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Coordination networks derived from antimony(III) halide complexes with thio- and seleno-ether ligation

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Antimony(III) halides form highly unusual infinite one- or two-dimensional networks when coordinated to dithio- or diseleno-ether ligands or macrocyclic selenoethers. The structures adopted are contrasted with those observed for related bismuth(III) species.

We have been interested for some time in the coordination chemistry of group 16 donor ligands. The vast majority of compounds involving thio-, seleno- or telluro-ether coordination incorporate d-block elements.[1] Also, we have shown that σ-donation towards low valent metal centres increases significantly as group 16 is descended.[2] However, there are relatively few examples of complexes involving p-block elements with these ligands. We have therefore extended our work to investigate the interaction of thio-, seleno- and telluro-ether ligands with p-block metalloids. These elements exhibit very different electronic environments compared to d-block elements and π-bonding effects are unimportant. Specifically in this communication we report the synthesis and structural characterisation of three antimony(III) halide complexes involving group 16 donor ligands, including the first examples containing selenoether ligation. Antimony(III) thioether complexes are rare, the only structurally characterised examples being [$SbCl_3$(1,4-dithiacycloheptane)], [$(SbI_3)_2$(1,4-dithiane)], [SbX_3([9]aneS_3)] (X = Cl or I) and [$(SbCl_3)_2$([18]aneS_6)] ([18]aneS_6 = 1,4,7,10,13,16-hexathiacyclooctadecane).[3]

Reaction of $SbBr_3$ with 1 mol equiv. of the dithioether $MeS(CH_2)_3SMe$ in anhydrous MeCN solution yields a pale yellow solid of empirical formula [$SbBr_3\{MeS(CH_2)_3SMe)\}$].† Crystals were obtained by slow evaporation from a solution of the compound in MeCN. The structure shows (Fig. 1)‡ that this species adopts a two-dimensional sheet array derived from distorted octahedral Sb(III) centres coordinated to three mutually *fac* terminal Br ligands and three S-donor atoms from different dithioether ligands, two of which, S(1) and S(1*), may be regarded as μ-bridging since they also form weak interactions to an adjacent Sb centre. While the Sb–Br distances are normal for primary Sb–Br ligation, the Sb–S distances are *ca.* 3.2 Å, suggesting secondary interactions. The second sulfur in each dithioether coordinates to a nearby, symmetry-related Sb centre to generate the infinite array. The *cis* angles at Sb lie in the range 80.3(1)–104.49(7)° and the angle at the bridging thioether, S(1), is 104.4(7)°. The Sb–S distances reported for known Sb(III) thioether species span a considerable range, *e.g.* in [SbX_3([9]aneS_3)], X = Cl (chain structure with seven-coordinate Sb) has *d*(Sb–S) = 3.156(3)–3.409(3), while X = I (discrete monomer with distorted octahedral Sb and *fac* [9]aneS_3) gives *d*(Sb–S) = 2.840(2)–2.895(2) Å, while for [$(SbI_3)_2$(1,4-dithiane)] (infinite chain with five-coordinate Sb} *d*(Sb–S) = 3.274 and 2.336 Å.[3] The Sb–S distances in our complex are comparable with those above.

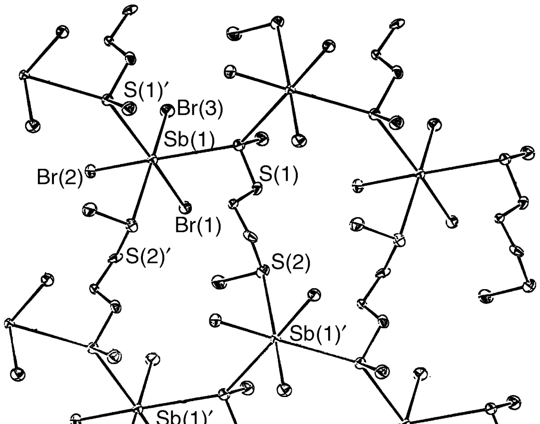

Fig. 1 View of a portion of the two-dimensional structure of [$SbBr_3\{MeS(CH_2)_3SMe\}$] with the atom numbering scheme. Selected bond lengths (Å): Sb–Br(1) 2.572(2), Sb–Br(2) 2.503(2), Sb–Br(3) 2.575(2), Sb–S(1) 3.253(5), Sb–S(2*) 3.155(5), Sb–S(1*) 3.291(5).

