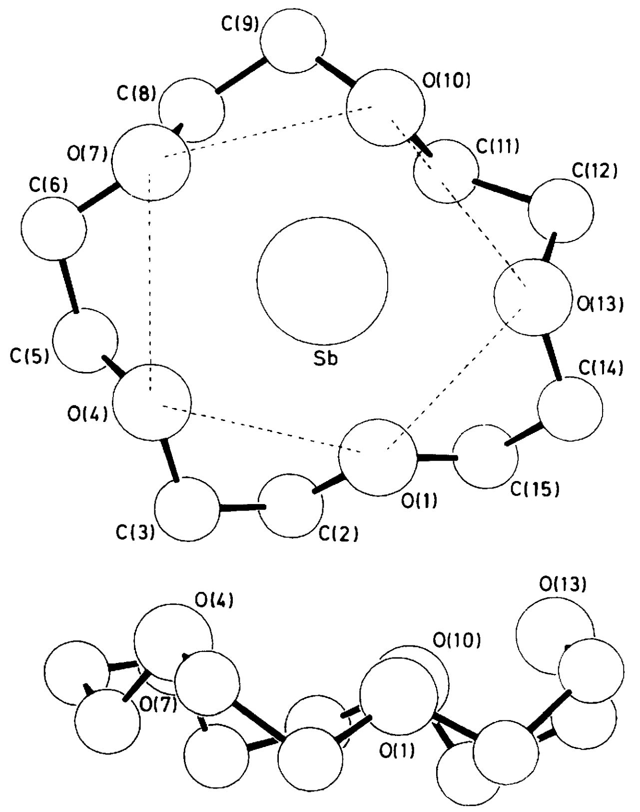

Figure 3. Top: the crown ether (hydrogen atoms omitted) viewed along the direction normal to the mean O$_5$ plane. Bottom: view along a direction in the mean plane

To a good approximation the conformation of the crown ether is characterised by the five oxygen atoms lying in a common plane. This is approximately parallel to that containing the three chlorine atoms. Therefore, the antimony atom is sandwiched between a three-membered ring of chlorines on the one side and a five-membered ring of oxygen atoms on the other.

The influence of the crown ether on the antimony lone pair is central to any discussion of this structure. That the SbCl$_3$ fragment retains much of its structural integrity (see above) lends support to the view that the lone pair retains much of its steric activity albeit somewhat modified by interaction with the five oxygen atoms of the ether. We find a similar arrangement in a complex formed between bismuth(III) chloride and 18-crown-6.[17] We omit a detailed discussion on the nature of the lone pair since the background for this has been recently presented in ref. 18 (and refs. therein).

The point symmetry is very close to C_s. The Sb–O bond distances are clearly long compared with the sum of the covalent radii (2.2 Å). Although the individual Sb–O distances suggest weak interactions, evidently the sum of these is large enough for a stable ligand–acceptor contact, and is sufficient to make the crown ether adopt the observed conformation. With an idealised C_s point symmetry the antimony atomic orbitals transform irreducibly as A' ($5s$, $5p_x$, $5p_y$) and A'' ($5p_z$). Group orbitals formed by combining the atomic orbitals on the oxygen and chlorine atoms transform as a series of A' and A'' and overlap with the corresponding orbitals on antimony. Thus, the lone pair is identified with contributions from the $5s$ and $5p_x$, $5p_y$ orbitals (as it is the admixture of *p*-and *s*-type wavefunctions which introduce directional characteristics and hence influence bond angles[18]) and is explicitly represented by the sum of antibonding *a′* molecular orbitals with varying antimony or ligand character. The stereochemical influence on Cl–Sb–Cl angles stems mainly from the balance between the series of bonding and antibonding *a′* molecular orbitals achieved by adjusting the molecular geometry.

The long Sb–O interactions must be primarily associated with those molecular orbital levels which are appreciably higher and antibonding, to those relating mainly to the Sb–Cl bonds. The significant decrease in the Cl–Sb–Cl bond angles is not due to any enhanced lone pair steric activity but is attributed to the systems desire to lower its total energy through maximum population of the 5*s* valence orbital on antimony[1,18] within the constraints imposed by ring conformation and lattice energy.

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