DALTON
PERSPECTIVE

# Macrocyclic and polydentate thio- and seleno-ether ligand complexes of the p-block elements

**William Levason and Gillian Reid**

*Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

***Received 5th July 2001, Accepted 12th September 2001***

**The diverse structures exhibited by complexes of p-block (Group 13–15) halides with acyclic and macrocyclic thio-, seleno-, and telluro-ethers are described. Examples range from six-coordinate monomers through to one-, two- or three-dimensional network infinite polymers with structural motifs often very different to those found with d-block elements.**

## Introduction

The coordination chemistry of macrocyclic and polydentate thioether and selenoether ligands has been studied in detail with elements from across the transition series, as detailed in several review articles which have appeared over the last decade.[1–4] In contrast, complexes of these ligands with elements from the p-block have been much less studied. This article aims to provide an overview illustrating recent results in the area. It is not intended to be comprehensive and will specifically focus on macrocyclic and polydentate (in practice bidentate and tripodal ligands) thio- and seleno-ether ligands only, and concentrates on those systems for which structural data are available. The inclusion of only bidentate telluroether complexes reflects the fact that while a small number of tritelluroether complexes with these elements have been prepared, none have yet been structurally characterised. While most of the discussion will deal with homoleptic ligands, occasional reference will be made to mixed-donor ligands where appropriate. We have chosen to concentrate on systems for which there are structural data since the p-block complexes are typically very labile and moisture/air sensitive in solution, hence the information derived from spectroscopic techniques is often very limited. Also, the presence of an electron pair on the p-block element which may or may not be stereochemically active and the frequent occurrence of 'secondary bonding interactions' (below) makes the structures much more difficult to predict reliably than for d-block complexes. As we show below however, the occurrence of one or both of these effects often leads to highly unusual and interesting structural motifs and polynuclear assemblies. It is worth noting that the structures discussed are of course only the species for which X-ray quality crystals were obtained. Other species may form under different reaction conditions or using different solvent systems.

## Bonding

Although it has received much less theoretical effort than in transition metal analogues, bonding in main group complexes where the octet rule is formally exceeded, has attracted considerable recent interest. The original model invoking *n*d orbital involvement leading to for example, central atom $sp^3d^2$ bonding

**Bill Levason**

*Bill Levason obtained his BSc and PhD from UMIST and was appointed to a lectureship in Southampton in 1976, promoted to senior lecturer 1988, reader 1994 and Professor of Inorganic Chemistry in 1999. His research interests include the synthesis and coordination chemistry of selenium, tellurium, antimony and bismuth donor ligands, early transition metal chemistry, main group coordination chemistry, and heteropolyanions. He has co-authored over 300 research papers.*

**Gill Reid**

*Gill Reid gained her BSc and PhD from the University of Edinburgh. Following a postdoctoral fellowship, she took up a lectureship in Inorganic Chemistry at the University of Southampton in 1991 and was promoted to senior lecturer in 1999. Her research interests are wide-ranging, encompassing many aspects of macrocyclic, transition metal and main group coordination chemistry, including the synthesis of macrocyclic and polydentate ligands involving Group 15 (P and As) and Group 16 (S, Se and Te) donor atoms, studies of their coordinating properties with metal ions and organometallic fragments and the synthesis and properties of metallocyclic species. She has co-authored over 120 research papers on aspects of this work.*

