Synchrotron X-Ray Absorption Studies on the 12-Crown-4 and 15-Crown-5 Complexes of Antimony(III) Chloride

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The extended X-ray absorption fine structure spectrum of powdered $SbCl_3 \cdot 12$-crown-4 has been measured at room temperature using synchrotron radiation. With the aid of standard full-matrix least-squares fitting methods and $SbCl_3 \cdot 15$-crown-5 as a model complex for extracting the amplitude and phase parameters for the Sb–Cl, Sb–O and Sb–C bonds, it was possible to show that the data are consistent with a pyramidal geometry for $SbCl_3$ that is complexed to the macrocycle through Sb–O bonds to all four oxygen atoms.

Although there is keen interest in the properties of macrocyclic polyethers, as evinced by the 300 or so structures already reported on their complexes with inorganic cations and molecules and neutral organic molecules, the complexes formed with p-block elements have been relatively little studied. However, the limited results to date show that interesting features are also evident for the latter. Thus, the recent literature reports [119]Sn Mössbauer spectroscopic[1] and X-ray crystallographic[2–4] studies on some tin(II) and tin(IV) complexes with 15-crown-5 (i.e. 1,4,7,10,13-pentaoxacyclopentadecane) and 18-crown-6 (or 1,4,7,10,13,16-hexaoxacyclooctadecane), and an extended X-ray absorption fine structure (EXAFS) spectroscopic investigation[5] on methanol solutions of tin(II) chloride and 12-crown-4 and 15-crown-5, together with X-ray crystallographic determinations[6,7] on the antimony(III) and bismuth(III) complexes with 15-crown-5 and 18-crown-6.

The work on the 15-crown-5 and the 18-crown-6 complexes with tin(II) chloride [$Sn(15$-crown-5$)_2^{2+}(SnCl_3^-)_2$ and $Sn(18$-crown-6$)Cl^+SnCl_3^-$] and the antimony(III) and bismuth(III) chloride adducts $SbCl_3 \cdot 15$-crown-5 and $BiCl_3 \cdot 18$-crown-6 shows that they differ considerably from those complexes that contain the smaller cyclic ethers, such as 1,4-dioxan,[8,9] in that the tin atoms are incorporated into molecular cations. Moreover, the $Sn(15$-crown-5$)_2^{2+}$ cation stands out because the tin lone pair is not sterically active.[6] The sandwich-like structure of the $Sn(15$-crown-5$)_2^{2+}$ cation is reminiscent of the neutral molecule decaphenylstannocene, [η^5-$(C_6H_5)_5C_5]_2Sn(II)$.[10] These two structures stand out because, with very few exceptions, a dominant feature of p-block elements in lower valence states is the role played by their lone pairs in producing irregular coordinations. To a significant extent, a similar effect is observed in the $Sn(18$-crown-6$)Cl^+SnCl_3^-$ complex, in which

the tin atom in the complex cation exhibits much reduced stereochemical activity.[5]

Although ideal Sn^{2+} and Sb^{3+} cations are isoelectronic, the fact that the ionisation energy for the latter is more than twice that of the former (being 2119.8 and 4872.0 kJ mol^{-1}, respectively)[11] must be a major factor governing the choice of the neutral discrete $SbCl_3 \cdot 15$-crown-5 adduct molecule rather than an ionic alternative which would have been analogous to the corresponding tin(II) systems.

The purpose of the present study is to exploit the advantage of EXAFS in probing the geometric environment of a specific element; in this case, to examine the coordination about antimony(III) as crown ethers with increasing coordinating capability are complexed to antimony(III) chloride. We were particularly interested in investigating the effect that decreased ring size has on the chelating behaviour of the smaller 12-crown-4 ligand towards the acceptor antimony(III) chloride molecule; it is known that with the even smaller cyclic ether 1,4-dioxan, the conformational requirements of the ring (the chair conformation) take precedence, with the result that polymeric complexes are formed rather than the molecular chelates that could be envisaged with the boat conformation.[8,9] Since X-ray diffraction quality crystals of $SbCl_3 \cdot 15$-crown-5 were obtained but not of $SbCl_3 \cdot 12$-crown-4, we decided to use the known crystal structure[6] of the former as the model compound in elucidating structural features about antimony in the latter complex.

Experimental

The complexes $SbCl_3 \cdot 12$-crown-4 and $SbCl_3 \cdot 15$-crown-5 were obtained as immediate flocculent precipitates on adding the ethers to solutions of antimony(III) chloride in

organic solvents. The crystal structure of $SbCl_3 \cdot 15$-crown-5 was determined[6] from a single crystal grown out of the mother liquor by very slow evaporation in a stoppered flask over several weeks.