The selenoether analogue [$SbCl_3\{MeSe(CH_2)_3SeMe\}$] was obtained similarly,† although this species is rather less stable, turning black over a period a few days even when stored in a N_2 purged dry-box. The structure of this complex (Fig. 2)‡ is markedly different from the thioether analogue above, adopting an infinite one-dimensional chain. The Sb centres exhibit a distorted octahedral coordination environment comprising two *cis* terminal Cl, two μ-Cl and two mutually *cis* Se atoms from different diselenoethers. Thus the chains are derived from weakly associated, asymmetric Sb_2Cl_6 units linked by bridging diselenoether ligands, Sb–Cl(2) 2.451(3), Sb–Cl(2*) 3.236(3) Å. Indeed, the Sb–Cl(2) distance is very similar to the terminal Sb–Cl(1) and Sb–Cl(3) distances, with a weak secondary Sb–Cl(2*) interaction. The Sb–Se distances of *ca.* 3.2 Å are very similar to the Sb–S distances in the dithioether species above, again suggesting rather weak, secondary interactions.

The coordination of Sb(III) to the tetraselenoether macrocycle [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane) was also probed to investigate the effect of the constrained cyclic ligand,

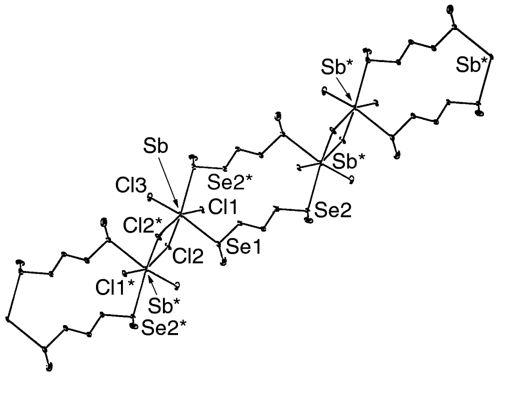

Fig. 2 View of a portion of the one-dimensional structure adopted by [$SbCl_3\{MeSe(CH_2)_3SeMe\}$] with the atom numbering scheme. Selected bond lengths (Å) and angles (°): Sb–Cl(1) 2.388(3), Sb–Cl(2) 2.451(3), Sb–Cl(3) 2.424(3), Sb–Cl(2*) 3.236(3), Sb–Se(1) 3.204(2), Sb–Se(2) 3.244(2) Å; Cl(2)–Sb–Cl(2*) 76.8(1).

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while retaining the trimethylene linkage between the donor atoms. Reaction of $SbBr_3$ with [16]aneSe_4 in MeCN affords a yellow powder of stoichiometry [$(SbBr_3)_2$([16]aneSe_4)].† The crystal structure of this species shows (Fig. 3)‡ a two-dimensional sheet array derived from [16]aneSe_4 molecules coordinated in an exocyclic configuration to four Sb centres each of which bridge to another selenacrown. The geometry at Sb can be described as five-coordinate *via* primary interactions to three *fac* terminal Br and secondary interactions to two *cis* Se atoms from different macrocycles to give a distorted square-pyramidal coordination environment. The Sb–Se distances in [$(SbBr_3)_2$([16]aneSe_4)] are shorter than those in [$SbCl_3${MeSe$(CH_2)_3$SeMe}] above, although this may be due to the lower coordination number at Sb in the former. The weak Sb–Se interactions in these systems are considerably longer than normal Sb–Se bond distances in, for example, [$Sb(SeMe)_3$] which average 2.580 Å.[4]

The main features which these new compounds have in common are the retention of the pyramidal SbX_3 unit observed in the parent antimony trihalide[5] and the occurrence of weak, secondary Sb–S or Sb–Se interactions on the opposite face which leads to the S or Se atoms occupying mutually *cis* coordination sites.

The very low solubilities exhibited by the new compounds, presumably associated with their polymeric nature, has severely hindered attempts to obtain solution NMR spectra, however the IR spectra show features associated with coordinated dithio- or diseleno-ether and ν(Sb–X).