DOI: 10.1039/b105973b

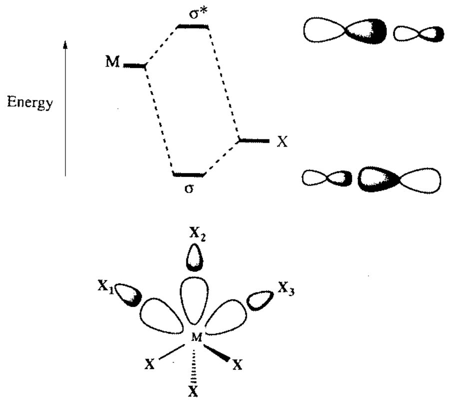

**Fig. 1** Schematic of the donor–acceptor bonding model.

in an octahedron, has fallen out of favour since the *n*d orbitals are now considered to be too high in energy and too diffuse to be a significant contribution,[5] and has been replaced by either *electron-rich multi-centre* bonding[6] or *donor–acceptor* bonding.[7,8] The concept of *secondary bonding* first introduced by Alcock,[9] is also very important in these systems. This recognised that, in addition to *normal* or *primary* bonds, many metalloid and non-metal compounds also exhibit longer directional interactions, shorter than van der Waals interactions but significantly longer than primary bonds. It has also been argued that the electron-rich three-centre and donor–acceptor bonding are not distinct approaches and are easily brought into correspondence.[10]

The qualitative donor–acceptor model is convenient and will be used in this Perspective. A good account as applied to Group 15 compounds has been provided by Carmalt and Norman.[11] The approach envisages primary M–X σ bonding (in the present article M is the main group element and X mostly halide) where the σ orbital is polarised towards the more electronegative X and the corresponding M–X σ* antibonding orbital is polarised towards M (Fig. 1). If the σ* lies low enough in energy it can behave as an acceptor orbital towards a Lewis base (in our case a thio- or seleno-ether) or a bridging halide from a neighbouring monomer unit. The extent and strength of the secondary bonding will vary with the electronegativity of both M and X and the match (or mismatch) in orbital size, since both are reflected in the energy of M–X σ*. Attempts to more quantitatively model secondary bonding of the heavy p-block elements appear to be difficult since the potential wells are very shallow.

A further factor effecting structures of the ($n$ − 2) oxidation state complexes is the extent of stereochemical activity of the lone pair, particularly in MX$_6$Y systems (here Y is the lone pair). The matter has been discussed in detail,[12] and here we just note that in the complexes discussed in this article, the geometries are often quite distorted, although it is difficult in many cases (particularly with M = Sb or Bi) to decide if this is the effect of the lone pair or a consequence of the ligand geometry and polymeric structures adopted.

## p-Block complexes with thioether and selenoether ligands

### Group 13

For the lighter Group 13 elements, it is surprising to note that although they were among the first examples of main group complexes with macrocyclic thioether ligands to be reported, [AlMe$_3$([12]aneS$_4$)]$_n$ ([12]aneS$_4$ = 1,4,7,10-tetrathiacyclododecane) and [(AlMe$_3$)$_4$([14]aneS$_4$)] ([14]aneS$_4$ = 1,4,8,11-tetrathiacyclotetradecane) remain the only aluminium examples. However, both species show structural features that recur frequently throughout the p-block complexes. The former exhibits *exo* coordination to the AlMe$_3$ fragment through one S-atom. The environment at Al(III) is then a distorted trigonal bipyramid *via* a further secondary Al···S interaction from an adjacent [AlMe$_3$([12]aneS$_4$)] unit. This leads to an infinite one-dimensional chain polymer. The primary Al–S bond distance (2.718(3) Å) is significantly shorter than that which we define as secondary (3.052(3) Å).[13] In marked contrast, [(AlMe$_3$)$_4$([14]aneS$_4$)] involves four terminal exocyclic AlMe$_3$ fragments, one coordinated to each of the S-donor atoms. This gives rise to the much more common tetrahedral geometry at Al(III) (Al–S = 2.512(2), 2.531(2) Å).[14]

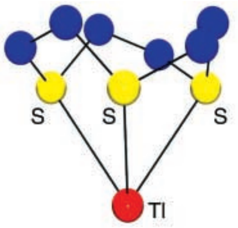

**Fig. 2** View of the [Tl([9]aneS$_3$)]$^+$ cation in the polymeric structure of [Tl([9]aneS$_3$)]PF$_6$, redrawn from ref. 17.