EXAFS transmission measurements of the two complexes at room temperature were carried out at the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, UK using the antimony K-edge ($0.406\,63$ Å, 30.49 keV). The short-wavelength X-rays were produced by the 5 T wiggler magnet and the facilities of station 9.2.

Theory, methods and results

Data were reduced to χ-curves by means of the EXCALIB and EXBACK programs from the SRS program library. All necessary data were transferred to Trondheim for structure refinement using the full-matrix least-squares curve fitting program TROLL (the Trondheim version of MO-LEX85), which employs a modified plane-wave approximation[12] (for K-edges) as given by eqn. (1), where i is the

$$\chi(k) = -\Sigma_j(N_j/kr^2_{ij})/F_j(k,\pi)/\sin\ [2k(r_{ij}- \Delta r_{ij})$$

$$+ \ \varphi_{ij}(k)]\exp\ (-2k^2\sigma^2_{ij} - 2r_{ij}\eta/k) \tag{1}$$

absorber, j is back-scattered, F_j is the back-scattering amplitude, φ_{ij} is a combined phase term adjusted to fit the experimental data for the reference compound, N_j is the multiplicity of the back-scatterer, r_{ij} is an interatomic distance, Δr_{ij} is the corresponding EXAFS phase correction, σ_{ij} is the relevant Debye–Waller parameter and η is the mean free path parameter. The variable k is the photoelectron wavevector. The modified phase term $\varphi_{ij}(k) = 2\ \varphi_i(k)$ $+ \ \varphi_{ij}(k)$. The functions F_j, φ_i and φ_j were calculated from partial-wave phase shifts δ_l obtained from the Daresbury database in numerical form. Data from the X-ray absorption near-edge structure (XANES) region, $E < 2.5$ hartree (1 hartree $= 27.211\,65$ eV), where E is the photoelectron energy above threshold, were excluded from all refinements. The upper energy limits for the spectra are 28 hartree.

The EXAFS refinements were arranged so as to follow the conventional strategy of gas-phase electron diffraction refinement,[13] a strategy that is incorporated in the TROLL EXAFS curve fitting program. In addition, TROLL contains a subroutine (DEPEND) which provides the flexibility and maximum user control, through the least-squares algorithm, for linking independent variables and dependent parameters in order to attain the best fit, whilst limiting parameter correlation and structural overdetermination. TROLL also contains a routine for Fourier transformation.

The model compound. From the molecular structure[6] of the 15-crown-5 antimony(III) trichloride complex, $SbCl_3 \cdot 15$-crown-5 (Fig. 1) it is evident that the $SbCl_3$ fragment retains the pyramidal geometry of the isolated $SbCl_3$ molecule and that the macrocycle coordinates to antimony via
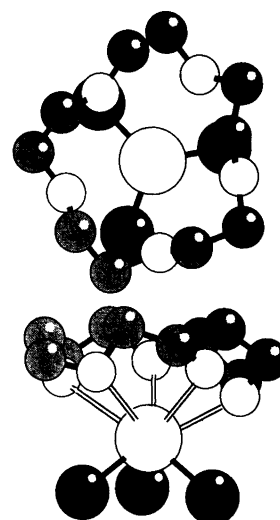

Fig. 1. The molecular structure of the model compound $SbCl_3 \cdot 15$-crown-5 viewed along the directions normal to the $(O)_5$ plane, and (bottom) along directions 90° to the top view.

all five oxygen atoms. For the purposes of EXAFS the three Sb–Cl, five Sb–O and ten Sb–C distances are averaged (Ref. 6), the differences being too subtle to resolve by the technique. We have recently shown[14] that the 12-crown-4 ligand also complexes some main group acceptors in a similar manner {one example being the adduct with lead(II) nitrate, in which lead is complexed as the $[Pb(12\text{-}crown\text{-}4)_2]^{2+}$ cation with the two 12-crown-4 ligands coordinating to lead via all of their oxygen atoms in the same way that 15-crown-5 bonds to tin(II) in $Sn(15\text{-}crown\text{-}5)_2^{2+}$ and to antimony(III) chloride in the model compound}.

