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Synthesis and structural properties of the first bismuth(III) telluroether complex

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The first donor–acceptor complexes of Sb(III) and Bi(III) with telluroether ligands are reported, together with the crystal structure of [BiBr$_3$(PhTeMe)].

Recently we have reported on a new series of main group coordination complexes involving Group 15 trihalides (MX$_3$, M = As, Sb, Bi; X = Cl, Br, I) with polydentate and macrocyclic thio- and seleno-ether ligands.[1–4] Within this class of compounds several unprecedented structural motifs have been characterised, the precise nature of which is apparently determined by a combination of primary and secondary bonding interactions and the degree of influence of the M-based lone pair of electrons. Highlights include the discrete 4 : 1 species [(AsCl$_3$)$_4$([24]aneSe$_6$)] ([24]aneSe$_6$ = 1,5,9,13,17,21-hexaselenacyclotetracosane)[3] where a weakly associated Cl$_2$-As(μ-Cl$_2$)AsCl$_2$ dimer unit lies within the ring and two AsCl$_3$ units lie *exo*, and [BiCl$_3${MeS(CH$_2$)$_3$SMe}] which contains pseudo-cubane Bi$_4$Cl$_4$ core units linked by bridging dithioethers into a 3-D network and containing large channels.[4] In view of the gross structural variations which occur through subtle modifications of the reagents or conditions, we were interested to examine the reactions of the heavier telluroether ligands with these Group 15 acceptors.

In general, telluroether chemistry is hampered by difficulties in the formation of Te–C linkages and their susceptibility to elimination of the organic units giving ditellurides and elemental tellurium.[5] Coordination to transition metal fragments, especially in high oxidation states, also tends to promote decomposition *via* reduction and dealkylation. At present their coordination chemistry is almost exclusively associated with middle to late transition metal ions in low or medium oxidation states, although it is clear that telluroether ligands are better σ-donors to low valent transition metals than their thio- or seleno-ether analogues.[6]

In terms of the p-block, the only examples of telluroether complexes are with SnX$_4$ (X = Cl or Br) and two examples, *cis*-[SnX$_4${*o*-C$_6$H$_4$(TeMe)$_2$}], have been structurally authenticated revealing distorted octahedral geometries.[7]

We have investigated the reactions of various MX$_3$ (M = As, Sb, Bi; X = Cl, Br, I) with MeTe(CH$_2$)$_3$TeMe in anhydrous MeCN solution (or thf for X = I). We were unable to isolate any solids from the As(III) reactions (probably owing to the poor Lewis acidity of AsX$_3$), however, using Sb and Bi salts allowed us to isolate orange–brown, analytically pure samples of a limited set of compounds, [SbX$_3${MeTe(CH$_2$)$_3$TeMe}] (X = Br or I), [BiCl$_3${MeTe(CH$_2$)$_3$TeMe}] and [BiBr$_3$(PhTeMe)] in modest to good yields.† These are the first examples of antimony and bismuth telluroether species, and, other than the tellurolate compounds [M{TeSi(SeMe$_3$)$_3$}$_3$] (M = Sb or Bi) synthesised by Arnold and co-workers,[8] they are the only known complexes involving Sb–Te or Bi–Te bonds.