There appear to be no reports of gallium complexes, however, [InCl$_3$([9]aneS$_3$)] ([9]aneS$_3$ = 1,4,7-trithiacyclononane) has been prepared by Wieghardt and co-workers. Although no structural data are available on this compound, it is likely to involve *fac*-coordination by [9]aneS$_3$ giving a pseudo-octahedral monomer.[15] The ligand 1,4-dithiane (L) gives [InMe$_3$(L)]$_n$, involving infinite chains of trigonal bipyramidal In(III), with equatorial Me groups and axial coordination to bridging dithiane ligands, In–S = 2.970(1), 3.134(1) Å.[16]

For thallium only the +1 oxidation state has been seen and the structures exhibit much less regular motifs and variable coordination numbers. Secondary interactions are a significant feature of the structures adopted. [Tl([9]aneS$_3$)]PF$_6$ shows tridentate [9]aneS$_3$ coordinated to a single thallium, Tl–S = 3.092(3), 3.110(3), 3.114(3) Å. There is a further secondary Tl···S interaction to an adjacent [Tl([9]aneS$_3$)]$^+$ unit, 3.431(3) Å, giving infinite chains. A further series of four weak, secondary Tl···F interactions to PF$_6^-$ anions cross-link these chains and give formally eight-coordinate Tl(I), Tl···F = 3.228(8), 3.389(8), 3.246(8), 3.272(9) Å.[17] The very long Tl–S distances give rise to acute S–Tl–S angles, 67.31–67.57° (Fig. 2). The corresponding complex with the hexathiacrown [18]aneS$_6$ (1,4,7,10,13,16-hexathiacyclooctadecane), [Tl([18]aneS$_6$)]PF$_6$ adopts a one-dimensional chain structure derived from two primary Tl–S bonds, 3.164(5), 3.205(7) Å and four secondary Tl···S interactions to one [18]aneS$_6$ molecule, 3.315(6), 3.347(7), 3.356(6), 3.370(5) Å. These [Tl([18]aneS$_6$)]$^+$ cations are then weakly associated to give the polymer through two much longer intermolecular Tl···S interactions, 3.689(6), 3.688(6) Å. The macrocyclic thioether ligand adopts a 'cradle-like' conformation with the Tl(I) ion occupying the bowl which is created.[18] A similar structure is seen for the mixed N/S-donor macrocyclic system [Tl([18]aneN$_2$S$_4$)]PF$_6$ ([18]aneN$_2$S$_4$ = 7,16-diaza-1,4,10,13-tetrathiacyclooctadecane).[18] The octathia macrocycle [24]aneS$_8$ (1,4,7,10,13,16,19,22-octathiacyclotetracosane) also gives a 1 : 1 Tl : L ratio even in the presence of excess TlPF$_6$. The structure of [Tl([24]aneS$_8$)]PF$_6$ shows a chain polymer, with [24]aneS$_8$ lying across a crystallographic inversion centre and coordinated to two Tl ions on opposite sides of the mean plane of the macrocycle. The Tl ions then occupy two-fold sites and are eight-coordinate through four primary Tl–S bonds (Tl–S = 3.2851(13), 3.2413(11) Å) and four secondary Tl···S interactions (Tl···S = 3.4305(14), 3.4734(14) Å) to give a sinusoidal polymer.[19]

There are no structural reports concerning macrocyclic or polydentate selenoether complexes of any of the Group 13 elements.

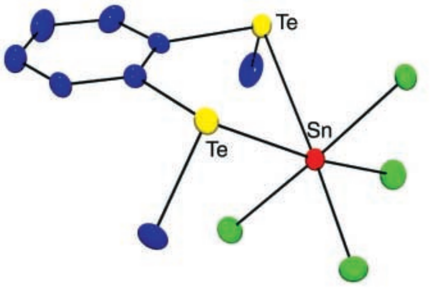

**Fig. 3** View of the crystal structure of $[SnCl_4\{o\text{-}C_6H_4(TeMe)_2\}]$.

## Group 14

No complexes of Si(IV) or Ge(IV) have been reported and *in situ* $^{29}Si$, $^{73}Ge$ and $^{77}Se$ NMR studies indicate no interaction in solutions of $MX_4$ and several mono- or bi-dentate thio- or seleno-ethers even at low temperature.[20] However, Sn(IV) halides readily coordinate two neutral S-, Se- or Te-donors to give pseudo-octahedral monomers.[20–24] In contrast to most of the systems discussed in this article, complexes of tin are well suited to solution NMR studies in that they are molecular and, at least at low temperature, ligand exchange is slow on the NMR time-scales. This allows identification of solution structures, including meso and DL invertomers for the chelating bidentate ligand complexes.

