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FULL PAPER

Synthesis and structures of bismuth(III) complexes involving thio- and seleno-ether ligands

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Bismuth trihalides (BiX_3, X = Cl, Br or I) reacted with a range of thio- and seleno-ether ligands L–L in anhydrous MeCN solution to yield compounds with either a 1:1, 1:2 or 2:1 Bi:L–L ratio. Structural studies on $[BiBr_3\{MeE(CH_2)_3EMe\}]$ (E = S or Se) and $[BiCl_3\{MeSe(CH_2)_3SeMe\}]$ revealed that all of these species adopt an infinite two-dimensional sheet array derived from planar Bi_2X_6 units linked by bridging dithio- or diseleno-ether ligands which occupy mutually *trans* co-ordination sites, giving a distorted octahedral geometry at Bi^{III}. The structure of $[BiBr_3\{MeS(CH_2)_2SMe\}_2]$ reveals a discrete molecular compound which adopts a 7-co-ordinate distorted pentagonal bipyramidal geometry involving two chelating $MeS(CH_2)_2SMe$ ligands. This arrangement is also found for the iodide analogue. Reaction of $BiBr_3$ with the Ph-substituted ligand $PhS(CH_2)_2SPh$ generated a very different structural arrangement in which chains of almost mutually orthogonal Bi_2Br_2 'rectangles' are cross-linked by bridging dithioether ligands to yield infinite sheets of formula $[Bi_2Br_6\{PhS(CH_2)_2SPh\}]$. With the tripodal ligands L^3 ($MeC(CH_2SMe)_3$ or $MeC(CH_2SeMe)_3$) compounds of stoichiometry $[BiX_3(L^3)]$ were obtained. The crystal structure of $[BiCl_3\{MeC(CH_2SeMe)_3\}]$ shows Bi_2Cl_6 subunits linked by bridging selenoether ligands to give a two-dimensional sheet. Each selenoether tripod functions as a bidentate chelate to Bi and bridges to an adjacent Bi *via* the third Se-donor, giving a distorted octahedral geometry at Bi^{III}. Although a rather poor quality structure, $[Bi_2I_6\{MeC(CH_2SeMe)_3\}_2]$ is not isostructural with its chloro analogue, but shows discrete dimers formed *via* Bi_2I_6 subunits, with each Bi also co-ordinated to a bidentate Se tripod and two terminal I ligands. The third Se-donor on each ligand remains non-co-ordinating. The influence of the Bi-based lone pair on the structures adopted by these complexes is discussed.

Introduction

While the chemistry of acyclic and macrocyclic thio- and seleno-ether ligands with d-block elements has received considerable attention over the last 15 years or so, derivatives of the p-block elements are much less well known. To some extent this may be attributed to the absence of good spectroscopic probes through which to monitor the chemistry, although the more labile nature of the p-block elements (compared certainly to the 4d and 5d metal complexes) may be expected to lead to very different co-ordinating characteristics. We recently reported the preparation and crystal structure of a highly unusual open-framework lattice, $[Bi_4Cl_{12}\{MeS(CH_2)_3SMe\}_4]\cdot H_2O$, incorporating pseudo-cubane Bi_4Cl_{12} units linked by bridging dithioether ligands to yield an infinite three dimensional array with large open channels.[1] We have now extended this work to investigate the interaction of bismuth(III) halides with a wider variety of thioether and also selenoether ligands. In this paper we report the synthesis and characterisation of a range of new bismuth(III) co-ordination compounds with these ligand types, including the crystal structures of $[BiBr_3\{MeS(CH_2)_3SMe\}]$, $[BiCl_3\{MeSe(CH_2)_3SeMe\}]$, $[BiBr_3\{MeSe(CH_2)_3SeMe\}]$, $[BiBr_3\{MeS(CH_2)_2SMe\}_2]$, $[Bi_2Br_6\{PhS(CH_2)_2SPh\}]$, $[BiCl_3\{MeC(CH_2SeMe)_3\}]$ and $[Bi_2I_6\{MeC(CH_2SeMe)_3\}_2]$.

There are no structurally characterised examples of bismuth(III) selenoether compounds, and examples of thioether derivatives are limited to $[Bi_4Cl_{12}\{MeS(CH_2)_3SMe\}_4]\cdot H_2O$ reported by us,[1] $[Me_3S]_2[Bi_2I_8(Me_2S)_2]$,[2] and a small number of macrocyclic thioether complexes including $[BiCl_3([12]aneS_4)]$, $[BiCl_3([15]aneS_5)]$, $[BiCl_3([18]aneS_6)]$ and $[(BiCl_3)_2([24]aneS_8)]$ ($[12]aneS_4$ = 1,4,7,10-tetrathiacyclododecane, $[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane, $[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane, $[24]aneS_8$ = 1,4,7,10,13,16,19,22-octathiacyclotetracosane).[3–5] It is significant that within the series of thiacrown complexes only one structural type is observed, *viz.* the structure is based on the arrangement identified in the parent $BiCl_3$[6] where the pyramidal $BiCl_3$ unit is retained, but the five weak, secondary Bi···Cl interactions are replaced by four, five or six weak, secondary Bi···S interactions of *ca.* 3.2 Å.[3–5] In these thiacrown species the weak thioether interactions form around the direction of the Bi-based lone pair. Similarly for crown ether and polyethylene glycol derivatives of BiX_3, the pyramidal BiX_3 unit is typically retained with the O-donor ligand capping the other face and giving weak Bi···O interactions,[7] although there are also examples of ether complexes of Bi^{III} in which Bi_2X_6 dimer units co-ordinate to the ether O-donors.[8] The only structurally characterised species involving Bi–Se bonds are the selenocyanate derivative, $[Bi(SeCN)_6]^{3-}$ (Bi–Se 2.881(3)–2.986(2) Å),[9] the selenobismuthate $[NEt_4][BiSe_2]$ (Bi–Se 2.590(5)–3.207(5) Å)[10] and $Ph_2BiSePh$ (Bi–Se 2.704(3) Å).[11]