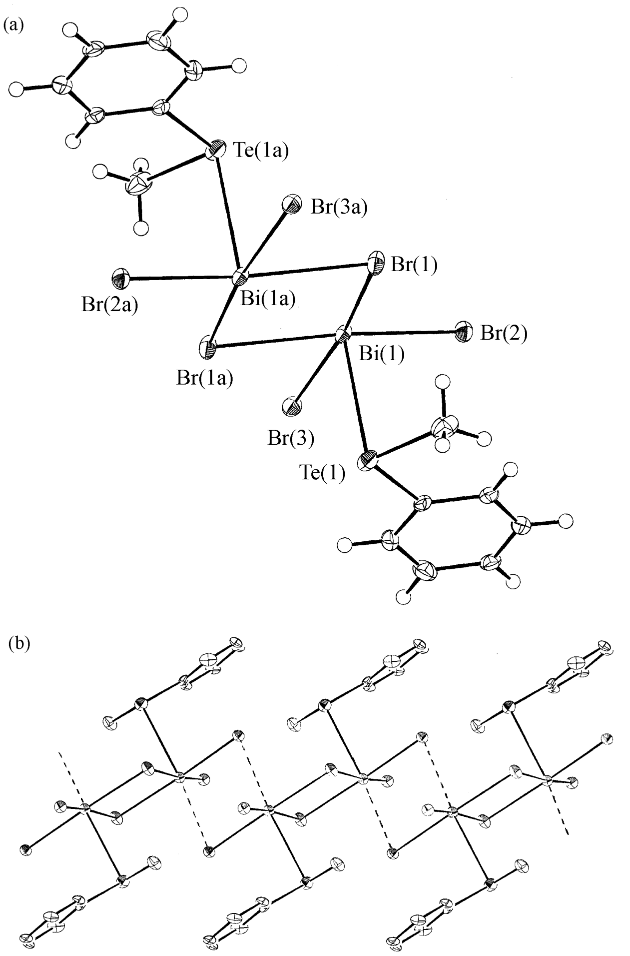

Fig. 1 (a) View of the crystal structure of the dimeric unit in [BiBr$_3$(PhTeMe)] with numbering scheme adopted. The symmetry related atoms Bi(1a) and Br(1a) are generated by the symmetry operation $1 - x, 1 - y, -z$. Ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (°): Bi(1)–Te(1) 3.0533(7), Bi(1)–Br(1) 2.8291(10), Bi(1)–Br(1a) 3.0810(10), Bi(1)–Br(2) 2.6497(9), Bi(1)–Br(3) 2.8570(9); Te(1)–Bi(1)–Br(1) 92.30(3), Te(1)–Bi(1)–Br(1a) 84.14(2), Te(1)–Bi(1)–Br(2) 90.92(2), Te(1)–Bi(1)–Br(3) 87.53(2), Br(1)–Bi(1)–Br(1a) 87.84(3), Br(1)–Bi(1)–Br(2) 92.45(3), Br(1)–Bi(1)–Br(3) 171.47(3), Br(1a)–Bi(1)–Br(2) 175.05(3), Br(1a)–Bi(1)–Br(3) 83.66(3), Br(2)–Bi(1)–Br(3) 96.08(3). (b) View of [BiBr$_3$(PhTeMe)] showing the interdimer Bi ··· Br contacts generating the infinite chains.

The isolated solids exhibit very poor solubility in chlorocarbons, MeCN and MeNO$_2$, hence severely hampering our attempts to obtain crystalline samples. We were however successful in obtaining red crystals of the compound [BiBr$_3$(PhTeMe)] by slow evaporation from an MeCN solution of BiBr$_3$ which had been layered with an equimolar solution of PhTeMe in CH$_2$Cl$_2$. The crystal structure‡ shows (Fig. 1a) a planar asymmetric Br$_2$Bi(μ-Br)$_2$BiBr$_2$ dimer unit with one PhTeMe ligand coordinated apically to each Bi and occupying mutually *anti* positions. Br(3) and Br(3b) form additional long contacts (3.16 Å) *via* the open Bi vertex and hence link adjacent units to give an infinite chain of Bi$_2$Br$_6$(PhTeMe)$_2$ dimers in a step-like arrangement (Fig. 1b). The Bi–(μ-Br) distances differ by *ca.* 0.25 Å, whereas in structurally related compounds such as the dianionic $[\mathrm{Bi_2I_8(SMe_2)_2}]$[2–9] and the selenacrown complex $[\mathrm{BiBr_3([16]aneSe_4)}]$ ($[16]\mathrm{aneSe_4}$ = 1,5,9,13-tetraselenacyclohexadecane)[2] the bridging halides are essentially symmetrical. The Bi centres in the present structure are therefore pseudo-octahedral and it seems likely that the Bi-based lone pair is probably directed out of the triangular face defined by Br(1a), Br(3) and Br(3b) *i.e.* involving the longer Bi–Br contacts.