While the bidentate ligands are constrained to give *cis*-coordination, $Me_2S$ and $Me_2Se$ give both *cis*- and *trans*-disubstituted species in solution. Unusually, the *cis*- and *trans*-$[SnBr_4(Me_2S)_2]$ co-crystallise, and the crystal structures of these, and also of the *trans*-$[SnX_4(Me_2Se)_2]$ (X = Cl or Br) have been described.[23,25] In contrast, although both $[SnCl_4(Me_2Te)_2]$ and $[SnBr_4(Me_2Te)_2]$ have been isolated, they are extremely unstable and very readily hydrolyse even as solids.[20] The crystal structures of $[SnX_4\{o\text{-}C_6H_4(TeMe)_2\}]$ (X = Cl or Br) have been obtained, confirming the presence of the meso form of the ditelluroether (Fig. 3).[20] Notably these species constitute the only structurally characterised telluroether complexes with the main group elements to-date. In all of these bidentate ligand (L–L) systems, *cis*-$[SnX_4(L–L)]$, the Sn–X bond distances *trans* to X are significantly longer than those *trans* to S/Se/Te. This is attributed to a *trans* influence on the hard Sn(IV) centre of X > S/Se/Te, which is the reverse of that well established with late transition metal ions. Also, the axial X–Sn–X angles are markedly less than the 180° expected for a regular octahedron, with the $SnX_2$ unit bending towards the neutral ligand.

Variable temperature multinuclear NMR studies ($^{1}H$, $^{119}Sn$, $^{77}Se$, $^{125}Te$) have been conducted on $[SnX_4(L–L)]$ (L–L = bidentate thio-, seleno- or telluro-ether) and demonstrate the acceptor ability $SnCl_4 > SnBr_4 \gg SnI_4$, and that dissociation in solution increases with donor type $S < Se \ll Te$. In fact, $SnI_4$ is a very poor Lewis acid and while some complexes have been identified at low temperature in solution, none have been isolated or structurally characterised.

Given the solution lability in these systems, it is very surprising that the two methylene-bridged ligands $MeSCH_2SMe$ and $MeSeCH_2SeMe$ form strained, four-membered ring chelate structures with $SnCl_4$.[24] These are the only structurally characterised examples of chelation by these ligands, which more commonly behave as bridging bidentate ligands to transition metal ions.

Without exception, the complexes of Sn(IV) with Group 16 donor ligands are six-coordinate, normally retaining the four Sn–X bonds. Thus, even with polythia macrocyclic ligands (except $[9]aneS_3$—see below), only two S atoms are taken up by the tin centre. The only reported (macro)cyclic thioether complexes with Sn are those involving $[9]aneS_3$, $[18]aneS_6$ and 1,5-dithiacyclooctane with Sn(IV). Thus, $[18]aneS_6$ reacts with one molar equivalent of $SnCl_4$ to give the 2 : 1 complex $[(SnCl_4)_2([18]aneS_6)]$, involving neutral $SnCl_4$ fragments coordinated in an *exo* fashion to two adjacent S-donor atoms of the macrocycle giving pseudo-octahedral coordination at tin, Sn–S = 2.535(10)–2.689(13) Å.[26] Perhaps surprisingly, rather than giving the chelate complex (or bridging $SnCl_4$ fragments), the cyclic dithioether 1,5-dithiacyclooctane (L) gives the centrosymmetric *trans*-$[SnCl_4(\eta^1\text{-}L)_2]$, *d*(Sn–S) = 2.602(1) Å.[27] On the other hand, $SnCl_4$ reacts with $[9]aneS_3$ in MeCN to give a product of stoichiometry $3SnCl_4{\cdot}2[9]aneS_3$ which has been shown to contain the cation–anion species $[SnCl_3([9]aneS_3)]_2[SnCl_6]$. The cation is six-coordinate with a *fac* $[9]aneS_3$ ligand, Sn–S = 2.618(3)–2.657(4) Å.[26] The formation of the Sn(IV) cationic $[SnCl_3([9]aneS_3)]^+$ may result from a combination of the exceptional ligating character of $[9]aneS_3$ (noted previously on complexes of many d-block elements) and the Lewis acid behaviour of further $SnCl_4$ which in the reaction abstracts a Cl to form the stable $[SnCl_6]^{2-}$. Since there is no solution spectroscopic information on this reaction system, the isolation of the salt may be mainly a consequence of its low solubility.

