Crown Thioether Complexes of p-Block Elements: Crystal and Molecular Structures of $SbCl_3 \cdot 9S3$ (9S3 = 1,4,7-trithiacyclononane) and $2SbCl_3 \cdot 18S6$ (18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane)

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The first crown thioether complexes of Sb^{III} and Bi^{III}, as representative p-block elements, have been isolated, *viz* $SbCl_3 \cdot 9S3$ **1**, $BiCl_3 \cdot 9S3 \cdot 0.5$ MeCN, $SbCl_3 \cdot 15S5$, $2SbCl_3 \cdot 18S6$ **2** and $BiCl_3 \cdot 18S6$;† X-ray crystal structure determinations of **1** and **2** establish full participation of ligand S-donor sites in metal · · · sulphur bonding in each case.

The ready ability of crown thioethers to bind metal ions provides simple and direct access to *S*-macrocyclic complexes of beguiling variety.[1] Most of the attention paid to these compounds has focused on transition metals (first-, second- and third-row) and the more familiar thioether ligands 9S3, 12S3, 14S4 and 18S6, which show a marked preference for the lower oxidation states of metal ions.[1,2] In this communication we describe the synthesis and X-ray structural characterisation of novel group Vb (15) crown thioether complexes incorporating $SbCl_3$ and $BiCl_3$ as exemplars of the p-block elements. Our interest in such compounds follows from recent studies of the complexation profile of MCl_3 (M = As, Sb, Bi) with the oxygen-containing crown ethers 12-crown-4, 15-crown-5 and 18-crown-6 where, with one exception, neutral adducts of the type $MCl_3 \cdot$crown based on a half-sandwich structure have been identified.[3] We reasoned that observation of a similar pattern for the crown thioethers would allow a direct comparison of coordination parameters, interpretable in a simplistic approach as involving 'hard' (O) *vs.* 'soft' (S) ligands.

The complexes $SbCl_3 \cdot 9S3$ **1**, $BiCl_3 \cdot 9S3 \cdot 0.5$ MeCN, $SbCl_3 \cdot 15S5$, $2SbCl_3 \cdot 18S6$ **2** and $BiCl_3 \cdot 18S6$ have been isolated and established by satisfactory IR and ^1H and ^{13}C NMR spectroscopic results and microanalytical data. In a typical preparation, dropwise addition of an acetonitrile solution of 9S3 (0.26 g, 1.46 mmol) to an ice-cold solution of $SbCl_3$ (0.33 g, 1.46 mmol) in acetonitrile maintained under an inert atmosphere of N_2 results in a clear solution. Slow concentration of this solution provided needle crystals of **1** (0.44 g, 74%) directly suitable for diffraction studies.‡ In the case of **2**

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† 9S3 = 1,4,7-trithiacyclononane, 15S5 = 1,4,7,10,13-pentathiacyclopentadecane, 18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane.

‡ *Crystal data*: **1** $C_6H_{12}S_3 \cdot SbCl_3$, $M = 408.5$, orthorhombic, $P2_12_12_1$, $a = 7.733(3)$, $b = 10.241(4)$, $c = 16.329(5)$ Å, $U = 1293.1(6)$ Å^3, $Z = 4$, $D_c = 2.10$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.71069$ Å, μ(Mo-Kα) = 32.0 cm^{-1}, $T = 290$ K, $R = 0.033$ for 1181 unique observed $[I/\sigma(I) \geqslant 2.0]$ reflections. **2** $C_{12}H_{24}S_6 \cdot 2SbCl_3$, $M = 816.9$, triclinic, $P\bar{1}$ $a = 8.291(4)$, $b = 8.450(3)$, $c = 11.587(6)$ Å $\alpha = 98.69(4)$, $\beta = 102.29(4)$, $\gamma = 115.86(3)°$, $U = 685.8(6)$ Å^3, $Z = 1$, $D_c = 1.98$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.71069$ Å, μ(Mo-Kα) = 32.0 cm^{-1}, $T = 290$ K, $R = 0.038$ for 2006 unique observed $[I/\sigma(I) \geqslant 2.0]$ reflections.

Data collected with a Nicolet $P2_1$ four-circle diffractometer in ω-2θ mode to maximum 2θ of 50°, corrected for absorption (Gaussian method). Structure solution by Patterson methods. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07$ Å^2, and inserted at calculated positions and not refined. For **1**, the absolute structure of the individual crystal chosen was checked by refinement of a $\delta f''$ multiplier. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