The EXAFS fitting. Qualitative inspection reveals that the EXAFS of the model and the unknown (Fig. 2) are so similar that it is difficult to detect any differences at all by eye. This in itself is significant, because it suggests that the molecular structures of both crown adducts are very similar. EXAFS calibration parameters, including corrections to back-scattering and adsorber phases (i.e. Δr_C, Δr_O, Δr_{Cl}) and the photoelectron energy zero, were extracted by fitting the EXAFS of the model compound, whose structural parameters are known from the crystallographic study.[6] The phases and Debye–Waller parameters so obtained were used to fit the $SbCl_3 \cdot 12$-crown-4 spectrum, this time holding phase corrections constant but now refining the Sb–Cl, Sb–O and Sb–C distances and, as before, the photoelectron energy zero. Table 1 expresses the minor differences between the spectra of the model and the unknown in terms of the parameters obtained from the curve fitting with the observed and difference EXAFS χ-curves shown in Fig. 2. The conventional residuals, R, obtained from the model and the unknown at convergence were 6.3 and 7.6 %, respectively, where $R = \Sigma|\chi|/|\chi_{obs}|$ (with $\Delta\chi = \chi_{obs} - \chi_{calc}$). Refining the relative coordination numbers for Sb–Cl, Sb–O and Sb–C gave the values 3.0(3), 4.0(3) and

(a)

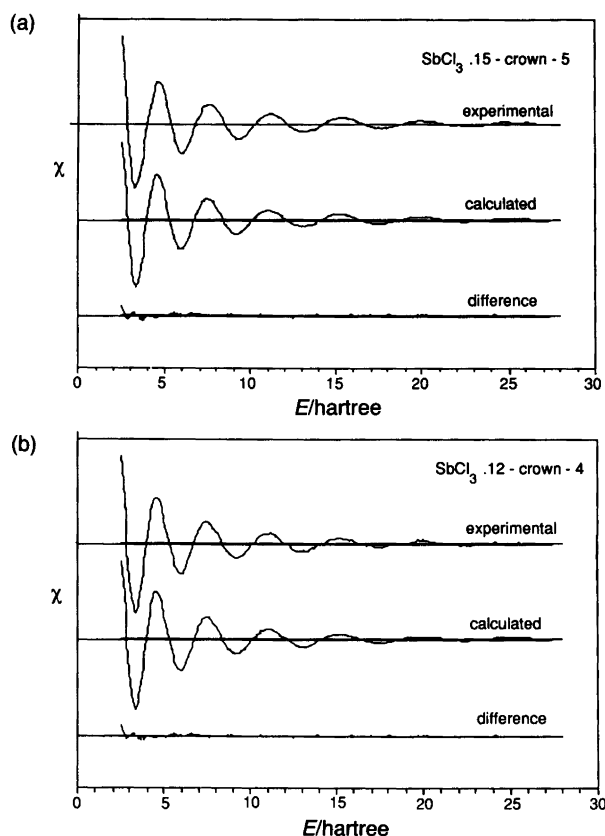**(b)**

Fig. 2. EXAFS χ-curves for (a) solid SbCl₃·15-crown-5 (the model compound) and (b) SbCl₃·12-crown-4.

Fig. 3. The molecular structure of the SbCl₃·12-crown-4 complex molecule, viewed along the directions normal to the (O)₄ plane, and (bottom) along directions 90° to the top view. Note that the actual orientation of the (Cl)₃ grouping about the principal axis of an idealised SbO₄ arrangement in the latter complex is not established.

4.7(8), respectively. (The carbon back-scatters were included for the sake of completeness, although the influence of such low-Z backscatterers at these distances, not surprisingly, was found to be but marginal.)

Table 1. Results of EXAFS curve-fitting.[a]

	SbCl₃·15-crown-5[b]	SbCl₃·12-crown-4	
Data range			
/hartree	2.5–28.0	2.5–28.0	
Sb–Cl/Å	2.409 (fixed)	2.41(1)	2.41(1)
N_{Cl}	3 (fixed)	3.0(3)	3 (fixed)
Δr(Sb–Cl)/Å	0.033(1)	0.033 (fixed)	0.033 (fixed)
σ(Sb–Cl)/Å	0.073(2)	0.073 (fixed)	0.075(3)
Sb–O/Å	2.89 (fixed)	2.85(2)	2.86(2)
N_O	5 (fixed)	4.0(3)	4 (fixed)
Δr(Sb–O)/Å	0.07(1)	0.07 (fixed)	0.07 (fixed)
σ(Sb–O)/Å	0.108(8)	0.108 (fixed)	0.102(6)
Sb–C/Å	3.75 (fixed)	3.62(9)	3.63(7)
N_C	10 (fixed)	4.7(8)	8 (fixed)
Δr(Sb–C)/Å	0.17(3)	0.17 (fixed)	0.17 (fixed)
σ(Sb–C)/Å	0.154(9)	0.154 (fixed)	0.176(8)
R/%	6.3	7.68	7.62

