9036 *Inorg. Chem.* **2010**, *49*, 9036–9048
DOI: 10.1021/ic101296e

Inorganic Chemistry
Article

Structural Diversity in Supramolecular Complexes of MCl_3 (M = As, Sb, Bi) with Constrained Thio- and Seleno-Ether Ligands

William Levason,[†] Seema Maheshwari,[†,‡] Raju Ratnani,[‡,§] Gillian Reid,*[,†] Michael Webster,[†] and Wenjian Zhang[†]

[†] *School of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K., and* [‡] *Department of Pure and Applied Chemistry, M. D. S. University, Ajmer-305009, India.* [§] *Deceased*

Received June 29, 2010

MCl_3 react with *o*-$C_6H_4(EMe)_2$ (E = S, Se) or *o*-$C_6H_4(CH_2ER)_2$ (E = S, R = Me or Et; E = Se, R = Me) in anhydrous CH_2Cl_2 or MeCN to give the yellow (Bi) or white (Sb) complexes, [MCl_3{*o*-$C_6H_4(EMe)_2$}], [$(MCl_3)_2${*o*-$C_6H_4(CH_2SMe)_2$}$_3$], [MCl_3{*o*-$C_6H_4(CH_2SEt)_2$}], and [$(BiCl_3)_4${*o*-$C_6H_4(CH_2SeMe)_2$}$_3$], which were characterized by IR/Raman, ^1H NMR spectroscopy, and microanalysis. The corresponding reactions with $AsCl_3$ gave oils. Using the tetrachalcogenoethers, 1,2,4,5-$C_6H_2(CH_2EMe)_4$ (E = S or Se), gave [$(MCl_3)_2${1,2,4,5-$C_6H_2(CH_2EMe)_4$}] (E = S: M = As, Sb or Bi; E = Se: M = As) as powdered solids. The structures adopted are extremely diverse within this related series. Crystal structure determinations show infinite chains for [MCl_3{*o*-$C_6H_4(EMe)_2$}] (M = Bi, E = S or Se; M = Sb, E = S), although the structures differ significantly in detail. [$BiCl_3${*o*-$C_6H_4(SMe)_2$}] is formed through chains of orthogonal μ-Bi_2Cl_2 units linked together, with one dithioether ligand chelating per Bi atom, and seven-coordinate Bi; [$SbCl_3${*o*-$C_6H_4(SMe)_2$}] comprises weakly associated Sb_2Cl_6 dimer units linked into chains by weakly bridging dithioethers, where both available lone pairs on each S atom are used. [$BiCl_3${*o*-$C_6H_4(SeMe)_2$}] comprises distorted square pyramidal units involving pyramidal $BiCl_3$ primary coordination and a weakly chelating diselenoether ligand, and assembled into infinite chains through long bridging Bi$\cdots$Cl interactions via all three Cl's. The 2:3 M:L complexes [$(MCl_3)_2${*o*-$C_6H_4(CH_2SMe)_2$}$_3$] (M = Bi or Sb) are isostructural, and also show one-dimensional polymers, but this time the coordination is based upon pyramidal MCl_3 units, with secondary bonding via three long M$\cdots$S contacts from bridging dithioethers, and a further long M$\cdots$Cl bridge which completes a distorted seven-coordinate environment at M. The Et-substituted thioether analogue gives the 1:1 [MCl_3{*o*-$C_6H_4(CH_2SEt)_2$}] for both Bi and Sb; the former showing a chain polymer structure based upon seven-coordinate Bi and bridging dithioethers and the latter a weakly Cl-bridged dimer with distorted octahedral coordination at Sb, with a chelating dithioether. The 4:3 [$(BiCl_3)_4${*o*-$C_6H_4(CH_2SeMe)_2$}$_3$] complexes are based upon a central $BiCl_6$ octahedron linked to each of the other three Bi atoms via two bridging Cl atoms; the outer Bi atoms are also bonded to two mutually *trans* Se donor atoms from distinct diselenoethers, and two terminal Cl atoms, giving a distorted octahedral coordination environment at Bi. One of the two crystallographically independent tetrabismuth units is discrete, while the other shows further Cl-bridges to adjacent units giving an infinite network. [$(AsCl_3)_2${1,2,4,5-$C_6H_2(CH_2SMe)_4$}] also forms an infinite network based upon square pyramidal As(III), and comprises pyramidal $AsCl_3$ units each weakly coordinated to two (mutually *cis*) S-donor atoms from two different thioether ligands. The Sb-analogue is structurally very similar; however, in this case a solvent MeCN occupies the sixth coordination site. Finally, [$(AsCl_3)_2${1,2,4,5-$C_6H_2(CH_2SeMe)_4$}] forms an infinite chain based upon distorted octahedral coordination at As through three terminal (pyramidal) Cl atoms, two Se atoms from κ^2-μ^2-selenoethers, although unexpectedly the chelation is through Se atoms that are mutually *meta* on the aromatic ring; with one Se atom on each ligand using both of its lone pairs to bridge (weakly) between two As atoms. These MCl_3-chalcogenoether adducts are mostly weakly associated, and lead to very diverse structures which result from a combination of intra- and intermolecular interactions and crystal packing.

Introduction

Although still less well developed than that of d-block complexes, the coordination chemistry of p-block Lewis acids has attracted renewed research interest over the past two decades.[1] This arises both from a desire to gain a better understanding of the properties of such complexes, for example, their structural features, the donor−acceptor bonding evidence, and, where relevant, the stereochemical consequences of the p-block element-based lone pair(s) of

---

*To whom correspondence should be addressed. E-mail: gr@soton.ac.uk.

(1) For examples see: (a) *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: New York, 2004; Vol. *3*; (b) Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2953–2960. (c) Rogers, R. D.; Bauer, C. B. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: New York, 1996; Chapter 8, pp 315−355.

Published on Web 09/02/2010 © 2010 American Chemical Society

electrons. Further motivation follows from the need for molecular reagents for the deposition of semiconductor materials for a range of applications via chemical vapor deposition techniques.[2]

Within the Group 15 elements the trivalent state is dominant, and carries one lone pair of electrons. Previous work has shown that the MX_3 (X = Cl, Br, or I) react with acyclic (saturated and flexible) neutral Group 16 donor ligands (thioethers, selenoethers, and telluroethers) to produce a range of structural motifs, usually based upon primary M−X bonds, with a variable number of secondary (longer and weaker) M···E (E = S or Se), and sometimes further M···X contacts, leading to a range of coordination numbers and geometries, and often giving supramolecular network assemblies.[3,4] The structural studies also demonstrate that the apparent stereochemical activity of the Group 15 element-based lone pair can vary quite considerably down Group 15, and not always in a regular or predictable way. For example, within the homologous series $[MCl_3([8]aneSe_2)]$ (M = As, Sb, or Bi; $[8]aneSe_2$ = 1,5-diselenocyclooctane) all of which adopt infinite ladder structures with planar M_2Cl_6 units, the As and Bi complexes show quite regular six-coordinate geometries, whereas in the Sb complex the very disparate Sb−Se distances are possibly a consequence of some stereochemical activity of the Sb-based lone pair.[4] The bond length and angle distributions in all of these compounds are largely consistent with the three-center-four-electron donor−acceptor bonding model as described by Carmalt and Norman.[5]

A number of other reports have described complexes of these Lewis acid fragments with saturated macrocyclic ligands containing Group 16 donor atoms, including, for example, the monomeric $[AsCl_3([9]aneS_3)]$,[3c] $[BiCl_3([12]aneS_4)]$, $[BiCl_3([15]aneS_5)]$, and $[BiCl_3([18]aneS_6)]$,[6] and the dinuclear $[(BiCl_3)_2([24]aneS_8)]$,[7] all of which contain pyramidal MCl_3 fragments, with longer, secondary M···S interactions. Using selenoether crowns gives the infinite ladder complex $[BiBr_3([16]aneSe_4)]$ comprising planar Bi_2Br_6 units linked by bridging selenacrowns,[4b] $[(MCl_3)_2([16]aneSe_4)]$ (M = As or Sb) which adopt sheet polymer structures with five-coordinate M(III) and *exocyclic* coordination of the selenoether crown,[3c,e] and the discrete molecular $[(AsCl_3)_4([24]aneSe_6)]$ which shows both *exo*- and *endocyclic* $AsCl_3$ coordination.[3c,8]

Further interest in these types of complexes arises from the observation that supramolecular networks based upon M(III) halide complexes containing large aromatic ligands with multiple chelating thioether groups, such as the 2,3,6,7,10,11-hexakis(alkylthio)triphenylene molecules (alkyl = Me, Et, or ^iPr) provide effective electronic coupling between the organic π-system and the metal center, leading to semiconductor properties and band gaps of around 1.64 to 2.18 eV, the lower dimensionality materials leading to larger band gaps.[9]

We report here the results of our investigation of how the introduction of rigid or semi-rigid aromatic backbones into the ligand architecture of thioethers and selenoethers in o-$C_6H_4(EMe)_2$ (E = S or Se), o-$C_6H_4(CH_2ER)_2$ (E = S; R = Me or Et; E = Se, R = Me) and 1,2,4,5-$C_6H_2(CH_2EMe)_4$ (E = S or Se), influences the structural properties of their complexes with MCl_3 (M = As, Sb, or Bi). This work therefore presents the remaining obvious architectural type within the family of chalcogenoether ligands. Owing to the very significant variability of the speciation (e.g., M:L ratios in the isolated products, ligand coordination modes) and in the structures observed, we have sought to support the discussion with single crystal X-ray structural data where this was possible, to provide the unequivocal evidence necessary.

Prior work with this series of aromatic di- and tetrathioether and -selenoether ligands has been concerned with transition metal complexes predominantly, and these studies have established a strong preference for bidentate chelation,[10] although a small number of complexes with o-$C_6H_4(CH_2SMe)_2$ (L-L) acting as a bridging ligand have also been reported, for example, $[\{(p\text{-cymene})RuCl_2\}_2(\mu^2\text{-L-L})]$,[10b] $[(MoO_2Cl_2)_2(\mu^2\text{-L-L})_2]$[11] and $[(NbCl_5)_2\{\mu^2\text{-L-L})]$.[12]

Experimental Section

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum100 spectrometer over the range 4000−200 cm^{-1}. Raman spectra were obtained using a Perkin-Elmer FT2000R with a Nd:YAG laser. Significant bands in the range 350−180 cm^{-1} are listed below. ^1H NMR spectra were recorded using a Bruker AV300 spectrometer. Microanalyses were outsourced to Medac Ltd. Several of the compounds reported are thermally unstable. For these, characterization was via low temperature spectroscopic and/or crystallographic data recorded from crystals grown from the reaction mixture at low temperature. Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques under a N_2 atmosphere. Anhydrous $AsCl_3$, $SbCl_3$, and $BiCl_3$ (Aldrich or Strem) were used as received. The thio- and seleno-ethers were made by literature methods.[10a,b,13]

---

(2) See, O'Brien, P.; Pickett, N. L. *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: New York, 2004; Vol. *9*, Chapter 23, pp 1005−1063.

(3) (a) Genge, A. R. J.; Levason, W.; Reid, G. *J. Chem. Soc., Chem. Commun.* **1998**, 2159–2160. (b) Barton, A. J.; Genge, A. R. J.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2000**, 859–865. (c) Hill, N. J.; Levason, W.; Reid, G. *Inorg. Chem.* **2002**, *41*, 2070–2076. (d) Barton, A. J.; Hill, N. J.; Levason, W.; Patel, B.; Reid, G. *Chem. Commun.* **2001**, 95–96. (e) Barton, A. J.; Hill, N. J.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1621–1627. (f) Levason, W.; Hill, N. J.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2002**, 4316–4317.