Results and discussion

A range of compounds of stoichiometry $[BiX_3(L\text{–}L)_2]$ (X = Cl, Br or I; L–L = $MeS(CH_2)_2SMe$), $[Bi_2X_6\{PhS(CH_2)_2SPh\}]$ (X = Cl or Br), $[BiX_3(L\text{–}L)]$ (L–L = $MeE(CH_2)_3EMe$ (E = S or Se) or $MeSe(CH_2)_2SeMe$) and $[BiX_3(L^3)]$ (L^3 = $MeC(CH_2SMe)_3$ or $MeC(CH_2SeMe)_3$) have been isolated from reaction of BiX_3 with L–L or L^3 in dry MeCN solution. The solid thioether complexes are relatively stable to moist air, whereas the selenoether complexes turn to black, viscous materials over a few weeks even when stored in a N_2-purged dry-box. Microanalytical data consistent with these formulations were obtained for all freshly prepared solids. The IR spectra of the chloro derivatives

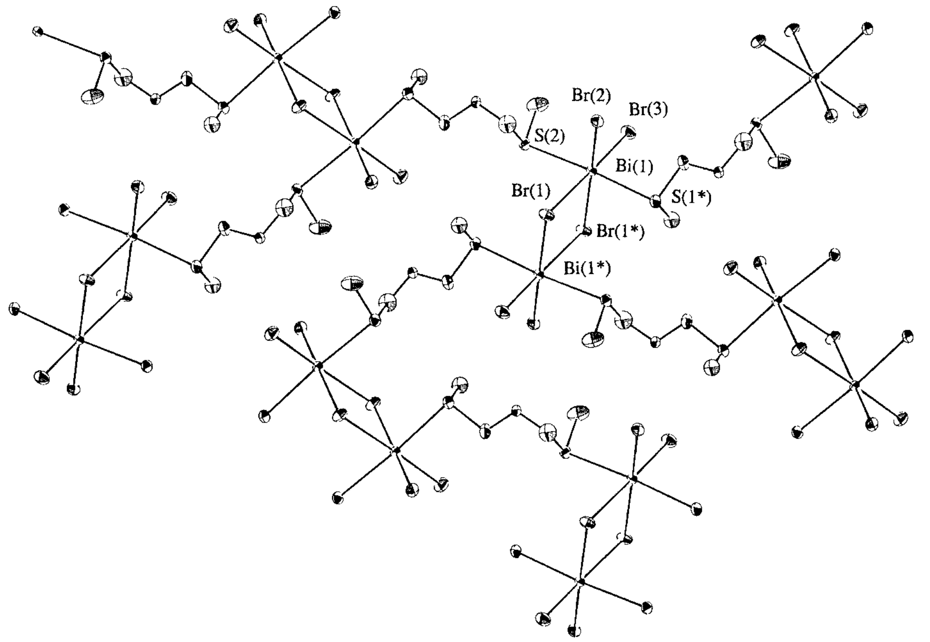

Fig. 1 View of a portion of the structure of [$BiBr_3${$MeS(CH_2)_3SMe$}] with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level in each figure.

show up to three peaks in the range 230–280 cm^{-1} assigned to ν(Bi–Cl); these compare to values of 242 and 288 cm^{-1} for the parent species, $BiCl_3$.[12] The very poor solubility of these compounds in non-co-ordinating solvents severely hindered attempts to obtain meaningful ^1H and ^{77}Se-{^1H} NMR spectra. Similar reaction of $BiCl_3$ with $MeSCH_2SMe$ gave a yellow solution, however we were unable to isolate a solid from this. Also, reaction of $BiCl_3$ with the ditelluroethers $MeTe(CH_2)_3TeMe$ and *o*-$C_6H_4(TeMe)_2$ yielded brightly coloured solutions which decomposed rapidly under these reaction conditions.

Crystallographic studies

In view of the lack of good spectroscopic probes to establish the precise nature of the products, we have obtained single crystal X-ray analyses on several examples. A weakly diffracting crystal was obtained from a sample of composition [$BiBr_3${$MeS(CH_2)_3SMe$}]. The crystal structure of this shows (Fig. 1, Table 1) Bi_2Br_6 units linked by four different, bridging dithioether ligands to give an infinite two-dimensional sheet. The co-ordination geometry at Bi^{III} is a distorted octahedron derived from two terminal Br (2.697(2), 2.719(2) Å), two bridging Br (2.980(2), 3.004(2) Å) and two S-donors from mutually *trans* bridging thioether ligands (2.880(4), 2.931(4) Å). The Bi_2Br_6 units are planar and, although the bonds within the Bi_2Br_2 ring are somewhat asymmetric, there is a crystallographic inversion centre at the midpoint of this ring. The orientation of the bismuth lone pair is implied from the elongated Bi–μ-Br distances. Sawyer and Gillespie[13] have noted previously that the weak interactions form around the direction of the maximum electron density of the lone pair, but not directly over it. While the Bi–Br distances are comparable with those in related compounds, the Bi–S distances are shorter than those in the previously reported Bi–thioether macrocyclic complexes,[3–5] indicating stronger interactions in the compound described here. The structure adopted for this compound contrasts starkly with that of the chloro analogue, [Bi_4Cl_{12}{$MeS(CH_2)_3SMe$}$_4$]·H_2O, which we reported earlier, the crystals of which were obtained from CH_2Cl_2 solution.[1]

Table 1 Selected bond lengths (Å) and angles (°) for [$BiBr_3${$MeS(CH_2)_3SMe$}]

Bi(1)–Br(1)	3.004(2)	Bi(1)–Br(3)	2.697(2)
Bi(1)–Br(1*)	2.980(2)	Bi(1)–S(1)	2.880(4)
Bi(1)–Br(2)	2.719(2)	Bi(1)–S(2)	2.931(4)
Br(1)–Bi(1)–Br(1*)	83.80(5)	Br(1*)–Bi(1)–S(2)	88.35(9)
Br(1)–Bi(1)–Br(2)	90.16(5)	Br(2)–Bi(1)–Br(3)	93.53(6)
Br(1)–Bi(1)–Br(3)	175.18(6)	Br(2)–Bi(1)–S(1)	89.0(1)
Br(1)–Bi(1)–S(1)	94.4(1)	Br(2)–Bi(1)–S(2)	93.53(9)
Br(1)–Bi(1)–S(2)	82.74(9)	Br(3)–Bi(1)–S(1)	88.8(1)
Br(1*)–Bi(1)–Br(2)	173.40(5)	Br(3)–Bi(1)–S(2)	93.9(1)
Br(1*)–Bi(1)–Br(3)	92.64(6)	S(1)–Bi(1)–S(2)	176.1(1)
Br(1*)–Bi(1)–S(1)	88.8(1)		

Table 2 Selected bond lengths (Å) and angles (°) for [$BiCl_3${$MeSe(CH_2)_3SeMe$}]