[a]See Ref. 17 for theory and definitions of σ and Δr. Estimated standard deviations are given in parentheses. [b]Model compound.[6]
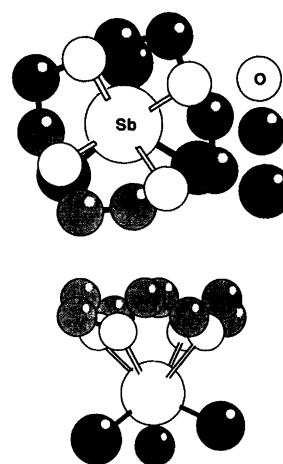
Since the coordination numbers are consistent with the formulation SbCl₃·12-crown-4, in which all four crown oxygen atoms are coordinated to antimony, and since the ligand is known to complex in this manner (see above), additional fits were carried out with the multiplicities fixed at 3, 4 and 8, respectively. The two choices of fit did not lead to any significant differences in the distances returned.

Discussion

The interaction between the crown ether donors and the SbCl₃ acceptor imposes conformations on the ethers that permit coordination through all ether oxygen atoms, so that the immediate environment around antimony in the 12-crown-4 complex is SbCl₃O₄, with three similar Sb–Cl and four essentially equivalent Sb–O bonds. The SbCl₃ unit in both complexes has longer bond lengths than those in the gas-phase molecule[15] [Sb–Cl 2.333(3) Å, Cl–Sb–Cl 97.2 (9)°]. The crown oxygens lie approximately in a common plane, thereby defining the conformation of the ligand, and the molecular structure (Fig. 3) is reminiscent of SbCl₃·15-crown-5 (Fig. 1).

Although the influence of complexation and crystal packing forces has only a minor effect on the Sb–Cl bonds, as shown by their lengths relative to those in the gas-phase SbCl₃ molecule,[15] the bond angles must deviate in the same way as already demonstrated by the X-ray structure analyses of the SbCl₃·15-crown-5 and BiCl₃·15-crown-5 complexes.[6]

Owing to the similarity in the lengths of the Sb(III)–O and Sb(III)–Cl bonds, which lie within the range 2.3–2.8 Å, values derived by EXAFS studies when these bonds are simultaneously present are liable to some correlation. We have recently shown[5] in a previous EXAFS study on some

tin(II) crown complexes that there is an alternative method, that makes no recourse to model compounds, of extracting structural information. [The procedure is described in detail by Beagley *et al.*,[16] who have shown that a similar treatment, applied to Mn(II)–I, Mn(II)–O and Mn(II)–P bonds, satisfactorily correlates the lengths of these bonds for a range of different environments.] This method is used here to check the structural information extracted here for the 12-crown-4 complex on the assumption that the 15-crown-5 complex is an appropriate structural model.

Using the same procedure as before,[5,16] the Sb–O and Sb–Cl distances are related to their respective coordination numbers through the bond-length versus bond-strength relationships of Brown and Shannon,[16] which take the form $s = s_0(R/R_0)^{-p}$. The parameters s_0 and R_0 are the standard bond strength and bond length values of a relevant reference system; s and R correspond to the same atom pair in another structure and p is an empirical constant (described below). In the present study two such relationships are

needed, one for the Sb(III)–O bonds and one for the Sb(III)–Cl bonds. The total bond strength for all the bonds around a trivalent antimony atom leads to eqn. (2), where

$$\Sigma s_{Cl} + \Sigma s_O = 3.00 \qquad (2)$$

s_{Cl} and s_O are the individual strengths for the bonds to chlorine and oxygen. With the corresponding coordination numbers N_{Cl} and N_O, eqn. (2) becomes eqn. (3).

$$\Sigma N_i s_i = N_{Cl} s_O = 3.00 \qquad (3)$$

Table 2 shows that if solid-state Sb_2O_3 and gas-phase $SbCl_3$ are used as reference systems,[15,19,20] the published Sb(III)–O and Sb(III)–Cl bond lengths in $SbCl_3 \cdot 5$-crown-5 satisfy eqn. (3) for chlorine and oxygen p-values of 6.0 and 5.0, respectively. The applicability of the equations for alkali halides with varying cation coordination numbers has also been demonstrated.[20,21]

Table 2. Agreements for known antimony(III) structures (including the EXAFS results for $SbCl_3 \cdot 12$-crown-4).[a]

(a) Reference values for Brown and Shannon equations:

Structure	Ref.	Bond	R_0	s_0	N
$SbCl_3$ (gas phase)	15	Sb–Cl	2.333	1.0	3.0
Sb_2O_3 (cubic)	19	Sb–O	1.977	0.875	3.0

The cubic oxide has a second, longer, Sb–O distance (R_1 of 2.917 Å, also with N = 3, so that s_1 = 1 − s_0 = 0.125. The constant p_O follows directly as (log 0.125 − log 0.875)/(log 1.977 − log 2.917) = 5.0. The combination s_0 = 0.875 and p_O = 5.0 fits the observed data for the orthorhombic oxide (see below), within limits of error. For Sb–Cl, p_{Cl} = 6.0 is self-consistent throughout this table.

(b) Agreement for known structures:

Compound	Ref.	Distances/Å	Bond strengths
(i) Structure with only Sb–O bonds [$s_O = s_0(R/R_0)^{-5.0}$]:			
Sb_2O_3(orthorhombic)	20	3×R(Sb–O) at 2.01(av) 1×R(Sb–O) at 2.519 1×R(Sb–O) at 2.618	$3s_O$ = 2.42 s_O = 0.26 s_O = 0.21 $\Sigma N_O s_O$ = 2.9(3.0)[b]
(ii) Structure with Sb–O and Sb–Cl bonds:			
$SbCl_3 \cdot 15$-crown-5	6	5×R(Sb–O) at 2.89 3×R(Sb–Cl) at 2.42	$5s_O$ = 0.66 $3s_{Cl}$ = 2.47 $\Sigma N_i s_i$ = 3.1(3.0)[b]

(c) Agreement from EXAFS parameters:

Compound	Ref.	Distances/Å	Bond strengths
$SbCl_3 \cdot 12$-crown-4	This work	4×R(Sb–O) at 2.85 3×R(Sb–Cl) at 2.41	$4s_O$ = 0.56 $3s_{Cl}$ = *2.47* $\Sigma N_i s_i$ = 3.0(3.0)[b]

[a]With p_{Cl} = 6.0 and p_O = 5.0; distances in Å. [b]Theoretical values in parentheses.

For the antimony(III) crown ether complexes for which we are interested in examining the variation of coordination numbers as well as the lengths of the bonds, the equations were used this time as as an aid in constraining the least-squares refinements but more as a means of checking the consistency of the results. This was achieved by considering the total coordination number ΣN_i of the samples, as well as the bond lengths $R(\text{Sb–Cl})$ and $R(\text{Sb–O})$, as independent variables. The dependent parameters, which include s_{Cl} and s_O, are then calculated from the refined bond lengths by substituting the s_0, R_0 and p values of Table 2 into the relationship of Brown and Shannon. Also dependent are the individual coordination numbers N_{Cl} and N_O because $N_{Cl} = \Sigma N_i - N_O$. This allows us to recast eqn. (3) into the form of eqn. (4), leading to eqn.

$$(N_i - N_O)s_{Cl} + N_O s_O = 3.00 \tag{4}$$

$$N_O = (3.00 - s_{Cl}\Sigma N_i)/(s_O - s_{Cl}) \tag{5}$$

(5). Table 2 shows that extracting structural information from the EXAFS spectrum for the $\text{SbCl}_3\cdot12\text{-crown-4}$ complex by means of the model compound (the $\text{SbCl}_3\cdot15\text{-crown-5}$ complex) yields results that are fully consistent with the method based on the relationship of Brown and Shannon.

The results of this EXAFS study show that the antimony atom in $\text{SbCl}_3\cdot12\text{-crown-4}$ is sandwiched between a three-membered ring of chlorines on one side and a four-membered oxygen-grouping, $(O)_4$, of the ether on the other; similar environments have been observed[6,7] for the bismuth atoms in $\text{BiCl}_3\cdot15\text{-crown-5}$ and $\text{BiCl}_3\cdot18\text{-crown-6}$ with $(O)_5$ and $(O)_6$ groupings, respectively, as well as for the model compound's $(O)_5$ grouping.

Indeed, both antimony structures can be compared to the above-mentioned $\text{Sn}(15\text{-crown-5})_2^{2+}$ cation, in which the two parallel $(O)_5$ groupings also form a sandwich; the non-stereochemical nature of the tin lone pair imposed by the centre of symmetry in this complex makes the comparison particularly interesting for the present structures because the symmetry of the antimony sites does not make the same imposition. Further discussion on the structure and bonding implications is curtailed here because the detailed discussions that are available in Refs 4 and 6 can be extended to the present situation.

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