(4) (a) Hill, N. J.; Levason, W.; Patel, R.; Reid, G.; Webster, M. *Dalton Trans.* **2004**, 980–981. (b) Barton, A. J.; Genge, A. R. J.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2000**, 2163–2166.

(5) Carmalt, C. J.; Norman, N. C. In *The Chemistry of Arsenic, Antimony and Bismuth*; Norman, N. C., Ed.; Blackie: London, 1998; Chapter 1.

(6) (a) Willey, G. R.; Lakin, M. T.; Ravindran, M.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1991**, 271–272. (b) Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1992**, 591–596. (c) Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1992**, 1339–1341.

(7) Blake, A. J.; Fenske, D.; Li, W.-S.; Lippolis, V.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3961–3958.

(8) Barton, A. J.; Hill, N. J.; Levason, W.; Reid, G. *J. Am. Chem. Soc.* **2001**, *123*, 11801–11802.

(9) (a) Huang, G.; Sun, Y.-Q.; Xu, Z.; Zeller, M.; Hunter, A. D. *Dalton Trans.* **2009**, 5083–5093. (b) Xu, Z. *Coord. Chem. Rev.* **2006**, *250*, 2745–2757. (c) Li, K.; Xu, Z.; Xu, H.; Ryan, J. M. *Chem. Mater.* **2005**, *17*, 4426–4437. (d) Li, K.; Xu, H.; Xu, Z.; Zeller, M.; Hunter, A. D. *Inorg. Chem.* **2005**, *44*, 8855–8860.

(10) (a) Levason, W.; Nirwan, M.; Ratnani, R.; Reid, G.; Tsoureas, N.; Webster, M. *Dalton Trans.* **2007**, 439–448. (b) Levason, W.; Ollivere, L. P.; Reid, G.; Tsoureas, N.; Webster, M. *J. Organomet. Chem.* **2009**, *694*, 2299–2308. (c) Levason, W.; Orchard, S. D.; Reid, G. *Coord. Chem. Rev.* **2002**, *225*, 159–199. (d) Black, J. R.; Champness, N. R.; Levason, W.; Reid, G. *Inorg. Chem.* **1996**, *35*, 1820–1824. (e) Gulliver, D. J.; Levason, W.; Smith, K. G.; Selwood, M. J.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1872–1878.

(11) Davis, M. F.; Levason, W.; Light, M. E.; Ratnani, R.; Reid, G.; Saraswat, K.; Webster, M. *Eur. J. Inorg. Chem.* **2007**, 1903–1910.

(12) Jura, M.; Levason, W.; Ratnani, R.; Reid, G.; Webster, M. *Dalton Trans.* **2010**, 883–891.

(13) (a) Hope, E. G.; Kemmitt, T.; Levason, W. *J. Chem. Soc., Perkin II* **1987**, 487–490. (b) Hartley, F. R.; Murray, S. G.; Levason, W.; Soutter, H. E.; McAuliffe, C. A. *Inorg. Chim. Acta* **1979**, *35*, 265–277.

Table 1. Crystal Data and Structure Refinement Details[a]

compound	$[BiCl_3\{o\text{-}C_6H_4\text{-}(SMe)_2\}]$	$[SbCl_3\{o\text{-}C_6H_4\text{-}(SMe)_2\}]$	$[BiCl_3\{o\text{-}C_6H_4\text{-}(SeMe)_2\}]$	$[(BiCl_3)_2\{o\text{-}C_6H_4\text{-}(CH_2SMe)_2\}_3]$	$[BiCl_3\{o\text{-}C_6H_4\text{-}(CH_2SEt)_2\}]$
formula	$C_8H_{10}BiCl_3S_2$	$C_8H_{10}Cl_3S_2Sb$	$C_8H_{10}BiCl_3Se_2$	$C_{30}H_{42}Bi_2Cl_6S_6$	$C_{12}H_{18}BiCl_3S_2$
M	485.61	398.38	579.41	1225.66	541.71
crystal syst	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$Pnma$ (no. 62)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a [Å]	8.9791(10)	7.538(3)	7.701(3)	10.323(2)	11.3264(10)
b [Å]	7.2095(10)	17.065(9)	12.409(4)	11.415(3)	7.7619(10)
c [Å]	20.905(2)	10.559(5)	14.026(6)	19.859(5)	19.630(2)
α [deg]	90	90	90	83.759(10)	90
β [deg]	98.574(10)	105.11(3)	90	84.587(15)	104.406(7)
γ [deg]	90	90	90	66.458(15)	90
U [Å^3]	1338.1(3)	1311.3(10)	1340.2(8)	2129.2(8)	1671.5(3)
Z	4	4	4	2	4
μ(Mo Kα) [mm^{-1}]	14.048	2.994	19.147	8.945	11.259
total reflns	18616	17104	12309	29694	21116
unique reflns	3063	3005	1607	8293	3824
R_{int}	0.054	0.116	0.073	0.062	0.063
no. of params, restraints	129, 0	129, 0	78, 21	403, 12	163, 0
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.025	0.053	0.042	0.053	0.033
R_1 [all data]	0.034	0.098	0.056	0.077	0.041
$wR_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.054	0.095	0.082	0.103	0.071
wR_2 [all data]	0.061	0.109	0.090	0.115	0.076

compound	$[SbCl_3\{o\text{-}C_6H_4\text{-}(CH_2SEt)_2\}]$	$[(BiCl_3)_4\{o\text{-}C_6H_4\text{-}(CH_2SeMe)_2\}_3]$	$[\{SbCl_3(MeCN)\}_2\{1,2,4,5\text{-}C_6H_2\text{-}(CH_2SMe)_4\}]$	$[(AsCl_3)_2\{1,2,4,5\text{-}C_6H_2\text{-}(CH_2SMe)_4\}]$	$[(AsCl_3)_2\{1,2,4,5\text{-}C_6H_2\text{-}(CH_2SeMe)_4\}]$
formula	$C_{12}H_{18}Cl_3S_2Sb$	$C_{30}H_{42}Bi_4Cl_{12}Se_6$	$C_{18}H_{28}Cl_6N_2S_4Sb_2$	$C_{14}H_{22}As_2Cl_6S_4$	$C_{14}H_{22}As_2Cl_6Se_4$
M	454.48	2137.72	856.86	681.10	868.70
crystal syst	monoclinic	trigonal	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P321$ (no. 150)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	7.283(3)	18.184(3)	9.546(3)	11.2413(15)	9.4033(10)
b [Å]	18.854(9)	18.184(3)	10.566(3)	7.0289(10)	8.8433(10)
c [Å]	12.653(6)	15.147(3)	15.728(3)	16.235(3)	15.4653(15)
α [deg]	90	90	90	90	90
β [deg]	90.38(4)	90	103.820(15)	93.360(10)	101.011(7)
γ [deg]	90	120	90	90	90
U [Å^3]	1737.3(14)	4337.4(13)	1540.5(6)	1280.6(3)	1262.4(2)
Z	4	3	2	2	2
μ(Mo Kα) [mm^{-1}]	2.272	16.487	2.558	3.562	9.050
total no. reflns	11004	37383	19499	17266	16134
unique reflns	3185	5680	3527	2931	2860
R_{int}	0.057	0.137	0.085	0.040	0.039
no. of params, restraints	164, 0	240, 69	148, 0	120, 0	120, 0
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.049	0.057	0.064	0.030	0.062
R_1 [all data]	0.054	0.081	0.097	0.038	0.066
$wR_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.130	0.111	0.114	0.069	0.160
wR_2 [all data]	0.137	0.123	0.130	0.072	0.162

[a] Common items: temperature = 120 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2 / \sum wF_o{}^4]^{1/2}$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $[BiCl_3\{o\text{-}C_6H_4(SMe)_2\}]$[a]

Bi1−Cl1	2.5232(12)	Bi1−Cl2	2.6618(11)
Bi1−Cl3	2.6262(11)	Bi1−Cl2a	2.8887(12)
Bi1−Cl3b	2.9776(11)	Bi1−S1	3.0075(11)
Bi1−S2	3.1542(12)		
Cl1−Bi1−Cl2	90.69(4)	Cl1−Bi1−Cl3	90.31(4)
Cl2−Bi1−Cl3	84.18(4)	Cl1−Bi1−Cl2a	88.29(4)
Cl2−Bi1−Cl2a	79.38(3)	Cl3−Bi1−Cl2a	163.47(3)
Cl1−Bi1−Cl3b	169.35(4)	Cl2−Bi1−Cl3b	85.47(4)
Cl3−Bi1−Cl3b	79.42(3)	Cl2a−Bi1−Cl3b	100.73(3)
Cl1−Bi1−S1	76.68(4)	Cl2−Bi1−S1	162.21(4)
Cl3−Bi1−S1	83.42(4)	Cl1−Bi1−S2	112.27(4)
Cl2−Bi1−S2	138.40(4)	Cl3−Bi1−S2	127.61(3)
S1−Bi1−S2	59.19(3)		

[a] Symmetry operations: a = 1 − x, −y, 1 − z; b = 1 − x, 1 − y, 1 − z.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for $[SbCl_3\{o\text{-}C_6H_4(SMe)_2\}]$[a]

Sb1−Cl1	2.377(2)	Sb1−Cl2	2.3566(19)
Sb1−Cl3	2.4198(18)	Sb1−S1	3.187(2)
Sb1−S2	3.569(2)	Sb1−S1a	3.836(2)
Sb1−S2a	3.453(2)	Sb1−Cl3b	3.464(2)
Cl1−Sb1−Cl2	94.23(7)	Cl1−Sb1−Cl3	90.58(6)
Cl1−Sb1−S1	82.13(5)	Cl2−Sb1−Cl3	92.84(6)
Cl2−Sb1−S1	83.00(6)	Cl3−Sb1−S1	171.29(6)
Cl1−Sb1−S2	133.79(5)	Cl2−Sb1−S2	82.57(6)
S1−Sb1−S2	51.68(4)	Cl3−Sb1−S2	135.53(5)
S1−Sb1−S1a	93.40(4)	S2−Sb1−S2a	92.88(5)
S2a−Sb1−S1a	47.64(4)	S2−Sb1−S1a	68.28(5)

[a] Symmetry operations: a = −x, 1 − y, − z; b = 1 − x, 1 − y, − z.

$[BiCl_3\{o\text{-}C_6H_4(SMe)_2\}]$. $BiCl_3$ (0.76 g, 2.4 mmol) was dissolved in MeCN (4 mL), and o-$C_6H_4(SMe)_2$ (0.41 g, 2.4 mmol) in CH_2Cl_2 (2 mL) was added dropwise with constant stirring. A light-yellow solution was formed immediately, and the solution was stirred for a further 4 h. A yellow solid precipitated out upon concentrating the solution in vacuo. This was filtered off and dried in vacuo. Yield: 0.78 g, 67%. Orange crystals suitable for X-ray diffraction studies were obtained from the filtrate which was kept in a refrigerator for several days. Anal. Calcd for $C_8H_{10}BiCl_3S_2$: C, 19.8; H, 2.1. Found: C, 19.8; H, 1.9. ^{1}H NMR (300 MHz, CD_2Cl_2): 2.55 (s, [6H], Me), 7.19−7.26 (m, [4H], Ar). IR (cm^{-1}, Nujol): 280(s), 243(s), 209(m). Raman (cm^{-1}): 272(s), 223(w).