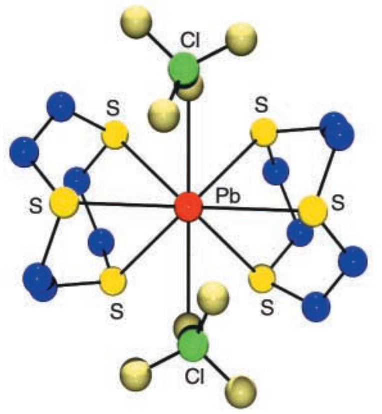

**Fig. 4** View of the crystal structure of $[Pb([9]aneS_3)_2(ClO_4)_2]$, redrawn from ref. 28.

In all of these systems the Sn–S bond distances are typically *ca.* 0.2–0.3 Å longer than the Sn–Cl distances and, although there is a spread of bond distances, there is no clearly defined distinction between primary and secondary bonding, such as has been observed in many of the compounds from Groups 13 and 15.

There are no complexes of the strongly oxidising Pb(IV), however $Pb(ClO_4)_2$ reacts with $[9]aneS_3$ and the octathia macrocycles $[24]aneS_8$ and $[28]aneS_8$ to afford $[Pb([9]aneS_3)_2(ClO_4)_2]$,[28] $[Pb_2([24]aneS_8)(ClO_4)_4]$ and $[Pb_2([28]aneS_8)(ClO_4)_4]$ ($[28]aneS_8$ = 1,4,8,11,15,18,22,25-octathiacyclooctacosane)[19] respectively. The structure of the trithia ligand complex shows eight-coordination at Pb(II) derived from two tridentate $[9]aneS_3$ ligands and two weakly associated $\eta^1$-coordinated $ClO_4^-$ ligands at 2.72(2) Å. The Pb–S bond distances lie in the range 3.015(5)–3.129(5) Å (Fig. 4). The overall geometry is a distorted square antiprism and the lone pair on Pb(II) is effectively stereochemically inactive—this contrasts with the structures of Pb(II)/$[9]aneN_3$ ($[9]aneN_3$ = 1,4,7-triazacyclononane) complexes where the lone pair is clearly stereochemically active.[28] The structure of $[Pb_2([28]aneS_8)(ClO_4)_4]$ shows very distorted eight-coordinate Pb(II) centres bonded to four adjacent thioether donor atoms, Pb–S = 2.861(2)–3.137(2) Å, two $\mu\text{-}O_2ClO_2$ and one $\eta^2\text{-}O_2ClO_2$ ligands complete the coordination environment.[19]

A substantial range of lead complexes involving mixed S/N- and S/O-donor macrocycles has also been reported. Subtle ligand modifications lead to significant changes in their selectivities for Pb(II).[29]

The chemistry of lead species with acyclic and macrocyclic selenoether and telluroether ligands has yet to be explored.