Surprisingly, the structures of the three new antimony species are each quite different from their bismuth(III) analogues. The thioether compound [Bi_4Cl_{12}{MeS$(CH_2)_3$SMe}$_4$]·H_2O forms a three-dimensional open-framework lattice incorporating pseudo-cubane Bi_4Cl_{12} units linked by bridging dithioether ligands, while [$BiBr_3${MeE$(CH_2)_3$EMe}] (E = S or Se) and [$BiCl_3${MeSe$(CH_2)_3$SeMe}] all adopt an infinite two-dimensional sheet array derived from planar Bi_2X_6 units linked by bridging dithio- or diseleno-ether ligands. Finally, [$BiBr_3$([16]aneSe_4)] adopts a one-dimensional ladder structure derived from almost planar Bi_2Br_6 'rungs', which are linked by bridging [16]aneSe_4 'uprights', leaving two mutually *trans* Se atoms within each crown uncoordinated.[6] These differences are unexpected given the subtle change from Bi(III) to Sb(III) and serve to extend further the diverse range of structures identified for thio- and seleno-ether complexes with p-block elements.

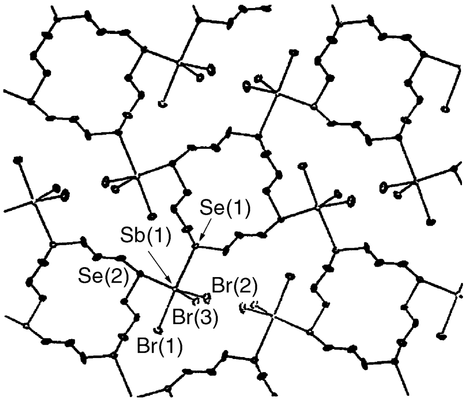

Fig. 3 View of a portion of the two-dimensional sheet adopted by [$(SbBr_3)_2$([16]aneSe_4)] with the atom numbering scheme. Selected bond lengths (Å) and angles (°) Sb–Br(1) 2.687(1), Sb–Br(2) 2.537(1), Sb–Br(3) 2.601(1), Sb–Se(1) 2.989(1), Sb–Se(2*) 3.193(1) Å; Se(1)–Sb–Se(2*) 82.55(3).

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Notes and references

† Satisfactory elemental analyses and IR spectroscopic data were obtained for the new compounds.

‡ Colourless {or yellow: [$(SbBr_3)_2$([16]aneSe_4)]} crystals were obtained by slow evaporation from a solution of the appropriate compound in MeCN. X-Ray crystallographic data were collected on a Rigaku AFC7S four-circle diffractometer, T = 150 K. Structure solution and refinement were routine.[7–10]

Crystal data: for [$SbBr_3${MeS$(CH_2)_3$SMe}]: $C_5H_{12}Br_3S_2Sb$, M = 497.73, orthorhombic, space group $Pna2_1$, a = 14.105(2), b = 9.446(1), c = 9.781(1) Å, V = 1303.2(3) Å^3, Z = 4, D_c = 2.537 g cm^{-3}, μ(Mo-Kα) = 116.11 cm^{-1}. 1364 unique reflections of which 1022 with $F > 4\sigma(F)$ were used in all calculations. Final R = 0.041, R_w = 0.049.

For [$SbCl_3${MeSe$(CH_2)_3$SeMe}]: $C_5H_{12}Cl_3SbSe_2$, M = 458.18, monoclinic, space group $P2_1/c$, a = 9.622(5), b = 12.882(3), c = 10.376(4) Å, β = 101.89(4)°, V = 1258.5(8) Å^3, Z = 4, D_c = 2.418 g cm^{-3}, μ(Mo-Kα) = 85.59 cm^{-1}. 2344 unique reflections of which 1934 with $F > 4\sigma(F)$ were used in all calculations. Final R = 0.041, R_w = 0.053.

For [$(SbBr_3)_2$([16]aneSe_4)]: $C_{12}H_{24}Br_6Sb_2Se_4$, M = 1207.08, monoclinic, space group $P2_1/n$, a = 10.276(2), b = 13.340(3), c = 10.755(2) Å, β = 113.71(1)°, V = 1370.1(4) Å^3, Z = 2, D_c = 2.926 g cm^{-3}, μ(Mo-Kα) = 160.58 cm^{-1}. 2536 unique reflections of which 1724 with $F > 4\sigma(F)$ were used in all calculations. Final R = 0.035, R_w = 0.039.

CCDC 182/1865. See http://www.rsc.org/suppdata/cc/b0/b007805k/ for crystallographic files in .cif format..

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