$[SbCl_3\{o\text{-}C_6H_4(SMe)_2\}]$. $SbCl_3$ (0.36 g, 1.6 mmol) was dissolved in MeCN (10 mL), and o-$C_6H_4(SMe)_2$ (0.27 g, 1.6 mmol)

Table 4. Selected Bond Lengths [Å] and Angles [deg] for $[BiCl_3\{o\text{-}C_6H_4(SeMe)_2\}]$[a]

Bi1−Cl1	2.609(2)	Bi1−Cl2	2.547(3)
Bi1−Cl1b	3.314(2)	Bi1−Cl2a	3.225(3)
Bi1−Se1	3.1376(13)		
Cl1−Bi1−Cl2	81.65(7)	Cl1−Bi1−Cl1c	94.31(10)
Cl1−Bi1−Se1c	155.31(6)	Cl2−Bi1−Se1	78.72(6)
Cl1−Bi1−Se1	97.49(6)	Se1−Bi1−Se1c	64.10(5)

[a] Symmetry operations: a = $x - 1/2, y, 1/2 - z$; b = $x - 1/2, 1/2 - y, 1/2 - z$; c = $x, 1/2 - y, z$.

Table 5. Selected Bond Lengths [Å] and Angles [deg] for $[(BiCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$[a]

Bi1−Cl1	2.526(3)	Bi2−Cl4	2.524(3)
Bi1−Cl2	2.522(3)	Bi2−Cl5	2.657(2)
Bi1−Cl3	2.626(3)	Bi2−Cl6	2.526(3)
Bi1−Cl5	3.307(2)	Bi2−Cl3b	3.303(3)
Bi1−S1	2.970(3)	Bi2−S2	3.095(3)
Bi1−S3	3.117(3)	Bi2−S4	3.188(3)
Bi1−S5a	3.150(3)	Bi2−S6	2.941(2)
Cl1−Bi1−Cl2	89.72(11)	Cl4−Bi2−Cl5	93.24(8)
Cl1−Bi1−Cl3	88.72(9)	Cl4−Bi2−Cl6	89.92(9)
Cl2−Bi1−Cl3	97.11(9)	Cl5−Bi2−Cl6	90.27(8)
S1−Bi1−S3	93.25(8)	S2−Bi2−S4	114.62(7)
S1−Bi1−S5a	112.42(7)	S2−Bi2−S6	107.86(7)
S3−Bi1−S5a	116.67(7)	S4−Bi2−S6	102.11(7)

[a] Symmetry operations: a = $x - 1, y, z$; b = $x + 1, y, z$.

Table 6. Selected Bond Lengths [Å] and Angles [deg] for $[BiCl_3\{o\text{-}C_6H_4(CH_2SEt)_2\}]$[a]

Bi1−Cl1	2.6422(14)	Bi1−Cl2	2.5508(15)
Bi1−Cl3	2.4862(15)	Bi1−S1	3.0889(15)
Bi1−S2	2.9323(15)	Bi1−Cl1a	3.2875(15)
Bi1−S1b	3.3159(14)		
Cl1−Bi1−Cl2	92.27(5)	Cl1−Bi1−Cl3	84.66(5)
Cl2−Bi1−Cl3	92.17(5)	S1−Bi1−S2	88.01(4)
Cl1−Bi1−S1	98.08(4)	Cl1−Bi1−S2	160.87(4)
Cl2−Bi1−S1	168.16(4)	Cl2−Bi1−S2	80.37(5)
Cl3−Bi1−S1	83.12(5)	Cl3−Bi1−S2	78.06(5)
S1−Bi1−S1b	120.32(3)	S2−Bi1−S1b	122.18(4)

[a] Symmetry operations: a = $-1/2 - x, 1/2 + y, 1/2 - z$; b = $-1/2 - x, -1/2 + y, 1/2 - z$.

Table 7. Selected Bond Lengths [Å] and Angles [deg] for $[SbCl_3\{o\text{-}C_6H_4(CH_2SEt)_2\}]$[a]

Sb1−Cl1	2.471(2)	Sb1−Cl2	2.360(2)
Sb1−Cl3	2.435(2)	Sb1−S1	2.968(2)
Sb1−S2	2.985(3)	Sb1−Cl1a	3.460(3)
Cl1−Sb1−Cl2	91.13(8)	Cl1−Sb1−Cl3	92.13(7)
Cl2−Sb1−Cl3	91.01(8)	Cl1−Sb1−S2	86.04(7)
Cl1−Sb1−S1	170.53(7)	Cl2−Sb1−S1	81.41(7)
Cl2−Sb1−S2	80.17(7)	Cl3−Sb1−S1	82.24(7)
Cl3−Sb1−S2	170.94(7)	S1−Sb1−S2	98.33(6)

[a] Symmetry operation: a = $1 - x, -y, 1 - z$.

Table 8. Selected Bond Lengths [Å] and Angles [deg] for $[(BiCl_3)_4\{o\text{-}C_6H_4(CH_2SeMe)_2\}_3]$[a]

Bi1−Cl1	2.697(5)	Bi2−Cl2	2.494(5)
Bi2−Cl1	2.974(6)	Bi2−Se1	3.006(2)
Cl1−Bi1−Cl1c	88.19(15)	Cl1−Bi1−Cl1a	92.0(2)
Cl2−Bi2−Cl2d	91.4(2)	Cl2−Bi2−Cl1d	172.92(17)
Cl2−Bi2−Cl1	93.96(15)	Cl1−Bi2−Cl1d	81.11(18)
Cl2−Bi2−Se1d	95.17(17)	Cl1−Bi2−Se1d	95.05(11)
Se1−Bi2−Se1d	173.92(10)	Bi1−Cl1−Bi2	93.63(15)

[a] Bi1 and Bi2 only. The second molecule is similar. Symmetry operations: a = $y, x, -z$; b = $-x + y, -x, z$; c = $-y, x - y, z$; d = $-x, -x + y, -z$.

Table 9. Selected Bond Lengths [Å] and Angles [deg] for $[(AsCl_3)_2\{1,2,4,5\text{-}C_6H_2(CH_2SMe)_4\}]$[a]

As1−Cl1	2.1814(7)	As1−Cl2	2.1996(7)
As1−Cl3	2.2221(8)	As1−S1	3.0189(8)
As1−S2b	3.2693(8)		
Cl1−As1−Cl2	98.20(3)	Cl1−As1−Cl3	95.86(3)
Cl2−As1−Cl3	95.35(3)	Cl1−As1−S1	86.33(2)
Cl2−As1−S1	84.80(3)	Cl3−As1−S1	177.76(3)
Cl1−As1−S2b	84.89(2)	Cl2−As1−S2b	170.55(2)
Cl3−As1−S2b	93.20(3)	S1−As1−S2b	86.50(2)

[a] Symmetry operations: a = $1 - x, -y, 1 - z$; b = $3/2 - x, 1/2 + y, 1/2 - z$.

Table 10. Selected Bond Lengths [Å] and Angles [deg] for $[\{SbCl_3(MeCN)\}_2\{1,2,4,5\text{-}C_6H_2(CH_2SMe)_4\}]$[a]

Sb1−Cl1	2.433(2)	Sb1−Cl2	2.4506(19)
Sb1−Cl3	2.3722(19)	Sb1−N1c	2.955(9)
Sb1−S1	3.059(2)	Sb1−S2b	3.001(2)
Cl1−Sb1−Cl2	88.43(7)	Cl1−Sb1−Cl3	93.80(8)
Cl2−Sb1−Cl3	94.07(7)	Cl3−Sb1−N1c	175.9(2)
Cl1−Sb1−N1c	82.1(2)	Cl2−Sb1−N1c	85.38(19)
Cl3−Sb1−S2b	79.71(7)	Cl1−Sb1−S2b	74.74(6)
Cl2−Sb1−S2b	161.50(7)	Cl3−Sb1−S1	77.47(7)
Cl1−Sb1−S1	166.41(7)	Cl2−Sb1−S1	81.91(7)
S1−Sb1−S2b	113.22(6)		

[a] Symmetry operations: b = $x - 1, 1/2 - y, z - 1/2$; c = $-x, y - 1/2, 1/2 - z$.

Table 11. Selected Bond Lengths [Å] and Angles [deg] for $[(AsCl_3)_2\{1,2,4,5\text{-}C_6H_2(CH_2SeMe)_4\}]$[a]

As1−Cl1	2.186(3)	As1−Cl2	2.215(3)
As1−Cl3	2.205(3)	As1···Se1	3.423(2)
As1···Se2	3.289(2)	As1···Se2a	3.603(2)
Cl1−As1−Cl3	97.84(11)	Cl1−As1−Cl2	96.26(11)
Cl3−As1−Cl2	93.71(11)	Se1···As1···Se2	114.22(4)
Se1···As1···Se2a	94.19(3)	Se2···As1···Se2a	94.84(3)

[a] Symmetry operation: a = $1 - x, 1 - y, -z$.

in MeCN (3 mL) was added dropwise to a stirred and chilled solution of $SbCl_3$. The resulting clear solution was stirred in an ice bath for 15 min, and then allowed to warm to room temperature overnight. The solvent was evaporated in vacuo, and the residual viscous liquid was dissolved in dichloromethane and layered with hexane. Transparent block crystals suitable for X-ray diffraction studies were obtained along with a cream-colored solid after 2 days. These solids were filtered off, washed with hexane, and dried in vacuo. Yield: 0.42 g, 66%. Anal. Calcd for $C_8H_{10}Cl_3S_2Sb \cdot CH_2Cl_2$: C, 22.4; H, 2.5. Found: C, 22.8; H, 2.2. ^1H NMR (300 MHz, $CDCl_3$): 2.44 (s, [6H], Me), 5.34 (s, CH_2Cl_2), 7.13−7.15 (m, [4H], Ar). IR (cm^{-1}, Nujol): 344(s), 322(s), 292(s).

$[BiCl_3\{o\text{-}C_6H_4(SeMe)_2]$. $BiCl_3$ (0.34 g, 1.09 mmol) was dissolved in MeCN (4 mL), and $o\text{-}C_6H_4(SeMe)_2$ (0.28 g, 1.09 mmol) in CH_2Cl_2 (2 mL) was added dropwise with constant stirring in an ice bath. A light yellow solution was formed instantaneously, and the solution was stirred for a further 3 h in an ice bath. No precipitate was obtained on concentrating in vacuo; hence the solvent was removed completely and hexane was added to the viscous liquid, followed by cooling to −78 °C. This led to formation of a yellow solid within ~15 min. The precipitate was filtered off and dried in vacuo. Yield: 0.51 g, 83%. Anal. Calcd for $C_8H_{10}BiCl_3Se_2$: C, 16.6; H, 1.7. Found: C, 16.7; H, 2.2. ^1H NMR (300 MHz, $CDCl_3$): 2.33 (s, [6H], Me), 7.15−7.18 (m, [2H], Ar), 7.32−7.35 (m, [2H], Ar). IR (cm^{-1}, Nujol): 305(w), 281(w), 273(m), 241(w). Raman (cm^{-1}): 305(m), 269(s), 217(s).