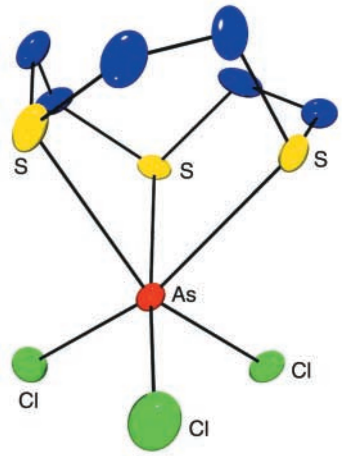

**Fig. 5** View of the crystal structure of [$AsCl_3$([9]ane$S_3$)].

## Group 15

There are no structural reports of thio-, seleno- or telluro-ether ligand complexes with $PX_3$ acting as a Lewis acid. However, examples are known for arsenic, antimony and bismuth. In many of these species secondary bonding interactions play an important role in directing the assembly of the structures as we will demonstrate below.

We have recently initiated an investigation of the coordination chemistry of $AsX_3$ (X = Cl, Br or I) with thio- and selenoether ligands and have isolated and characterised the first such adducts, including complexes with $MeS(CH_2)_2SMe$, [9]ane$S_3$, [14]ane$S_4$, [8]ane$Se_2$ (1,5-diselenacyclooctane), [16]ane$Se_4$ (1,5,9,13-tetraselenacyclohexadecane) and [24]ane$Se_6$ (1,5,9,13,17,21-hexaselenacyclotetracosane).[30] Attempts to isolate complexes with $MeSe(CH_2)_2SeMe$ and $MeC(CH_2EMe)_3$ (E = S or Se) have yielded only oils, which may reflect the poorer Lewis acidity of $AsX_3$ compared to the heavier $SbX_3$ and $BiX_3$ for which a much wider range of complexes has been isolated—see below.

The crystal structure of [$AsCl_3$([9]ane$S_3$)] (Fig. 5) shows six-coordinate monomers involving distorted octahedral $S_3X_3$-coordination at As(III), with the lone pair effectively stereochemically inactive, As–S = 2.720(4)–2.861(4) Å.[30] In contrast, the structure of [($AsCl_3$)([8]ane$Se_2$)] shows an infinite one-dimensional ladder with [8]ane$Se_2$ 'uprights' and planar $As_2Cl_6$ μ-chloro bridged dinuclear units functioning as 'rungs'. The Se atoms therefore adopt mutually *trans* coordination sites and there is no obvious stereochemically active lone pair on the arsenic.[30] This structure resembles that of [($BiCl_3$)([8]ane$Se_2$)] below.[30] With the tetraselenoether ligand [16]ane$Se_4$ we obtained the 2 : 1 [$(AsCl_3)_2$([16]ane$Se_4$)] which adopts a sheet polymer structure with five-coordinate As(III) coordinated to three terminal Cl's and two Se donor atoms from *exo* coordination to two different macrocyclic rings. This five-coordinate geometry approximates to an 'octahedron' with one vacant vertex which we assume is occupied by the As-based lone pair, As–Se = 2.922(3), 3.164(3) Å.[30] This species is similar to [$(SbBr_3)_2$([16]ane$Se_4$)]—see Fig. 9.

Although complexes of [24]ane$Se_6$ with antimony and bismuth have been prepared, only the arsenic chloride derivative, which has an unexpected 4 : 1 As : ligand stoichiometry, has given X-ray quality crystals. The [$(AsCl_3)_4$([24]ane$Se_6$)] (Fig. 6) is extremely unusual, displaying a new structural type in that it shows both *endo* and *exo* coordination of the As(III) centres and forms discrete molecules.[31] An unusual feature is the occurrence of an asymmetric $As_2Cl_6$ μ-chloro bridged dinuclear unit coordinated within the macrocyclic ring, giving a distorted octahedral $Se_2Cl_4$ coordination environment at the *endo* As atoms. Interestingly, the *exo* As centres adopt a different coordination number and geometry. Those *exo* to the ring form four-coordinate distorted sawhorse units through coordination to three terminal Cl's and a single Se atom. The lone pair on the *exo* As atoms is assumed to occupy the third equatorial vertex of a 'trigonal bipyramid'. The hexaselenoether macrocycle therefore uses all six Se donor atoms to bind to the As centres; two mutually *trans* pairs of adjacent Se atoms chelate to the As centres of the endocyclic dinuclear fragment, with each of the two remaining, mutually *trans* Se atoms coordinating $\eta^1$ (*exo*) to discrete $AsCl_3$ units, As–Se(*endo*) = 2.994(2), 3.005(2); As–Se(*exo*) = 3.091(2) Å.[31]