Bi(1)–Se(1)	3.036(2)	Bi(1)–Cl(2)	2.566(4)
Bi(1)–Se(2)	2.988(2)	Bi(1)–Cl(3)	2.826(4)
Bi(1)–Cl(1)	2.554(4)	Bi(1)–Cl(3*)	2.884(4)
Se(1)–Bi(1)–Se(2)	173.19(4)	Se(2)–Bi(1)–Cl(3*)	86.97(9)
Se(1)–Bi(1)–Cl(1)	89.95(9)	Cl(1)–Bi(1)–Cl(2)	89.7(1)
Se(1)–Bi(1)–Cl(2)	97.3(1)	Cl(1)–Bi(1)–Cl(3)	90.3(1)
Se(1)–Bi(1)–Cl(3)	83.56(10)	Cl(1)–Bi(1)–Cl(3*)	172.2(1)
Se(1)–Bi(1)–Cl(3*)	92.57(9)	Cl(2)–Bi(1)–Cl(3)	179.1(1)
Se(2)–Bi(1)–Cl(1)	89.65(9)	Cl(2)–Bi(1)–Cl(3*)	97.3(1)
Se(2)–Bi(1)–Cl(2)	89.5(1)	Cl(3)–Bi(1)–Cl(3*)	82.6(1)
Se(2)–Bi(1)–Cl(3)	89.65(10)		

Crystals were also obtained from a 1 : 1 ratio of $BiCl_3$ and $MeSe(CH_2)_3SeMe$ in MeCN. The structure of this compound shows (Fig. 2, Table 2) a very similar two-dimensional sheet array to [$BiBr_3${$MeS(CH_2)_3SMe$}] above, with edge-shared bioctahedral Bi_2Cl_6 dimers linked by diselenoether ligands which bridge between staggered Bi_2Cl_6 units, with Bi–Se 3.036(2), 2.988(2) Å. The Se(1)–Bi–Se(2) angle is 173.19(4)°. The compound [$BiBr_3${$MeSe(CH_2)_3SeMe$}] (Fig. 3, Table 3) is isostructural with [$BiBr_3${$MeS(CH_2)_3SMe$}] above, with Bi–Se distances of 3.028(2) and 2.978(3) Å. These species represent the first structurally characterised bismuth(III) compounds involving selenoether co-ordination. Significantly, the Bi–Se distances in these compounds are shorter than (or, in some cases similar to) the Bi–S distances in the macrocyclic thioether complexes, *e.g.* [$BiCl_3$([15]aneS_5)] [*d*(Bi–S) = 3.146(4)–3.225(4) Å] and [$BiCl_3$([18]aneS_6)] [*d*(Bi–S) = 3.134(2)–3.313(2) Å].[3,4] This suggests that while the Bi–S interactions are described as weak, secondary interactions, those involving Se are considerably stronger, and presumably reflect the orientation of the

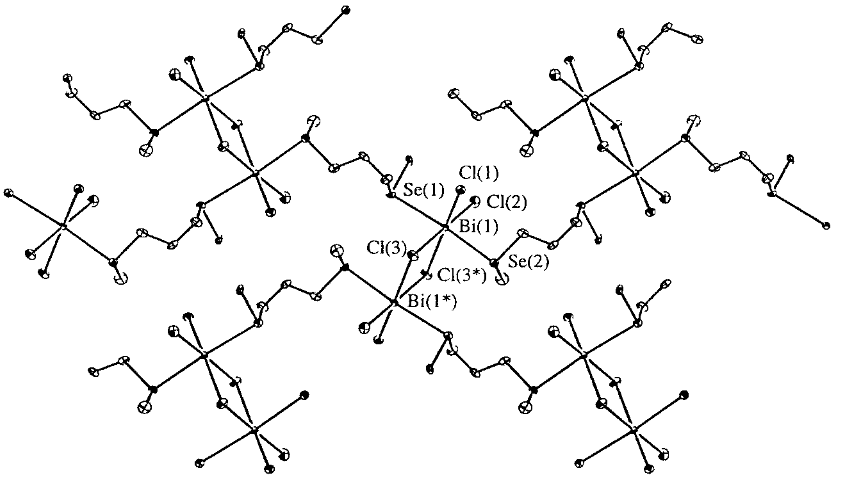

Fig. 2 View of a portion of the structure of [BiCl$_3${MeSe(CH$_2$)$_3$SeMe}] with the numbering scheme adopted.

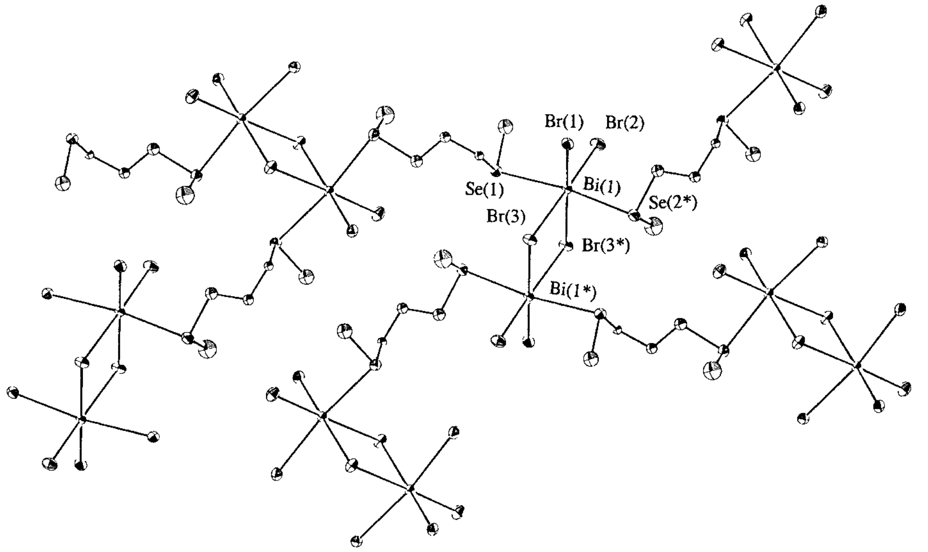

Fig. 3 View of a portion of the structure of [BiBr$_3${MeSe(CH$_2$)$_3$SeMe}] with the numbering scheme adopted.