$[SbCl_3\{o\text{-}C_6H_4(SeMe)_2\}]$. $SbCl_3$ (0.18 g, 0.80 mmol) was dissolved in MeCN (5 mL), and $o\text{-}C_6H_4(SeMe)_2$ (0.21 g, 0.80 mmol) in MeCN (2 mL) was added dropwise with constant stirring in an ice bath. A light yellow solution was formed immediately, and the solution was stirred for a further 4 h in an ice bath. No precipitate was obtained on concentrating the

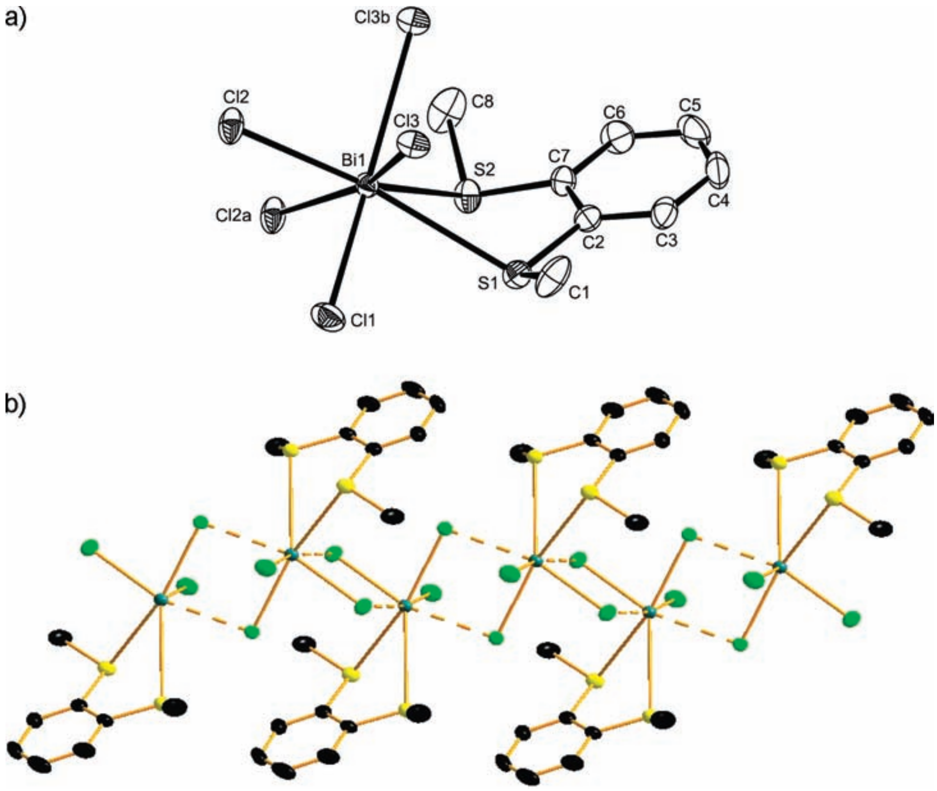

Figure 1. Structure of [$BiCl_3\{o\text{-}C_6H_4(SMe)_2\}$] (a) showing the atom numbering scheme. H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. The coordination of Bi1 is also shown. Symmetry operations: a = $1 - x, -y, 1 - z$; b = $1 - x, 1 - y, 1 - z$. (b) View of the chain polymer structure via the weak Bi···Cl interactions. Teal = Bi, green = Cl, yellow = S, black = C.

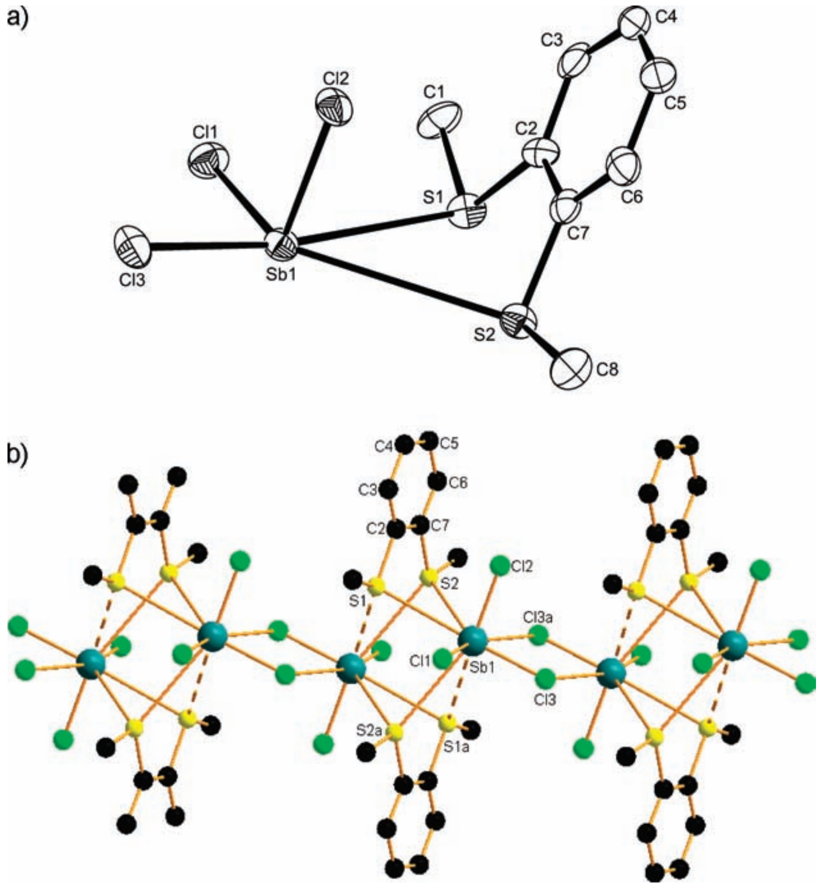

Figure 2. (a) Structure of [$SbCl_3\{o\text{-}C_6H_4(SMe)_2\}$] showing the atom numbering scheme. H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. (b) View of the chain polymer. Teal = Sb, green = Cl, yellow = S, black = C.

solution, so the solvent was evaporated to dryness to give a yellow viscous oil which was washed with CH_2Cl_2 and hexane. Anal. Calcd for $C_8H_{10}Cl_3SbSe_2 \cdot CH_2Cl_2$: C, 18.7; H, 2.1. Found: C, 18.3; H, 2.0. ^{1}H NMR (300 MHz, $CDCl_3$): 2.32 (s, [6H], Me), 7.13−7.16 (dd, [2H], Ar), 7.26−7.29 (dd, [2H], Ar). IR (cm^{-1}, Nujol): 318(br s).

$[(BiCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$. $BiCl_3$ (0.31 g, 1.0 mmol) was dissolved in MeCN (4 mL), and o-$C_6H_4(CH_2SMe)_2$ (0.20 g, 1.0 mmol) in CH_2Cl_2 (2 mL) was added dropwise with constant stirring. A light yellow solution was formed instantaneously, and the solution was stirred for a further 1 h. A yellow solid precipitated out on concentrating the solution; this was filtered off and dried in vacuo. Yellow needle-shaped crystals suitable for X-ray diffraction studies were obtained from the filtrate which was kept in a refrigerator for several days. Yield: 0.31 g, 75%. Anal. Calcd for $C_{30}H_{42}Bi_2Cl_6S_6$: C, 29.4; H, 3.4. Found: C, 28.9; H, 3.4. ^{1}H NMR (300 MHz, $CDCl_3$): 2.28 (s, [6H], Me), 4.03 (s, [4H], CH_2); 7.26 (br s, [4H], Ar). IR (cm^{-1}, Nujol): 283(m), 264(m), 230(m). Raman (cm^{-1}): 298(w), 281(s), 269(m), 231(m), 214(m).

$[(SbCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$. $SbCl_3$ (0.20 g, 0.88 mmol) was dissolved in MeCN (10 mL), and o-$C_6H_4(CH_2SMe)_2$ (0.17 g, 0.88 mmol) in MeCN (3 mL) was added dropwise to a stirred and chilled solution of $SbCl_3$. The resulting clear solution was stirred in an ice bath for 10 min, and then at room temperature overnight. A white solid precipitated out on placing the solution in the refrigerator overnight. This was collected by filtration and dried in vacuo. Transparent needle-shaped crystals suitable for X-ray diffraction studies were obtained from the filtrate from the original reaction upon layering with hexane and cooling in a refrigerator for several days. The bulk material was then recrystallized by dissolving in hexane and cooling the solution in the freezer for several days. Yield: 0.20 g, 63%. Anal. Calcd for $C_{30}H_{42}Cl_6S_6Sb_2 \cdot C_6H_{14}$: C, 38.1; H, 5.0. Found: C, 38.7; H, 4.6. ^{1}H NMR (300 MHz, CD_3CN): 2.03 (s, [6H], Me), 3.84 (s, [4H], CH_2) 7.22−7.28 (m, [4H], Ar), IR (cm^{-1}, Nujol): 296(w), 281 (m), 265 (m).

$[BiCl_3\{o\text{-}C_6H_4(CH_2SEt)_2\}]$. $BiCl_3$ (0.21 g, 0.66 mmol) was dissolved in MeCN (4 mL), and o-$C_6H_4(CH_2SEt)_2$ (0.30 g, 1.33 mmol) in CH_2Cl_2 (2 mL) was added dropwise with constant stirring. A deep-yellow solution was formed instantaneously, and the solution was stirred for a further 3 h. No precipitate was observed on concentrating the solution, so the solvent was removed completely and the yellow viscous residue was dissolved in CH_2Cl_2 again. A cream solid appeared after 1 day in the freezer. This was filtered off and dried in vacuo. Needle-shaped crystals suitable for X-ray diffraction studies were obtained on keeping this filtrate in the freezer for several days. Yield: 0.25 g, 70%. Anal. Calcd for $C_{12}H_{18}BiCl_3S_2 \cdot CH_2Cl_2$: C, 24.9; H, 3.2. Found: C, 24.2; H, 3.5. ^{1}H NMR (300 MHz, $CDCl_3$): 1.25 (t, [6H], Me), 3.02 (q, [4H], CH_2); 4.26 (s, [4H], CH_2), 5.33 (s, CH_2Cl_2), 7.29−7.31 (m, [4H], Ar). IR (cm^{-1}, Nujol): 303(m), 253(m), 227(w).

$[SbCl_3\{o\text{-}C_6H_4(CH_2SEt)_2\}]$. $SbCl_3$ (0.33 g, 1.4 mmol) was dissolved in MeCN (10 mL), and o-$C_6H_4(CH_2SEt)_2$ (0.33 g, 1.4 mmol) in MeCN (4 mL) was added dropwise with constant stirring. The resulting clear solution was stirred in an ice bath for 10 min, and then stirred at room temperature overnight. A white solid precipitated out on placing the solution in the refrigerator overnight; this was filtered off and dried in vacuo. Transparent needle-shaped crystal suitable for X-ray diffraction studies were grown from the filtrate upon layering with hexane and storing in a refrigerator for several days. Yield: 0.56 g, 84%. Anal. Calcd for $C_{12}H_{18}Cl_3S_2Sb \cdot 1/2CH_2Cl_2$: C, 30.2; H, 3.8. Found: C, 30.1; H, 3.7. ^{1}H NMR (300 MHz, $CDCl_3$): 1.27 (t, [6H], Me), 2.54 (q, [4H], CH_2); 3.90 (s, [4H], CH_2), 5.34 (s, CH_2Cl_2), 7.18−7.26 (m, [4H], Ar). IR (cm^{-1}, Nujol): 291(m), 269(m).