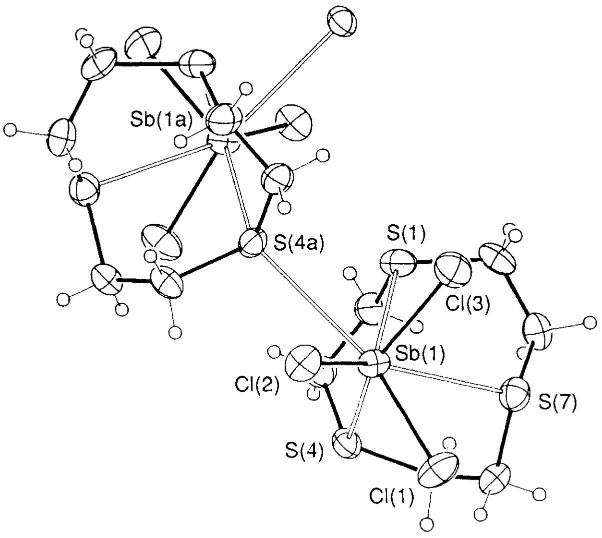

Fig. 1 Structure of $SbCl_3 \cdot 9S3$ **1** showing the atom numbering scheme. Distances are: Sb(1)–Cl (range) 2.374(3)–2.451(3); Sb(1)–S(1), 3.409(3), Sb(1)–S(4), 3.396(3), Sb(1)–S(7), 3.156(3), Sb(1)–S(4a), 3.171(3) Å.

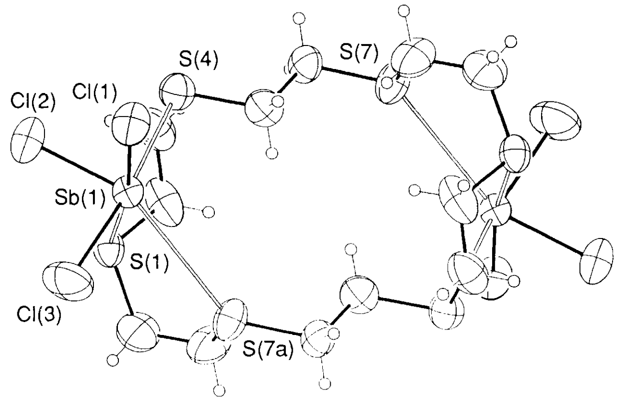

Fig. 2 Structure of $2SbCl_3 \cdot 18S6$ **2** showing the atom numbering scheme. Distances are: Sb(1)–Cl (range) 2.381(3)–2.471(2); Sb(1)–S(1), 2.968(2), Sb(1)–S(4), 3.061(3), Sb(1)–S(7a), 3.460(3) Å.

several recrystallisations from $MeCN-CH_2Cl_2$ at low temperature finally provided fine needle crystals.[‡] The ^1H and ^{13}C NMR spectroscopic data indicate fluxional species in solution: each complex shows a characteristic singlet for the $-CH_2-CH_2-$ backbone in the room temperature spectra (CD_3CN solution), *e.g.* for $SbCl_3 \cdot 15S5$, δ 2.77 and δ 33.26 (δ32.50, singlet, at 233 K) respectively. In the IR spectra broad bands characteristic of metal–halogen stretching modes dominate the far-IR region (400–200 cm^{-1}), *e.g.* for $SbCl_3 \cdot 15S5$ ν(Sb–Cl) 263, 291, 312 cm^{-1}.

In both complexes, **1** (Fig. 1) and **2** (Fig. 2), the Sb atoms are weakly coordinated to the sulphur atoms with Sb–S distances in the range 2.968(2)–3.460(3) Å. The Sb–Cl distances in **1** [2.374(3)–2.451(3)] and **2** [2.381(3)–2.471(2) Å] are similar to those of the pyramidal core unit in crystalline $SbCl_3$ itself [2.340(2) and 2.368(1) Å (2)].[4] In **2** the antimony centres are six coordinate with each of the three crown sulphur atoms *trans* to a chlorine atom in an irregular *fac*-octahedral array. One of the trio of sulphur atoms is noticeably further away from the metal centre [Sb(1)–S(7a) 3.460(3) Å] than the other two [2.968(2), 3.061(3) Å]. A similar [2 + 1] Sb–S bonding mode has been noted in $SbCl_3(EtNH \cdot CS \cdot CS \cdot NHEt)_{1.5}$[5] and $SbCl_3(S_2C_5H_{10})$[6] ($S_2C_5H_{10}$ = 1,4-dithiacycloheptane) suggesting that this is a stable geometry for Sb^{III}. In **1** the metal centres adopt a completely different stereochemistry and there is a chain structure; each $SbCl_3$ unit is irregularly bound to the three sulphur donors of one 9S3 crown [Sb–S 3.409(3), 3.396(3) and the much shorter 3.156(3) Å] and to a further sulphur from an adjacent ring *viz*, seven coordinate Sb^{III} embraced by two crown rings. Remarkably the intermolecular distance Sb(1)–S(4a), 3.171(3) Å, which produces the chain structure in the crystal is one of the shortest (mean, Sb–S 3.283 Å). As a general comparison the Sb–S distances (above) are quite similar to the Sb–O distances in the analogous $SbCl_3$·crown ether complexes, *e.g.* $SbCl_3 \cdot$12-crown-4 (2.66–2.98 Å), $SbCl_3 \cdot$15-crown-5 (2.79–3.00 Å) and $SbCl_3 \cdot$18-crown-6·MeCN (2.99–3.40 Å) indicating a relative order of binding thiocrown > oxa-crown.

The various group Vb–crown thioether complexes discussed above represent an important extension of the coordination chemistry of macrocyclic polythioethers into the p-block domain.

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