Table 3 Selected bond lengths (Å) and angles (°) for [BiBr$_3${MeSe-(CH$_2$)$_3$SeMe}]

Bi(1)–Br(1)	2.723(2)	Bi(1)–Br(3*)	2.978(2)
Bi(1)–Br(2)	2.711(3)	Bi(1)–Se(1)	3.028(2)
Bi(1)–Br(3)	2.994(2)	Bi(1)–Se(2)	2.978(2)
Br(1)–Bi(1)–Br(2)	93.11(8)	Br(2)–Bi(1)–Se(2)	90.79(8)
Br(1)–Bi(1)–Br(3)	89.89(7)	Br(3)–Bi(1)–Br(3*)	83.42(7)
Br(1)–Bi(1)–Br(3*)	172.59(8)	Br(3)–Bi(1)–Se(1)	81.87(6)
Br(1)–Bi(1)–Se(1)	94.67(7)	Br(3)–Bi(1)–Se(2)	92.03(7)
Br(1)–Bi(1)–Se(2)	89.41(8)	Br(3*)–Bi(1)–Se(1)	87.56(6)
Br(2)–Bi(1)–Br(3)	175.91(8)	Br(3*)–Bi(1)–Se(2)	87.65(7)
Br(2)–Bi(1)–Br(3*)	93.74(7)	Se(1)–Bi(1)–Se(2)	172.64(7)
Br(2)–Bi(1)–Se(1)	95.10(7)		

bismuth lone pair which is towards the thioether ligand in the macrocyclic derivatives, but towards the bridging Br ligands in the compounds reported here. The Bi–Se distances are also within the sum of the formal ionic radii of Bi^{3+} and Se^{2-} (3.01 Å). The Bi–Cl distances are comparable with those in other related compounds.

Crystals were also obtained for the 1 : 2 Bi : dithioether compound, [BiBr$_3${MeS(CH$_2$)$_2$SMe}$_2$]. The structure of this species is quite different from those described above, showing (Fig. 4, Table 4) discrete mononuclear molecular units. In this case the bismuth(III) species is seven-co-ordinate and adopts a distorted pentagonal bipyramidal geometry. The donor set is derived from three terminal Br and four S-donors from two chelating dithioethers, with Bi–S 2.918(5)–3.090(5) Å. The Br ligands are arranged in an approximately meridional fashion, occupying the axial sites and one equatorial site, with the mutually *trans* Br ligands giving an angle of 164.63(7)° at Bi. Interestingly while one of the dithioether ligands adopts the *meso* form, the other takes the DL configuration. There is only one other structure where both invertomers occur in the same discrete molecule,

Table 4 Selected bond lengths (Å) and angles (°) for [BiBr$_3${MeS-(CH$_2$)$_2$SMe}$_2$]

Bi(1)–Br(1)	2.813(2)	Bi(1)–S(2)	3.090(5)
Bi(1)–Br(2)	2.826(2)	Bi(1)–S(3)	3.004(5)
Bi(1)–Br(3)	2.787(2)	Bi(1)–S(4)	2.918(5)
Bi(1)–S(1)	2.963(5)		
Br(1)–Bi(1)–Br(2)	98.86(7)	Br(2)–Bi(1)–S(2)	87.2(1)
Br(1)–Bi(1)–Br(3)	96.07(7)	Br(2)–Bi(1)–S(3)	77.4(1)
Br(1)–Bi(1)–S(1)	76.8.(1)	Br(2)–Bi(1)–S(4)	93.0(1)
Br(1)–Bi(1)–S(2)	146.3(1)	Br(3)–Bi(1)–S(1)	92.1(1)
Br(1)–Bi(1)–S(3)	145.2(1)	Br(3)–Bi(1)–S(2)	78.4(1)
Br(1)–Bi(1)–S(4)	73.1(1)	Br(3)–Bi(1)–S(3)	92.1(1)
Br(2)–Bi(1)–Br(3)	164.63(7)	Br(3)–Bi(1)–S(4)	94.5(1)
Br(2)–Bi(1)–S(1)	88.3(1)	S(1)–Bi(1)–S(2)	70.3(2)
S(1)–Bi(1)–S(3)	136.8(2)	S(1)–Bi(1)–S(4)	149.7(2)
S(2)–Bi(1)–S(3)	68.5(1)	S(2)–Bi(1)–S(4)	140.1(1)
S(3)–Bi(1)–S(4)	72.6(1)		

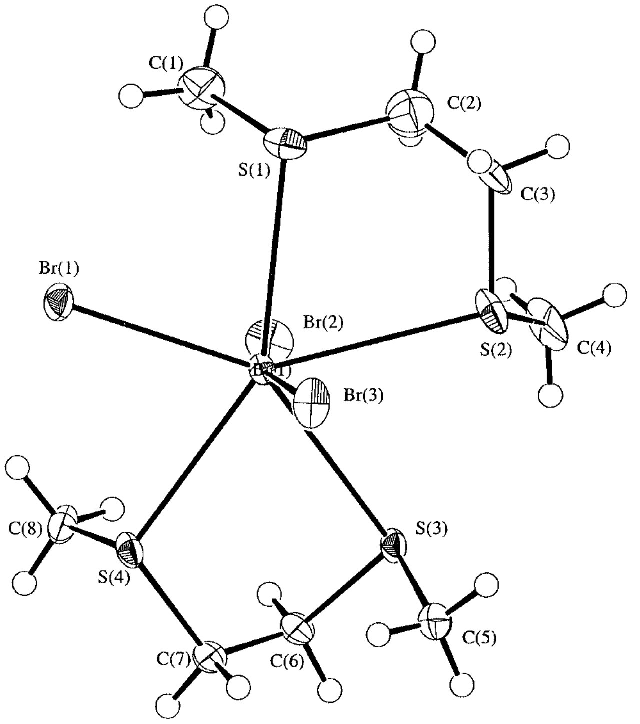

Fig. 4 View of the structure of $[BiBr_3\{MeS(CH_2)_2SMe\}_2]$ with the numbering scheme adopted.

$[RuCl(PPh_3)\{MeTe(CH_2)_3TeMe\}_2]PF_6$.[14] The S–Bi–S angles within the five-membered chelate rings are 70.3(2) and 72.6(1)°, considerably lower than the bite angle usually observed for this ligand (*ca.* 85°), although the vast majority of examples known involve octahedral d-block complexes. Two of the Bi–S distances (involving S(1) and S(4)) in this species are at the lower end of those observed for macrocyclic thioether complexes. Within each bidentate ligand there is asymmetry in *d*(Bi–S), probably reflecting the position of the Bi-based lone pair, pointing between S(2) and S(3).