$[(BiCl_3)_4\{o\text{-}C_6H_4(CH_2SeMe)_2\}_3]$. $BiCl_3$ (0.27 g, 0.86 mmol) was dissolved in MeCN (4 mL) and o-$C_6H_4(CH_2SeMe)_2$ (0.25 g, 0.86 mmol) in CH_2Cl_2 (2 mL) was added dropwise with constant stirring in an ice bath. A yellow precipitate was formed instantaneously, and the reaction mixture was stirred for a further 2 h while maintaining the temperature below 0 °C in an ice bath. The precipitate was filtered off and dried in vacuo. Yield: 0.43 g, 84%. Note that the yellow solid turned green upon storing under dry N_2 in the glovebox; hence samples were stored under N_2 in the freezer. Yellow block crystals suitable for X-ray diffraction studies were obtained by slow evaporation from an MeCN solution of $BiCl_3$ which had been layered by equimolecular solution of ligand in CH_2Cl_2, and placed in the refrigerator for several days. ^{1}H NMR (300 MHz, $CDCl_3$): 2.07 (s, [6H], Me), 4.01 (s, [4H], CH_2), 7.17−7.21 (m, [4H], Ar). IR (cm^{-1}, Nujol): 294(m), 265(br,m), 221(w). The isolated complex is thermally unstable, turning green over a few hours at room temperature; hence, microanalytical data were not obtained. Green solid: ES$^+$ mass spectrum (MeCN): m/z = 125 $[Me_3Se]^+$, 199 $[o\text{-}C_6H_4(CH_2)_2SeMe]^+$; ES$^-$ mass spectrum (MeCN): m/z = 351 $[BiCl_4]^-$.

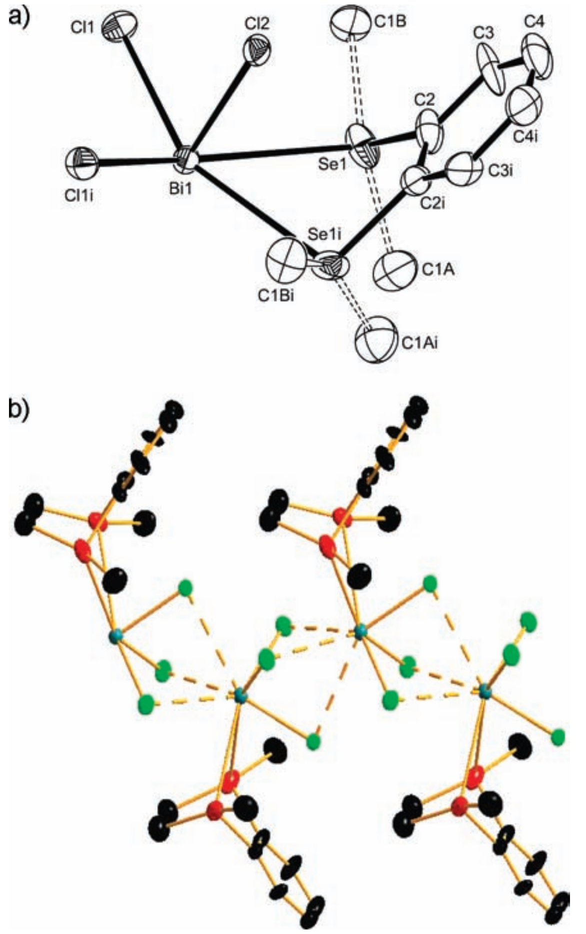

Figure 3. (a) Structure of $[BiCl_3\{o\text{-}C_6H_4(SeMe)_2\}]$ showing the atom numbering scheme. H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. Atoms C1A and C1B are two alternative positions for the disordered Me substituents (equal occupancy). Symmetry operation: i = x, $1/2 - y$, z. (b) View of the chain polymer showing the long Bi···Cl contacts. Teal: Bi; green: Cl; red: Se; black: C. Note that both positions for the disordered terminal Me C atoms are shown (each has 50% site occupancy).

Reaction of $SbCl_3$ with o-$C_6H_4(CH_2SeMe)_2$. $SbCl_3$ (0.28 g, 1.25 mmol) was dissolved in MeCN (10 mL), and o-$C_6H_4(CH_2SeMe)_2$ (0.36 g, 1.25 mmol) in CH_2Cl_2 (5 mL) was added dropwise with constant stirring in an ice bath. The solution was stirred for a further 2 h in an ice bath. A white solid precipitated out on concentrating the solution; this was filtered off and dried in vacuo. All these processes were carried out in an ice bath. ^{1}H NMR (300 MHz, CD_3CN): 1.94 (s, [6H], Me), 3.89 (s, [4H], CH_2), 7.16−7.23 (m, [4H], Ar). IR (cm^{-1}, Nujol): 296(w), 274(w). Note that this white solid turned brown over 1 to 2 h

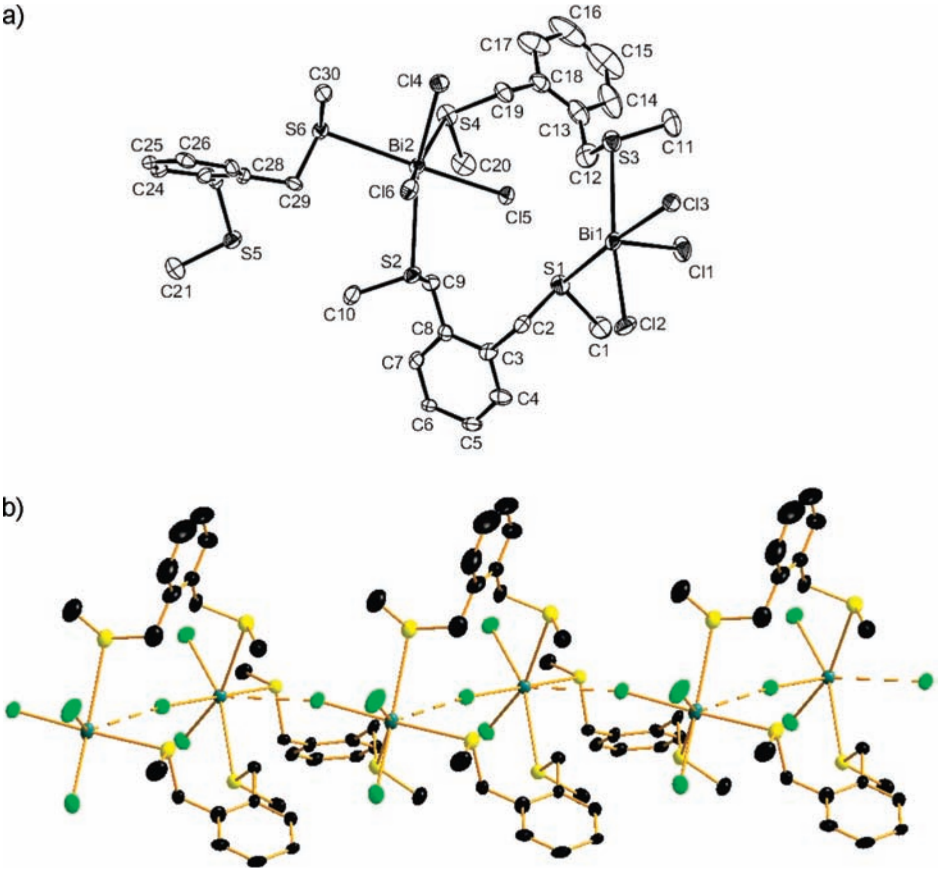

Figure 4. (a) Structure of [$(BiCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3$] showing the atom labeling scheme. H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. Symmetry operation: b = $x + 1, y, z$. (b) View of the chain polymer structure.

at room temperature even when stored under dry N_2, precluding microanalytical measurements. Brown solid: ES^+ mass spectrum (MeCN): m/z = 199 [$o\text{-}C_6H_4(CH_2)_2SeMe]^+$; ES^- mass spectrum (MeCN): m/z = 262 $[SbCl_4]^-$, 490 $[Sb_2Cl_7]^-$.

[$(AsCl_3)_2\{$1,2,4,5-$C_6H_2(CH_2SMe)_4\}$]. $AsCl_3$ (0.24 g, 1.33 mmol) was dissolved in CH_2Cl_2 (5 mL), and the tetrathioether (0.21 g, 0.66 mmol) in CH_2Cl_2 (5 mL) was added dropwise with constant stirring. The reaction mixture was stirred for a further 4 h to ensure the completion of the reaction. Block shaped crystals suitable for X-ray diffraction studies and a pale yellow solid appeared after cooling the reaction mixture in a freezer overnight. These were filtered off and dried in vacuo. Yield: 0.27 g, 81%. The complex dissociates very easily in solution, and repeated attempts to recrystallize it to obtain an analytically pure sample led to increasing amounts of "free" ligand. ^1H NMR (300 MHz, $CDCl_3$): 2.07 (s, [12H], Me), 3.83 (s, [8H], CH_2), 7.14 (s, [2H], Ar). IR (cm^{-1}, Nujol): 358(s), 303(m), 321(s), 303(s).

[$(SbCl_3)_2\{$1,2,4,5-$C_6H_2(CH_2SMe)_4\}$]. $SbCl_3$ (0.32 g, 1.41 mmol) was dissolved in MeCN (10 mL), and tetrathioether (0.22 g, 0.68 mmol) in CH_2Cl_2 (5 mL) was added dropwise with constant stirring. A white solid appeared immediately after the addition. The reaction mixture was stirred for a further 2 h to ensure the completion of the reaction. The white solid was filtered off and dried in vacuo. Transparent needle-shaped crystals were obtained from the filtrate on layering with hexane and cooling in a refrigerator for a few days. Yield: 0.46 g, 86% Anal. Calcd for $C_{14}H_{22}Cl_6S_4Sb_2$: C, 21.7; H, 2.9. Found: C, 22.3; H, 3.2. ^1H NMR (300 MHz, $CDCl_3$): 2.08 (s, [12H], Me), 3.82 (s, [8H], CH_2), 7.17 (s, [2H], Ar). IR (cm^{-1}, Nujol): 299(br,s), 278(s), 260(sh).

[$(BiCl_3)_2\{$1,2,4,5-$C_6H_2(CH_2SMe)_4\}$]. $BiCl_3$ (0.30 g, 0.95 mmol) was dissolved in MeCN (4 mL), and tetrathioether (0.15 g, 0.47 mmol) in CH_2Cl_2 (2 mL) was added dropwise with constant stirring. Yellow solid appeared immediately after the addition. The reaction mixture was stirred for a further 2 h to ensure the completion of the reaction. The yellow solid was filtered off and dried in vacuo. Yield: 0.40 g, 90%. Anal. Calcd for $C_{14}H_{22}Bi_2Cl_6S_4 \cdot MeCN$: C, 19.4; H, 2.5; N, 1.4. Found: C, 20.2; H, 2.5; N, 2.1. ^1H NMR (300 MHz, $CDCl_3$): poor solubility. IR (cm^{-1}, Nujol): 2293, 2256 (MeCN), 305(m), 276(m), 231(s). Raman (cm^{-1}): 302(s), 248(s), 236(sh), 222(sh).

[$(AsCl_3)_2\{$1,2,4,5-$C_6H_2(CH_2SeMe)_4\}$]. $AsCl_3$ (0.22 g, 1.21 mmol) was dissolved in CH_2Cl_2 (5 mL), and the tetraselenoether (0.30 g, 0.60 mmol) in CH_2Cl_2 (10 mL) was added dropwise with constant stirring. A pale pink solid appeared immediately after the addition. The reaction mixture was stirred for a further 4 h to ensure the completion of the reaction. The solid was filtered off, washed with dry hexane, and dried in vacuo. Yield: 0.42 g, 80%. This product proved to be very unstable, and we were unable to obtain an analytically pure sample. ^1H NMR (300 MHz, $CDCl_3$): 1.97 (s, [12H], Me), 3.86 (s, [8H], CH_2), 7.01 (s, [2H], Ar). IR (cm^{-1}, Nujol): 385(m), 320(w), 290(w).