The Bi–Te distance of 3.0533(7) Å indicates that this is a strong bond, only marginally longer than the sum of the covalent radii of the elements (2.89 Å). As these are the first structural data on a Bi–Te bonded species and there are no direct analogues with thio- or seleno-ether ligands, meaningful comparisons are difficult. However, the dianion $[\mathrm{Bi_2I_8(SMe_2)_2}]^{2-}$ in which the $\mathrm{SMe_2}$ ligands are also *anti* (but *trans* to I), shows d(Bi–S) = 3.054(8) Å[9] and $[\mathrm{BiBr_3([16]aneSe_4)}]$, which also contains a planar $\mathrm{Br_2Bi(\mu\text{-}Br)_2BiBr_2}$ unit (but mutually *trans* Se atoms)[2] gives d(Bi–Se) = 2.952(2) and 3.095(2) Å. Thus, the bismuth–chalcogen bond distances in these compounds are not significantly different from the title compound despite the much larger radius of Te *vs.* Se and S. The availability of bismuth telluroether complexes and the relatively strong Bi–Te bonds may indicate that such compounds could function as single source precursors to the thermoelectric material $\mathrm{Bi_2Te_3}$.[10]

The infinite structure identified for $[\mathrm{BiBr_3(PhTeMe)}]$ is unprecedented in Group 15 halide-chalcogenoether chemistry. Structurally the closest analogues are with phosphine and arsine ligands, *e.g.* the discrete dimer $[\mathrm{As_2Cl_6(AsEt_3)_2}]$,[11] the polymeric $[\mathrm{AsCl_3(PMe_3)}]$[10] and especially $[\mathrm{SbI_3(PMe_3)}]$[13] which shows a very similar packing arrangement within the crystal lattice.

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Notes and references

† $[\mathrm{SbBr_3\{MeTe(CH_2)_3TeMe\}}]$: To an anhydrous MeCN solution of $\mathrm{SbBr_3}$ (0.09 g, 0.25 mmol) was added an equimolar quantity of $\mathrm{MeTe(CH_2)_3TeMe}$ in MeCN. The resulting orange solution was stirred at RT for 30 min and then concentrated *in vacuo* to afford an orange powder which was filtered, washed with anhydrous $\mathrm{CH_2Cl_2}$ and dried *in vacuo*. Yield 74%. (Calc. for $\mathrm{C_5H_{12}Br_3SbTe_2}$: C, 8.7; H, 1.7. Found: C, 8.5; H, 1.9%).

$[\mathrm{SbI_3\{MeTe(CH_2)_3TeMe\}}]$: Procedure as above but using thf. Yield 82%. Red powder. (Calc. for $\mathrm{C_5H_{12}I_3SbTe_2}$: C, 7.2; H, 1.5. Found: C, 7.2; H, 2.1%).

$[\mathrm{BiCl_3\{MeTe(CH_2)_3TeMe\}}]$: Procedure as above and using MeCN. Yield 44%. Brown powder. (Calc. for $\mathrm{C_5H_{12}BiCl_3Te_2}$: C, 9.3; H, 1.9. Found: C, 9.4; H, 2.1%).

$[\mathrm{BiBr_3(PhTeMe)}]$: Procedure as above. Yield 22%. Red–brown powder. (Calc. for $\mathrm{C_7H_8BiBr_3Te}$: C, 12.6; H, 1.2. Found: C, 12.3; H, 0.9%).

‡ Crystal data for $[\mathrm{BiBr_3(PhTeMe)}]$: $\mathrm{C_7H_8BiBr_3Te}$ (M_r = 668.43), monoclinic, $P2_1/n$, a = 8.4820(2), b = 6.7592(2), c = 22.5808(8) Å, β = 100.6760(10)°, V = 1272.18(6) Å^3, Z = 4, D_c = 3.490 g cm^{-3}, μ(Mo-Kα) = 25.486 cm^{-1}, T = 120 K, R = 0.039, R_w = 0.037 for 109 parameters against 2144 reflections with $I > 2\sigma(I)$ out of 2956 unique reflections. Structure solution and refinement were routine.[14–16] CCDC reference number 194426. See http://www.rsc.org/suppdata/dt/b2/b209321a/ for crystallographic data in CIF or other electronic format.

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