Several rather weakly diffracting, diamond-shaped crystals of the analogous iodo-complex, $[BiI_3\{MeS(CH_2)_2SMe\}_2]$, were also obtained upon concentrating an acetonitrile solution containing a 1:2 ratio of BiI_3 and $MeS(CH_2)_2SMe$. Two datasets were collected on different samples, both of which turned out to be rather weakly diffracting. The structure was found to be enantiomorphic, crystallising in either the space group $P4_12_12$ or $P4_32_12$, and the correct choice of enantiomorph was not clear. Additionally, there was evidence of disorder of the C atoms in the dithioether ligands. The combination of these factors precluded satisfactory solution and refinement. However, refinement of the heavy atom positions was sufficient to confirm that the arrangement of the ligands around Bi^{III} was the same as for $[BiBr_3\{MeS(CH_2)_2SMe\}_2]$ above. In contrast, the products obtained from reaction of BiX_3 with selenoether ligand $MeSe(CH_2)_2SeMe$ are the 1:1 species $[BiX_3\{MeSe(CH_2)_2SeMe\}]$ (even with an excess of $MeSe(CH_2)_2SeMe$). Unfortunately to-date we have not been able to obtain crystals of any of these selenoether species.

Altering the terminal substituent on the dithioether ligand also has a dramatic effect upon the structure adopted. Crystals were obtained from a 1:1 mixture of $BiBr_3$ and $PhS(CH_2)_2SPh$. The crystal structure however shows (Fig. 5, Table 5) that the sample contains a 2:1 Bi:dithioether stoichiometry. The species adopts an infinite 2-dimensional sheet structure which incorporates infinite chains of almost orthogonal Bi_2Br_6 dimer units cross-linked by bridging $PhS(CH_2)_2SPh$ ligands to give a two-dimensional sheet. The donor set around the bismuth ions comprises four bridging Br (2.693(3)–3.274(3) Å), one terminal Br (2.596(2) Å) and one thioether S-donor (3.082(6) Å), giving a distorted octahedral geometry. The thioether donor is *cis* to the terminal Br ligand. It is clear from the Bi–μ-Br bond distances that the Bi_2Br_2 rectangles are very asymmetric and only weakly associated and, as for $[BiX_3\{MeE(CH_2)_3EMe\}]$ (E = S or Se) above, the longer Bi–Br distances probably reflect the orientation of the Bi-based lone pair. The dihedral angle between adjacent Bi_2Br_2 rectangles is 82.65(7)°.

Table 5 Selected bond lengths (Å) and angles (°) for $[Bi_2Br_6\{PhS(CH_2)_2SPh\}]$

Bi(1)–Br(1)	2.596(2)	Bi(1)–Br(3)	2.693(3)
Bi(1)–Br(2)	2.751(2)	Bi(1)–Br(3*)	3.274(3)
Bi(1)–Br(2*)	3.149(3)	Bi(1)–S(1)	3.082(6)
Br(1)–Bi(1)–Br(2)	94.94(8)	Br(2)–Bi(1)–S(1)	174.7(1)
Br(1)–Bi(1)–Br(2*)	97.04(8)	Br(2)–Bi(1)–Br(3*)	168.53(7)
Br(1)–Bi(1)–Br(3)	94.19(8)	Br(2*)–Bi(1)–Br(3)	80.82(6)
Br(1)–Bi(1)–Br(3*)	176.62(8)	Br(2*)–Bi(1)–S(1)	94.8(1)
Br(1)–Bi(1)–S(1)	90.3(1)	Br(3)–Bi(1)–Br(3*)	87.85(7)
Br(2)–Bi(1)–Br(2*)	85.46(8)	Br(3)–Bi(1)–S(1)	87.5(1)
Br(2)–Bi(1)–Br(3)	91.29(8)	Br(3*)–Bi(1)–S(1)	92.4(1)
Br(2)–Bi(1)–Br(3*)	82.31(7)		

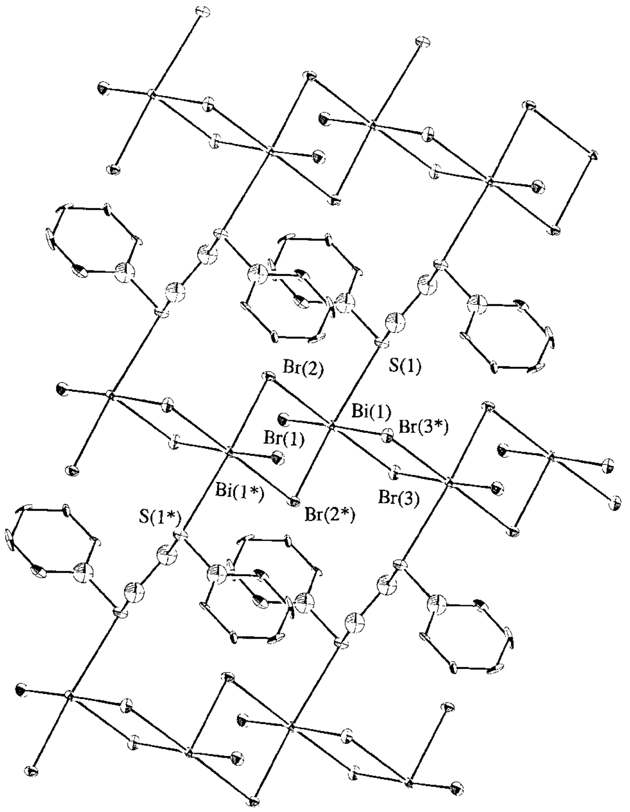

Fig. 5 View of a portion of the structure of $[Bi_2Br_6\{PhS(CH_2)_2SPh\}]$ with the numbering scheme adopted.