X-ray Crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals were obtained as described above. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated (confocal mirrors) Mo-K_α X-radiation (λ = 0.71073 Å). Crystals were held at 120 K in a nitrogen gas stream. Structure solution and refinement were generally routine,[14,15] except as described

---

(14) Sheldrick, G. M. *SHELXS-97, Program for crystal structure solution*; University of Göttingen: Göttingen, Germany, 1997.

(15) Sheldrick, G. M. *SHELXL-97, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

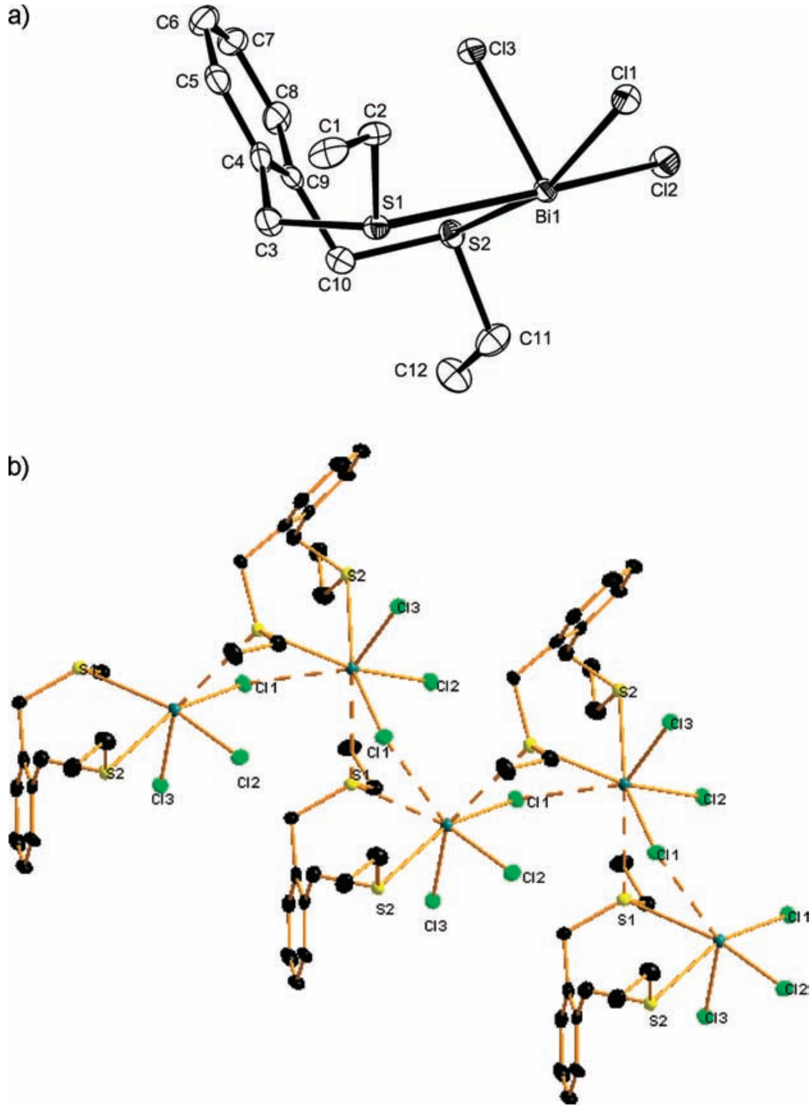

Figure 5. (a) Structure of $[BiCl_3\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ showing the atom labeling scheme. H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. (b) View of the chain polymer showing the long Bi$\cdots$Cl and Bi$\cdots$S contacts. Teal = Bi, green = Cl. yellow = S, black = C.

below, with hydrogen atoms on C added to the model in calculated positions and using the default C−H distance. The crystal of $[(SbCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]\cdot{}^1/_2MeCN$ was of modest quality; however, the compound has the same core geometry as the Bi analogue (except for the presence of MeCN in the former), although detailed analysis of bond lengths and angles should be treated cautiously. The unit cell for $[SbCl_3\text{-}\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ is pseudo orthorhombic ($\beta = 90.375(7)°$) and was originally collected using an orthorhombic strategy. During solution and refinement the true monoclinic symmetry was identified (along with a twin law emulating the pseudo orthorhombic symmetry) and as a result the completeness is low 0.94 ($2\theta = 52°$). The data were reprocessed to obtain the correct β angle and to redo the multiscan absorption correction. Selected bond lengths and angles are given in Tables 2 to 11.

CCDC reference numbers 782404−782414 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

This work investigates the structural consequences of coordinating a series of dithio-, diseleno-, tetrathio-, and tetraselenoether ligands incorporating rigid or semi-rigid aromatic linking groups with MCl_3 (M = As, Sb, or Bi). The main aim was to establish how the rigid, preorganized *o*-phenylene ($o\text{-}C_6H_4(EMe)_2$) and semi-rigid *o*-xylylene backbones ($o\text{-}C_6H_4(CH_2ER)_2$, E = S, R = Me or Et; E = Se, R = Me) and tetrabenzyl ($1,2,4,5\text{-}C_6H_2(CH_2EMe)_4$) (E = S or Se) in the ligands would influence the structures of the resulting complexes and to allow comparison with earlier studies on corresponding MX_3 thio- and seleno-ether complexes with flexible polymethylene backbones.[3]

All of the preparations were conducted in non-coordinating (CH_2Cl_2) or weakly coordinating (MeCN) solvents under anhydrous conditions to minimize competition for coordination to the Lewis acid MCl_3 (M = As, Sb or Bi), see Experimental Section for details. The bismuth and antimony complexes were mostly white through to yellow solids and were all moisture sensitive to some extent. Hence the products were stored and handled in a dry, O_2-free glovebox. Far-IR data

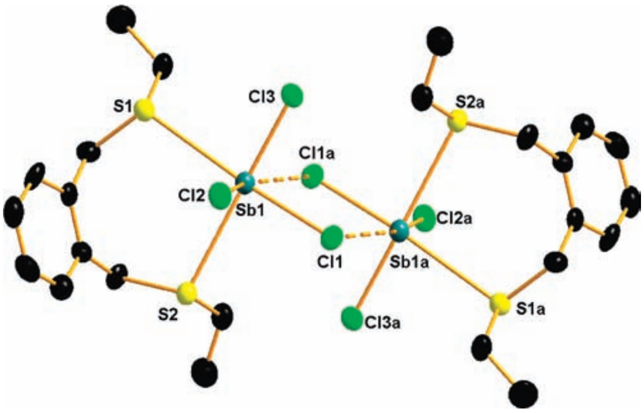

Figure 6. Structure of [$SbCl_3\{o\text{-}C_6H_4(CH_2SEt)_2\}$] showing the atom labeling scheme and the weakly associated dimer structure (dashed lines represent the long Sb···Cl contacts). H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. Symmetry operation: a = 1 − *x*, −*y*, 1 − *z*.

provide evidence of M−Cl bonds, but do not readily identify structural units. Raman spectra were also recorded for the complexes; in general the data obtained were complementary and corroborate the IR assignments, although in some cases the compounds fluoresce or decompose in the laser. As expected, proton NMR spectra are simple, showing small high frequency coordination shifts, consistent with labile systems in which the polymeric structures present in the solid state (vide infra) undergo significant dissociation in solution.

In contrast, with $AsCl_3$ the dithio- and diseleno-ethers gave colorless or pale-yellow oils, and attempts to obtain crystals from some of these produced only "free" ligand. These products are not discussed here since in the absence of crystallographic evidence for complexation it is not possible to ascertain the structural motifs present, and given the significant differences observed even between Bi and Sb homologues, structures cannot be inferred from the heavier analogues. However, the tetrathio- and tetraseleno-ethers, 1,2,4,5-$C_6H_2(CH_2EMe)_4$ (E = S or Se) gave solids, the spectroscopic and structural properties of which are described below.

Dithioether and Diselenoether Complexes. Reaction of a CH_2Cl_2 solution of the dithioether *o*-$C_6H_4(SMe)_2$ with $BiCl_3$ in MeCN solution under anhydrous conditions affords [$BiCl_3\{o\text{-}C_6H_4(SMe)_2\}$] as a yellow solid in good yield. The far-IR spectrum shows three peaks around 350 to 290 cm^{-1}, tentatively assigned as Bi−Cl stretching vibrations.

The crystal structure of [$BiCl_3\{o\text{-}C_6H_4(SMe)_2\}$] (Figure 1, Table 2) shows a chain polymer formed through orthogonally disposed Bi_2Cl_2 units, with one dithioether ligand chelating per Bi atom. The distorted seven-coordinate environment at each Bi atom comprises three short (primary, mutually *cis*) Bi−Cl bonds (2.5232(12)−2.6618(11) Å), two longer Bi···Cl interactions (2.8887(12), 2.9776(11) Å), and two long, secondary Bi···S contacts (3.0075(11), 3.1542(11) Å). The S−Bi−S angle within the five-membered chelate ring is very acute (59.19(3)°), as a consequence of the very long bond distances, with the Me substituents adopting a *meso* configuration.

A similar reaction produces the homologous [$SbCl_3\{o\text{-}C_6H_4(SMe)_2\}$] (Figure 2, Table 3). However, while this compound also adopts a chain polymer structure, it is quite different in detail from the Bi species above. [$SbCl_3\{o\text{-}C_6H_4(SMe)_2\}$] comprises pyramidal $SbCl_3$ units linked into *anti* Sb_2Cl_6 via asymmetric (μ-Cl)$_2$ bridges. These dimers are then linked into chains by weakly bridging dithioethers. Asymmetric coordination within each dithioether is also evident, with each SMe forming long (secondary) bonds to two different Sb atoms and then each have an even longer contact to a neighboring antimony, such that each S atom essentially uses both of the available lone pairs. How much of the asymmetry in Sb−S distances is due to the constrained ligands and crystal packing is unclear. We note that even the short *d*(Sb−S) (3.187(2) Å) is much longer than Bi−S in [$BiCl_3\{o\text{-}C_6H_4(SMe)_2\}$] above, and compares with *d*(Sb−S) (3.09 to 3.29 Å) in [$SbCl_3\{MeS(CH_2)_2SMe\}$].[3e]

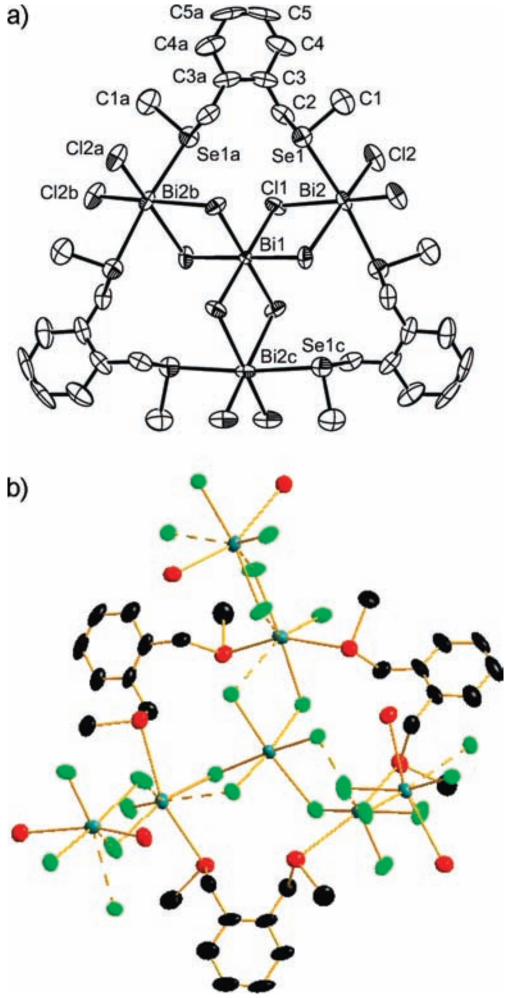

Figure 7. (a) Structure of the Bi1 centered crystallographically independent [$(BiCl_3)_4\{o\text{-}C_6H_4(CH_2SeMe)_2\}_3$] unit showing the atom labeling scheme. H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. Symmetry operations: a = *y*, *x*, −*z*; b = −*x* + *y*, − *x*, *z*; c = −*y*, *x* − *y*, *z*. (b) View of the polymeric structure adopted by the Bi3 centered [$(BiCl_3)_4\{o\text{-}C_6H_4(CH_2SeMe)_2\}_3$] unit showing the weak Cl-bridging through Cl5 to adjacent molecules. Teal = Bi, green = Cl, red = Se, black = C.

The yellow selenoether complex, [$BiCl_3\{o\text{-}C_6H_4(SeMe)_2\}$], is obtained in good yield via an analogous method, although the Sb analogue produced a viscous yellow oil. Both products show simple ^1H NMR spectra, shifted slightly to high frequency of the selenoether itself. The structure of [$BiCl_3\{o\text{-}C_6H_4(SeMe)_2\}$] shows (Figure 3a,

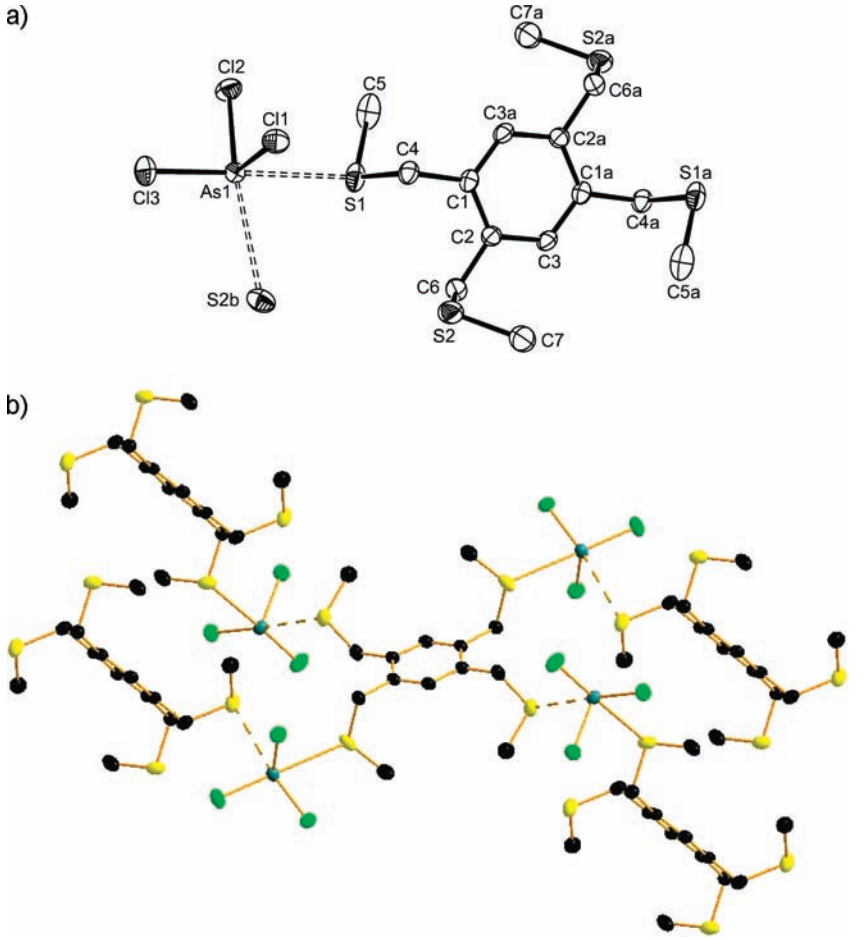

Figure 8. (a) Structure of $[(AsCl_3)_2\{1,2,4,5\text{-}C_6H_2(CH_2SMe)_4\}]$ showing the atom numbering scheme and the two long As···S bonds (dotted). Ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity. The tetrathioether ligand has a center of symmetry. Symmetry operations: a = $1 - x, -y, 1 - z$; b = $3/2 - x, 1/2 + y, 1/2 - z$. (b) View of the 3-dimensional polymer showing the tetrathioether ligand bridging four different $AsCl_3$ units. Teal = As, green = Cl, yellow = S, black = C.

Table 4) distorted square pyramidal units involving pyramidal $BiCl_3$ primary coordination (Bi−Cl = 2.547(3), 2.609(2) Å), and a weakly chelating diselenoether ligand completing the equatorial coordination plane, Bi···Se = 3.1376(13) Å, Se−Bi−Se = 64.10(5)°. The Bi···Se distances are about 0.1 Å longer than in trimethylene-linked diselenoethers or macrocycles.[3b,4b] Each of the Me C-atoms is disordered (50:50) over two positions; however, the C1A···C1Ai distance is only 1.93(5) Å; hence, it is clear that the complex adopts the *DL* form (since if ClA is present, ClBi is required). These monomer units are assembled into infinite chains through long asymmetric bridging Bi···Cl interactions via the three Cl ligands, 3.225(3), 3.314(2) Å, leading to eight-coordinate Bi (Figure 3b).

Reaction of a CH_2Cl_2 solution of o-$C_6H_4(CH_2SMe)_2$ with $BiCl_3$ in MeCN solution affords a yellow solid with stoichiometry $[(BiCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$ from microanalytical measurements. The ^1H NMR spectrum is simple, probably indicating an exchanging system, with the resonances shifted to high frequency of the ligand itself; however, the IR and Raman spectra show several peaks below 300 cm^{-1} consistent with Bi−Cl stretching vibrations.

The crystal structure of $[(BiCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$ shows (Figure 4, Table 5) each Bi atom coordinated to three mutually *cis* Cl ligands (pyramidal $BiCl_3$) with Bi−Cl = 2.522(3) − 2.657(2) Å, constituting the primary bonding. There are then three long (secondary) Bi···S interactions on the opposite face, 2.941(2)−3.188(3) Å, involving three distinct o-xylyl dithioether ligands which bridge adjacent Bi atoms. Atoms Cl3 and Cl5 also form long bridging contacts to the next Bi atom, Bi1···Cl5 = 3.307(2), Bi2···Cl3b = 3.303(3) Å, leading to a very distorted seven-coordinate bismuth center.

The corresponding antimony complex $[(SbCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$ (see Supporting Information) shows the same core geometry, although it also incorporates half a molecule of MeCN solvent per formula unit which occupies the large voids generated in the lattice; however, the crystal quality was modest, and hence, detailed comparisons on geometric parameters are not justified.

Using the ethyl substituted analogue, o-$C_6H_4(CH_2SEt)_2$, with $BiCl_3$ or $SbCl_3$ gives the 1:1 complexes $[MCl_3\{o\text{-}C_6H_4\text{-}(CH_2SEt)_2\}]$. The structure of $[BiCl_3\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ reveals (Figure 5, Table 6) a polymeric assembly again based upon seven-coordinate Bi. There is a primary pyramidal $BiCl_3$, one chlorine of which is involved in bridging to a second Bi, with a chelating dithioether, one S of which forms a bridging interaction to a second bismuth which is ~0.4 Å longer than the Bi−S distance involving the nonbridging sulfur. The different structural motif found here compared to $[(BiCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]$ probably reflects the extra steric requirements of the ethyl groups, since electronically the two ligands will be very similar. The extra bulk of the ethyl substituted ligand is also apparent in the large voids seen in this structure.

The corresponding antimony complex, [SbCl$_3${*o*-C$_6$H$_4$(CH$_2$SEt)$_2$}] (Figure 6, Table 7) is based upon five-coordinate Sb, coordinated via a pyramidal SbCl$_3$ unit with three primary Sb−Cl bonds (2.360(2)−2.471(2) Å) and two S-donor atoms from a weakly chelating dithioether (Sb−S = 2.968(2), 2.985(3) Å; angle S−Sb−S = 98.33(6)°). These units are very loosely assembled into centrosymmetric dimers via bridging at Cl1 (Sb···Cl1 = 3.460(3) Å), hence giving a distorted octahedral coordination environment at each Sb atom. Although this Sb$_2$Cl$_6$ unit is unusual within the present series of compounds and with other thio- and seleno-ethers, it is the common motif in phosphine and arsine complexes.[16]

Reaction of the *o*-xylyl-diselenoether, *o*-C$_6$H$_4$(CH$_2$SeMe)$_2$, with BiCl$_3$ in CH$_2$Cl$_2$/MeCN or SbCl$_3$ in MeCN at ice temperature gives thermally sensitive yellow or colorless solids, respectively. Solution ^{1}H NMR spectra of freshly prepared samples reveal resonances corresponding to coordinated *o*-C$_6$H$_4$(CH$_2$SeMe)$_2$, but (unlike the complexes with *o*-C$_6$H$_4$(SeMe)$_2$ described above) these solutions also degrade over a short period of time at room temperature. Positive and negative electrospray mass spectra (MeCN) on the decomposition products show the presence of the known[17] cyclic selenonium cation [*o*-C$_6$H$_4$(CH$_2$)$_2$SeMe]$^+$ and [Me$_3$Se]$^+$ and the [MCl$_4$]$^-$ anions (and in the case of the Sb compound, [M$_2$Cl$_7$]$^-$) as the dominant species, consistent with degradation of the ligand via Se−C cleavage.

However, it was possible to grow crystals of the bismuth selenoether complex from the reaction mixture maintained at −18 °C over a few days. The structure shows this species is the very unusual [(BiCl$_3$)$_4${*o*-C$_6$H$_4$(CH$_2$SeMe)$_2$}$_3$], markedly different from that containing the analogous thioether (above). This compound crystallizes in a trigonal space group and contains two independent tetrabismuth units within the asymmetric unit. The first (involving Bi1/Bi2) is discrete (Figure 7a, Table 8) with 3-fold symmetry (D_3), comprising a central BiCl$_6$ octahedron linked to each of the other three Bi atoms via two aymmetrically bridging Cl atoms (Bi1−Cl1 = 2.697(5), Bi2−Cl1 = 2.974(6) Å). The outer Bi atoms (Bi2) are also bonded to two mutually *trans* Se donor atoms from distinct diselenoethers (Bi2−Se1 = 3.006(2) Å) and two terminal Cl atoms (Bi2−Cl2 = 2.494(5) Å), and therefore adopt a distorted octahedral coordination geometry. The Bi−Se distances are unremarkable. The diselenoethers lie on the outside of the trigonal array of Bi atoms, bridging adjacent Bi atoms, and with the SeMe groups *anti*. The second tetrabismuth species in the asymmetric unit (involving Bi3/Bi4) shows a similar structure (symmetry C_3) within the unit itself, but with additional long, secondary bonds for example, Bi4···Cl5′ (symm: ′ = *y*, *x*, 1 − *z*) of 3.084(4) Å, which link these into a polymeric array (Figure 7b).