We were also able to obtain crystals of $[BiCl_3\{MeC(CH_2SeMe)_3\}]$ and $[Bi_2I_6\{MeC(CH_2SeMe)_3\}_2]$ from solutions of the respective complex in MeCN. The crystal structure of the former shows (Fig. 6, Table 6) centrosymmetric Bi_2Cl_6 units linked by tripodal selenoether ligands. The bismuth(III) ions are 7-co-ordinate, with the donor set comprising two bridging Cl (2.776(8), 3.151(10) Å), two terminal Cl (2.622(9), 2.55(1) Å), one bidentate selenoether (2.962(4), 3.156(4) Å) and one monodentate selenoether (3.117(4) Å). This product may be considered as Bi_2Cl_6 units with additional bidentate selenoether co-ordination at each Bi, with the third Se-donor from each tripod cross-linking these to give a 2-dimensional sheet, with an Se_3Cl_4 donor set at each Bi. The co-ordination of the third Se-donor results in a severe twisting of the Bi_2Cl_6 unit from planarity. The crystals of $[Bi_2I_6\{MeC(CH_2Se-$

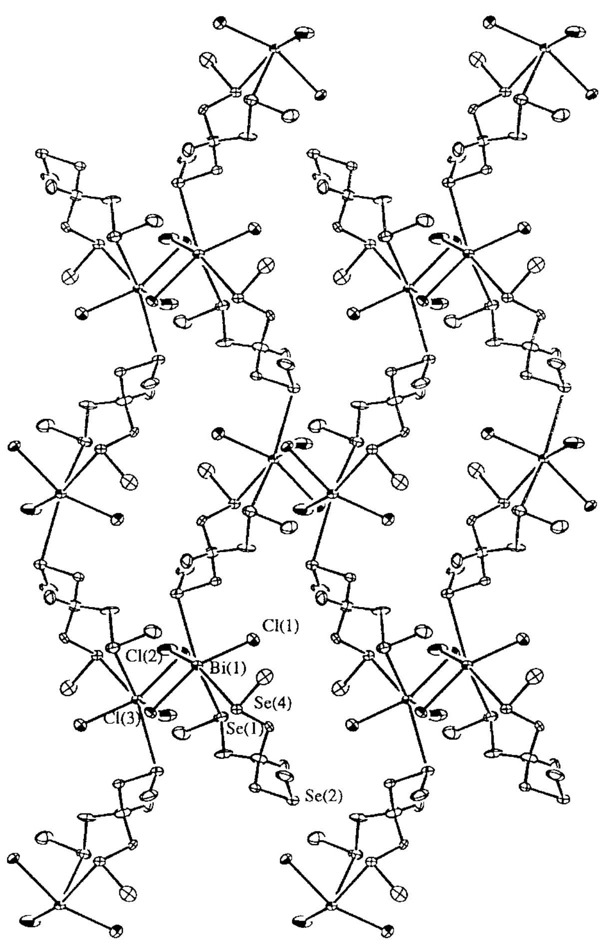

Fig. 6 View of a portion of the structure of [$BiCl_3${MeC(CH_2SeMe)$_3$}] with the numbering scheme adopted.

Me)$_3$}$_2$]† were very weakly diffracting, and hence the structure quality is rather poor. However, while comparisons of bond lengths and angles are not warranted, it is worth noting that this species is different from [$BiCl_3${MeC(CH_2SeMe)$_3$}] above, showing (Fig. 7) a discrete dimeric species derived from twisted Bi_2I_6 units with one bidentate tripod selenoether co-ordinated to each Bi. The geometry at Bi is therefore a distorted octahedron.

Conclusion

By their very nature, the characterisation of these bismuth(III) species is restricted to analytical data, IR spectroscopy and single crystal X-ray diffraction. While the stoichiometry of the products is not in question, the structural motifs described here represent those species which yielded suitable quality crystals. For the Me-substituted ligand MeS(CH_2)$_2$SMe discrete monomers are obtained with chelating dithioethers, whereas for MeS(CH_2)$_3$SMe and MeSe(CH_2)$_3$SeMe two-dimensional networks are observed in which the Group 16 donor ligands bridge between Bi_2X_6 dimers. It is interesting that complexes of the form [Bi_2X_6(L)$_4$] and [Bi_2X_6(L–L)$_2$] (L and L–L = phosphine ligands) invariably adopt bioctahedral structures in which the L and L–L ligands occupy mutually *cis* co-ordination sites.[15] Examples of related bismuth(III) halide compounds incorporating *trans* related ligands (as in [BiX_3{MeE(CH_2)$_3$EMe}] above) are much rarer, the most general class being where L = pyridine-based ligands.[16] In previous work we have shown that a similar set of dithioether and diselenoether ligands produces infinite lattice structures with silver(I) and copper(I) salts; MeSe(CH_2)$_2$SeMe yields a discrete mononuclear cation, [Ag{MeSe(CH_2)$_2$SeMe}$_2$]BF_4, possibly reflecting the preference of the dimethylene linked bidentate ligand to act as a chelate.[17] The fact that PhS(CH_2)$_2$SPh does not yield a monomeric species like its Me-substituted analogue may be due to the added steric bulk of the Ph groups and the weaker σ-donor ability of this ligand. With the tripod ligands, while we might have anticipated formation of a discrete octahedral species, [BiX_3(L^3)], we again observe the occurrence of the dinuclear Bi_2X_6 subunit, with the selenoether ligand functioning as a bidentate chelate and, in the case of [$BiCl_3${MeC(CH_2SeMe)$_3$}], the third arm bridging to an adjacent Bi. With the exception of [Bi_4Cl_{12}{MeS(CH_2)$_3$SMe}$_4$]·H_2O reported recently by us,[1] the compounds described here are the first examples of bismuth–thioether or bismuth–selenoether species which adopt infinite, polymeric structures. All of the compounds reported here are markedly different in structure from the thiacrown bismuth(III) derivatives reported previously.[3–5] Other work investigating the factors which govern the topologies adopted by these bismuth(III) adducts is currently underway.

Table 6 Selected bond lengths (Å) and angles (°) for [$BiCl_3${MeC(CH_2SeMe)$_3$}]

Bi(1)–Se(1)	2.962(4)	Bi(1)–Cl(2)	2.55(1)
Bi(1)–Se(2)	3.117(4)	Bi(1)–Cl(3)	2.776(8)
Bi(1)–Se(4*)	3.156(4)	Bi(1)–Cl(3*)	3.151(10)
Bi(1)–Cl(1)	2.622(9)		
Se(1)–Bi(1)–Se(2*)	153.6(1)	Se(2*)–Bi(1)–Cl(2)	79.4(2)
Se(1)–Bi(1)–Se(4)	78.0(1)	Se(2*)–Bi(1)–Cl(3)	115.6(2)
Se(1)–Bi(1)–Cl(1)	81.1(2)	Se(2*)–Bi(1)–Cl(3*)	65.9(2)
Se(1)–Bi(1)–Cl(2)	80.3(3)	Se(4)–Bi(1)–Cl(1)	85.4(2)
Se(1)–Bi(1)–Cl(3)	81.0(2)	Se(4)–Bi(1)–Cl(2)	157.5(2)
Se(1)–Bi(1)–Cl(3*)	140.0(2)	Se(4)–Bi(1)–Cl(3)	80.5(2)
Se(2*)–Bi(1)–Se(4)	123.2(1)	Se(4)–Bi(1)–Cl(3*)	64.8(2)
Se(2*)–Bi(1)–Cl(1)	85.0(2)	Cl(1)–Bi(1)–Cl(2)	97.1(4)
Cl(1)–Bi(1)–Cl(3)	159.2(3)	Cl(1)–Bi(1)–Cl(3*)	108.8(3)
Cl(2)–Bi(1)–Cl(3)	90.3(3)	Cl(2)–Bi(1)–Cl(3*)	133.7(3)
Cl(3)–Bi(1)–Cl(3*)	79.0(3)		

Experimental

Infrared spectra were measured as Nujol mulls between CsI plates using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}, ^1H NMR spectra in $CDCl_3$ at 300 MHz unless otherwise stated, using a Bruker AM300 spectrometer. All preparations used the same general method, which is detailed for one example below. Standard Schlenk methods were used.

Preparations

[$BiBr_3${MeS(CH_2)$_3$SMe}]. The compound $BiBr_3$ (0.16 g, 0.35 mmol) was treated with MeS(CH_2)$_3$SMe (0.05 g, 0.35 mmol) in MeCN (10 cm^3) to give a yellow solution. Concentration *in vacuo* afforded a yellow solid which was filtered off, washed with CH_2Cl_2 and dried *in vacuo*. Yield 0.16 g, 76%. Required for $C_5H_{12}BiBr_3S_2$: C, 10.3; H, 2.1%. Found: C, 10.4; H, 2.0%.

[BiI_3{MeS(CH_2)$_3$SMe}]. Dark red powder. Yield 59%. Required for $C_5H_{12}BiI_3S_2$: C, 8.3; H, 1.7. Found: C, 8.5; H, 1.9%.

[$BiCl_3${MeSe(CH_2)$_3$SeMe}]. Yellow powder. Yield 75%. Required for $C_5H_{12}BiCl_3Se_2$: C, 11.0; H, 2.2. Found: C, 10.8; H, 2.3%. IR/cm^{-1}: 238, 252, 263.

[$BiBr_3${MeSe(CH_2)$_3$SeMe}]. Bright yellow powder. Yield 64%. Required for $C_5H_{12}BiBr_3Se_2$: C, 8.9; H, 1.8. Found: C, 9.1; H, 2.1%.

[$BiCl_3${MeS(CH_2)$_2$SMe}$_2$]. Yellow powder. Yield 67%. Required for $C_8H_{20}BiCl_3S_4$: C, 17.2; H, 3.6. Found: C, 17.2; H, 3.3%. IR/cm^{-1}: 227, 250, 281.

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† $C_8H_{18}BiI_3Se_3$, $M = 940.80$, monoclinic space group, $P2_1/c$, $a = 10.59(1)$, $b = 8.717(4)$, $c = 21.40(1)$ Å, $\beta = 97.93(6)°$, $V = 1956(2)$ Å^3, $Z = 2$, $D_{calc} = 3.194$ g cm^{-3}, μ(Mo-Kα) = 192.95 cm^{-1}, 2961 unique data, 700 with $F > 4\sigma(F)$, $R = 0.084$, $Rw = 0.074$.

Table 7 Crystallographic data collection and refinement parameters

	[BiBr$_3${MeS-(CH$_2$)$_3$SMe}]	[BiCl$_3${MeSe-(CH$_2$)$_3$SeMe}]	[BiBr$_3${MeSe-(CH$_2$)$_3$SeMe}]	[BiBr$_3${MeS-(CH$_2$)$_2$SMe}$_2$]	[Bi$_2$Br$_6${PhS-(CH$_2$)$_2$SPh}]	[BiCl$_3${MeC-(CH$_2$SeMe)$_3$}]
Formula	$C_5H_{12}BiBr_3S_2$	$C_5H_{12}BiCl_3Se_2$	$C_5H_{12}BiBr_3Se_2$	$C_8H_{20}BiBr_3S_4$	$C_{14}H_{14}Bi_2Br_6S_2$	$C_8H_{18}BiCl_3Se_3$
M	584.96	545.41	678.76	693.18	1104.77	666.45
Space group	$C2/c$	$P2_1/c$	$C2/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/a$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
a/Å	12.9497(4)	8.653(6)	13.013(2)	13.040(1)	9.267(3)	11.402(7)
b/Å	11.8967(3)	12.024(5)	12.012(2)	14.493(2)	6.981(2)	16.919(5)
c/Å	18.0227(4)	12.600(6)	18.305(4)	9.883(2)	18.340(5)	11.893(6)
β/°	102.895(2)	107.70(5)	103.64(2)	90	93.94(2)	99.23(4)
V/Å^3	2706.5(1)	1249(1)	2780.5(9)	1867.8(5)	1183.6(6)	2264(1)
Z	8	4	8	4	2	4
μ(Mo-Kα)/cm^{-1}	221.51	205.11	264.99	162.85	251.53	129.28
Unique obs. reflections	2873	2317	2998	1907	2277	4136
Obs. reflections with $[I_o > 2\sigma(I_o)]$	2138	1721	1056	1548	1212	1880
R	0.065	0.045	0.037	0.035	0.044	0.060
R_w	0.077	0.049	0.039	0.044	0.049	0.088