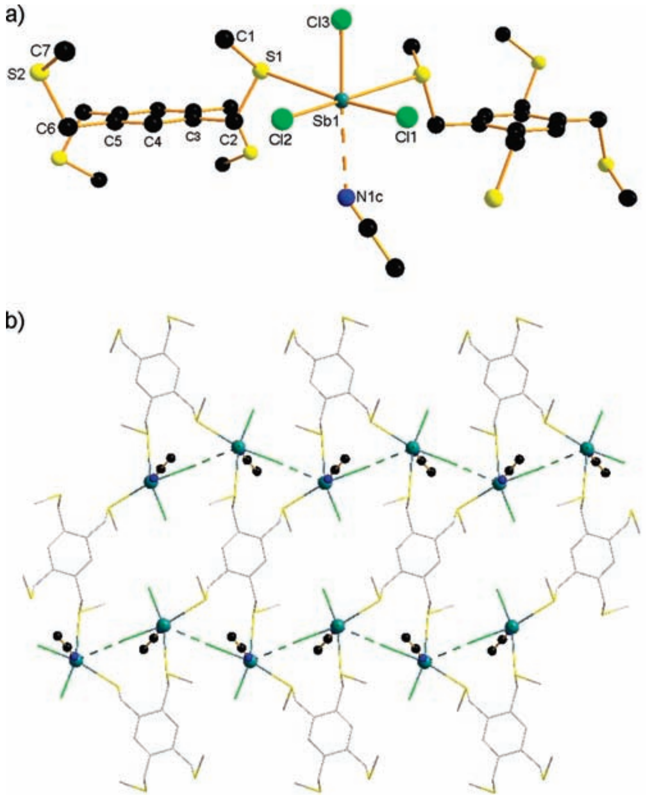

Figure 9. (a) Structure of [{SbCl$_3$(MeCN)}$_2${1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$}] showing the atom numbering scheme. H atoms are omitted for clarity, and displacement ellipsoids are shown at the 50% probability level. Symmetry operations: b = $x-1$, $1/2-y$, $z-1/2$; c = $-x$, $y-1/2$, $1/2-z$. (b) View of the 3-dimensional polymer. Teal = Sb, green = Cl, yellow = S, blue = N, black = C.

Tetrathioether and Tetraselenoether Complexes. The tetrathioether 1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$ reacts with two mol. equiv of MCl$_3$ in CH$_2$Cl$_2$ (As) or CH$_2$Cl$_2$/MeCN (Sb) to give [(AsCl$_3$)$_2${1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$}] and [{SbCl$_3$(MeCN)}$_2${1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$}], respectively, as pale yellow solids. The successful isolation of a powdered solid from the AsCl$_3$ reaction contrasts with the viscous oils obtained using the dithio- and diseleno-ether ligands above. The structure of the former shows (Figure 8, Table 9) the pyramidal AsCl$_3$ fragments (As−Cl = 2.1814(7)−2.2221(8) Å) each weakly coordinated to two (mutually *cis*) S-donor atoms from two different thioether ligands (As···S = 3.0189(8), 3.2693(8) Å), leading to a network polymer arrangement. The S$_2$Cl$_3$ donor set at As leads to an approximately square pyramidal coordination environment, with the longest As−Cl (Cl3) lying *trans* to the shorter As···S and the S−As−S angle is 86.50(2)°. The As···S distances in this complex are significantly longer than those in *fac*-[AsCl$_3$([9]aneS$_3$)] (2.720(4)−2.861(4) Å) and [AsX$_3${MeS(CH$_2$)$_2$SMe}] (X = Br or I: range 2.70 to 2.88 Å).[3c] There is no evidence of π-stacking interactions between the aromatic rings.

[{SbCl$_3$(MeCN)}$_2${1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$}] (Figure 9, Table 10) adopts a very similar overall arrangement to that of [(AsCl$_3$)$_2${1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$}], except for an additional weakly coordinated MeCN ligand at Sb (Sb···N = 2.955(9), Sb···S = 3.001(2), 3.059(2) Å,

---

(16) (a) Clegg, W.; Elsegood, M. R. J.; Graham, V.; Norman, N. C.; Pickett, N. L.; Tavakkoli, K. *Dalton Trans.* **1994**, 1753–1757. (b) Clegg, W.; Elsegood, M. R. J.; Graham, V.; Norman, N. C.; Pickett, N. L. *Dalton Trans.* **1993**, 997–998. (c) Genge, A. R. J.; Hill, N. J.; Levason, W.; Reid, G. *Dalton Trans.* **2001**, 1007–1012.

(17) (a) Gurnani, C.; Levason, W.; Ratnani, R.; Reid, G.; Webster, M. *Dalton Trans.* **2008**, 6274–6282. (b) Levason, W.; Ollivere, L. P.; Reid, G.; Webster, M. *J. Organomet. Chem.* **2010**, *695*, 1346–1352.

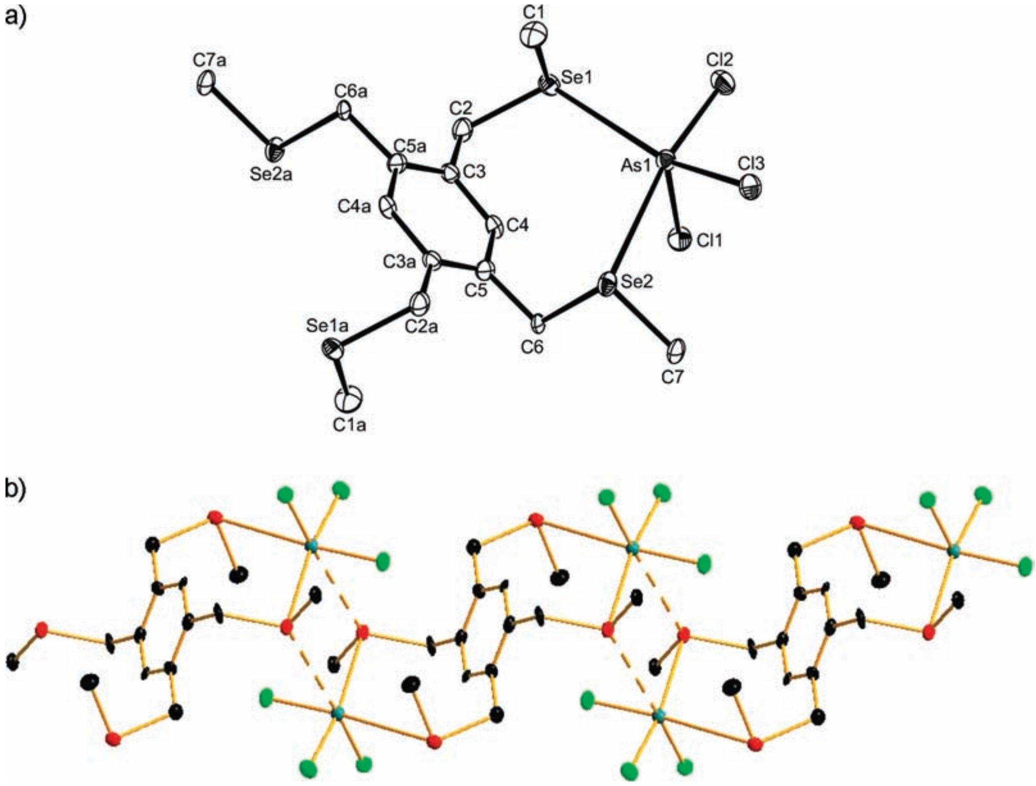

Figure 10. (a) Structure of [$(AsCl_3)_2\{1,2,4,5\text{-}C_6H_2(CH_2SeMe)_4\}$] showing the atom numbering scheme and the long As···Se bonds. Ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity. Symmetry operation: a = 1 − *x*, 2 − *y*, −*z*. (b) View of the chain polymer structure. Teal = As, green = Cl, red = Se, black = C.

S−Sb−S = 113.22(6)°), leading to a distorted six-coordinate geometry.

The conformation of the coordinated tetrathioether ligand in these complexes is very similar to that observed in the uncomplexed form, with the S atoms directed outward and the CH_2SMe groups on adjacent ring carbon atoms on opposite sides of the ring.[10b]

[$(AsCl_3)_2\{1,2,4,5\text{-}C_6H_2(CH_2SeMe)_4\}$] was obtained as a light pink solid by a similar reaction. The structure confirms (Figure 10, Table 11) the 2:1 As:ligand ratio; however, in this compound the selenoether ligand is weakly chelating to the pyramidal $AsCl_3$ units, surprisingly via the Se donor atoms in the 2,4- and 1,5- positions (i.e., the two chelating Se atoms are in *meta* relationship in each case, forming eight-membered chelate rings), with the Me substituents in the *DL* configuration with respect to the As1Se1Se2 plane. This is a very unusual coordination mode for this ligand, typically chelation of the 1,2,4,5-$C_6H_2(CH_2EMe)_4$ ligands occurs via the *ortho*-disposed donor atoms (1,2- and 4,5-positions), forming seven-membered chelate rings.[11] This leads to a chain polymer (Figure 10b) with bridging tetraselenoethers linking the $AsCl_3$ units and one Se atom on each ligand (Se2) using both of its lone pairs to bridge (weakly) between two As atoms. This gives rise to a very distorted octahedral coordination environment at each As atom, via three primary As−Cl and three long, secondary As···Se interactions. The secondary As···Se distances are in the range 3.289(2) to 3.602(2) Å, the sum of the van der Waals radii As + Se = 3.75 Å.[18] These are considerably longer than *d*(As−Se) observed in other selenoether complexes with As(III), for example, [$(AsCl_3)_4([24]aneSe_6)$] (2.994(2), 3.005(2); As−Se(*exo*) = 3.091(2) Å) and [$(AsCl_3)_2([16]aneSe_4)$] (As−Se = 2.922(3), 3.164(3) Å) and [$(AsCl_3)([8]aneSe_2)$] (2.7940(7) Å) ([24]aneSe$_6$ = 1,5,9,13,17,21-hexaselenacyclotetracosane, [16]aneSe$_4$ = 1,5,9,13-tetraselenacyclohexadecane, [8]aneSe$_2$ = 1,5-diselenacyclooctane).[3b,8]

Conclusions

This study has revealed a number of structural motifs previously unknown within complexes of the Group 15 halides, perhaps the most notable example being the [$(BiCl_3)_4\{o\text{-}C_6H_4(CH_2SeMe)_2\}_3$]. The wide range of structural motifs evident in these systems is consistent with shallow potential wells associated with the complexes, such that very small variations in the systems, for example, through changes in the donor atom type, linking groups, ligand denticity, and steric requirements play a significant role in determining the precise network structure adopted by a particular complex. The structures also depend upon the nature of the Group 15 acceptor element, and the data are consistent with increasing Lewis acidity as Group 15 is descended. It is also notable that while a range of M:L ratios has been observed within the new series of complexes, only one species has been observed in each MCl_3-ligand system. Consideration of the M to S/Se distances reveals that when M = Bi these fall within a relatively narrow range around 3.0 Å, and do not change with the increase in covalent radius of Se versus S.[18] In contrast, when M = Sb, the range is wider, and the geometries about M are often much less regular, which may well be due to some

---

[18] See web-site: www.ccdc.cam.ac.uk/products/csd/radii/ for values used by the CCDC and literature references: Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverria, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

stereochemical activity at Sb, whereas for Bi the data suggest the lone pair occupies the 6s orbital. A similar pattern has been observed in the series [MCl_3([8]aneSe$_2$)].[4a] For M = As far fewer (only two) complexes could be isolated, and in both cases the core geometry is based upon a square pyramid, with the lone pair possibly in the vacant coordination site.

Acknowledgment. We thank the Commonwealth Commission U.K. for the award of a scholarship to S.M. and EPSRC for support. We also thank Drs. M. Jura and M. Rogers for assisting with the crystallographic data collection.

Supporting Information Available: Cif files for the crystal structures described. Also, crystallographic details for the compound [$(SbCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}_3]\cdot{}^1/_2MeCN$, together with a figure of the structure. This material is available free of charge via the Internet at http://pubs.acs.org.