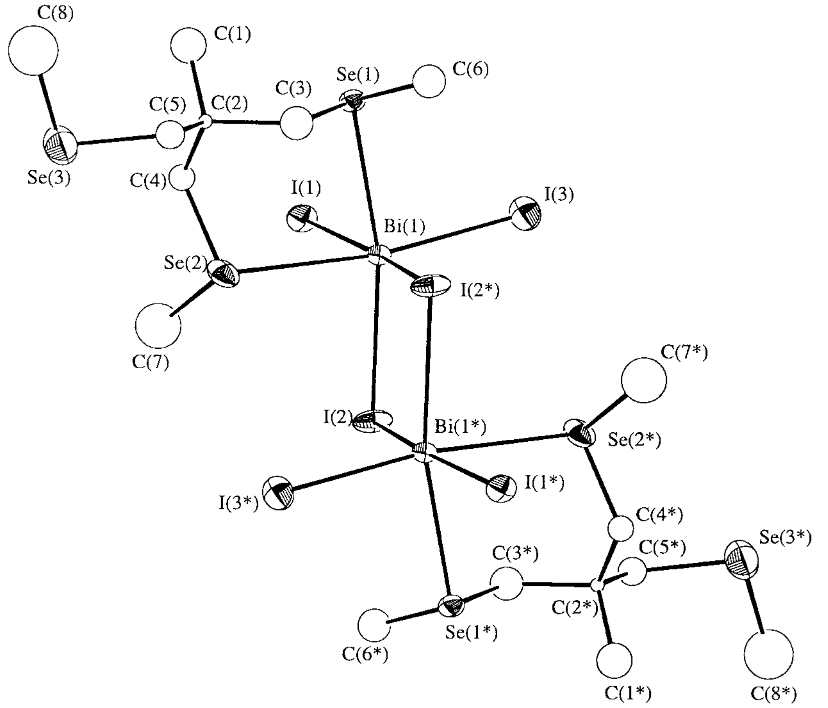

Fig. 7 View of the structure of [Bi$_2$I$_6${MeC(CH$_2$SeMe)$_3$}$_2$] with the numbering scheme adopted. Selected bond lengths: Bi(1)–I(1) 2.923(7), Bi(1)–I(2) 3.133(7), Bi(1)–I(2*) 3.260(7), Bi(1)–I(3) 2.917(9), Bi(1)–Se(1) 2.96(1), Bi(1)–Se(2) 3.19(1) Å.

[BiBr$_3${MeS(CH$_2$)$_2$SMe}$_2$]. Bright yellow powder. Yield 61%. Required for $C_8H_{20}BiBr_3S_4$: C, 13.9; H, 2.9. Found: C, 13.5; H, 2.6%.

[BiI$_3${MeS(CH$_2$)$_2$SMe}$_2$]. Dark red powder. Yield 37%. Required for $C_8H_{20}BiI_3S_4$: C, 11.5; H, 2.4. Found: C, 11.7; H, 2.5%.

[BiCl$_3${MeSe(CH$_2$)$_2$SeMe}]. Yellow powder. Yield 57%. Required for $C_4H_{10}BiCl_3Se_2$: C, 9.7; H, 2.0. Found: C, 10.0; H, 2.1%. IR/cm^{-1}: 234, 256, 279.

[BiBr$_3${MeSe(CH$_2$)$_2$SeMe}]. Bright yellow powder. Yield 46%. Required for $C_8H_{20}BiBr_3Se_2$: C, 7.2; H, 1.5. Found: C, 7.0; H, 1.5%.

[BiI$_3${MeSe(CH$_2$)$_2$SeMe}]. Dark red powder. Yield 16%. Required for $C_4H_{10}BiI_3Se_2$: C, 6.0; H, 1.2. Found: C, 6.4; H, 1.4%.

[Bi$_2$Cl$_6${PhS(CH$_2$)$_2$SPh}]. Orange powder. Yield 67%. Required for $C_7H_7BiCl_3S$: C, 19.2; H, 1.6. Found: C, 19.6; H, 1.7%. IR/cm^{-1}: 219, 234, 271.

[Bi$_2$Br$_6${PhS(CH$_2$)$_2$SPh}]. Dark orange powder. Yield 54%. Required for $C_7H_7BiBr_3S$: C, 13.6; H, 1.1. Found: C, 13.4; H, 1.2%.

[BiCl$_3${MeC(CH$_2$SMe)$_3$}]. Yellow solid. Yield 35%. Required for $C_8H_{18}BiCl_3S_3$: C, 14.6; H, 2.7. Found: C, 14.4; H, 2.5%. IR/cm^{-1}: 233, 246.

[BiCl$_3${MeC(CH$_2$SeMe)$_3$}]. Yellow solid. Yield 77%. Required for $C_8H_{18}BiCl_3Se_3$: C, 14.4; H, 2.7. Found: C, 14.0; H, 2.8%. IR/cm^{-1}: 230, 246.

[BiBr$_3${MeC(CH$_2$SeMe)$_3$}]. Yellow-orange solid. Yield 46%. Required for $C_8H_{18}BiBr_3Se_3$: C, 12.0; H, 2.3. Found: C, 12.3; H, 2.4%.

[BiI$_3${MeC(CH$_2$SeMe)$_3$}]. Dark red solid. Yield 38%. Required for $C_8H_{18}BiI_3Se_3$: C, 10.2; H, 1.9. Found: C, 10.0; H, 1.7%.

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 7. The crystals were grown by slow evaporation from solutions of the complexes in MeCN. The selected crystal was coated with mineral oil and placed in a stream of N_2 gas at 150 K. Data collection used a Rigaku AFC7S four-circle diffractometer (except for [BiBr$_3${MeS-

$(CH_2)_3SMe\}]$ which used an Enraf-Nonius Kappa-CCD diffractometer) and graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.71073$ Å). No significant crystal decay or movement was observed. The AFC7S data were corrected for absorption using ψ-scans (except for $[Bi_2Br_6\{PhS(CH_2)_2SPh\}]$, $[BiCl_3\{MeSe(CH_2)_3SeMe\}]$ and $[BiBr_3\{MeSe(CH_2)_3SeMe\}]$ for which ψ-scans did not provide a satisfactory correction, hence with the model at isotropic convergence, the data were corrected for absorption using DIFABS[18]). For $[BiBr_3\{MeS(CH_2)_3SMe\}]$ the data were corrected for absorption using SORTAV.[19] The structures were solved by direct methods[20] (except $[BiCl_3\{MeC(CH_2SeMe)_3\}]$, heavy atom methods[21]) and developed by iterative cycles of full-matrix least-squares refinement and Fourier difference syntheses.[22] All fully occupied non-H atoms were refined anisotropically (except $[BiBr_3\{MeSe(CH_2)_3SeMe\}]$ for which the C atoms were refined isotropically and $[BiBr_3\{MeS(CH_2)_3SMe\}]$ for which attempts to refine C(1) anisotropically led to non-positive definite thermal parameters, both most likely a consequence of the scattering being dominated by the heavy Bi and Br atoms). For $[BiBr_3\{MeS(CH_2)_3SMe\}]$ atom C(5) is disordered across two sites, giving C(5) 60% occupancy and C(5B) 40% occupancy. Atom C(5) in $[BiBr_3\{MeSe(CH_2)_3SeMe\}]$ also shows a high thermal parameter, however attempts to model this disorder were unsuccessful. The H atoms were placed in fixed, calculated positions with d(C–H) = 0.96 Å. The Flack parameter indicated the correct choice of enantiomorph for $[BiBr_3\{MeS(CH_2)_2SMe\}_2]$.[23]

CCDC reference number 186/1826.

See http://www.rsc.org/suppdata/dt/a9/a909803h/ for crystallographic files in .cif format.

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