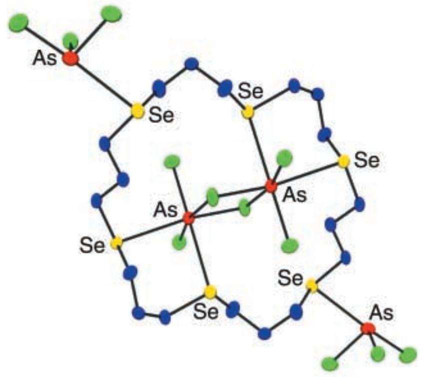

**Fig. 6** View of the crystal structure of [$(AsCl_3)_4$([24]ane$Se_6$)].

As mentioned earlier, the only acyclic dithio- or diselenoether complexes to be isolated are [$AsX_3\{MeS(CH_2)_2SMe\}$] (X = Cl, Br or I). The crystal structures of the bromo and iodo species reveal discrete asymmetric μ-dibromo bridged $As_2X_6$ units with a chelating dithioether on each As centre in the meso arrangement.[30] These molecules are in the *isomer A* form according to the nomenclature used by Norman and coworkers for phosphine complexes of antimony and bismuth trihalides.[11] Although only a small range of arsenic(III) adducts has been characterised, these exhibit a surprising structural diversity and incorporate a variety of motifs. Furthermore, the dimeric structure and $X_4S_2$ donor set in these As(III) species contrasts with the two-dimensional network and $Cl_3S_3$ donor set seen for [$SbCl_3\{MeS(CH_2)_2SMe\}$] and the mononuclear $Cl_3S_4$ donor set for [$BiCl_3\{MeS(CH_2)_2SMe\}_2$]—below.

Unlike in the arsenic systems above, $SbX_3$ (X = Cl, Br or I) react readily with a wide range of cyclic and acyclic bidentate and tripodal thio- and seleno-ether ligands in anhydrous MeCN or thf to afford the 1 : 1 species [$SbX_3$(L)]. Similarly, reaction of $MeTe(CH_2)_3TeMe$ or $MeC(CH_2TeMe)_3$ (L) with one molar equivalent of $SbX_3$ yields orange/brown powdered solids of stoichiometry [$SbX_3L$], although no structural data have been obtained for the telluroether species to-date.[32] In contrast to the tin(IV) systems, attempts to record multinuclear NMR spectra of these antimony complexes have been largely unsuccessful since most are polymeric and poorly soluble in non-coordinating solvents. In the few cases where data were obtained, the spectra closely resembled those of the uncoordinated ligand, suggesting substantial dissociation and/or fast exchange. The solids range in colour from white through yellow, to deep orange/red depending on the halide. The diffuse reflectance UV-visible spectra show ill-defined charge transfer transitions tailing into the visible region, but these do not appear to provide a structural fingerprint.[33]

The dithio- and diseleno-ether compounds, [$SbCl_3\{MeS(CH_2)_2SMe\}$], [$SbBr_3\{MeS(CH_2)_3SMe\}$] and [$SbCl_3\{MeSe(CH_2)_3SeMe\}$], exhibit unusual infinite one- or two-dimensional structures derived from primary Sb–X bonding with weak, secondary Sb–Se(S) interactions to bridging thio- or seleno-ethers.[33,34] The structure of [$SbCl_3\{MeS(CH_2)_2SMe\}$] shows a distorted octahedral coordination environment at Sb derived from three terminal Cl's and three S atoms from different dithioethers, one terminal and two μ-bridging.[33] On each dithioether the second S atom coordinates to an adjacent Sb

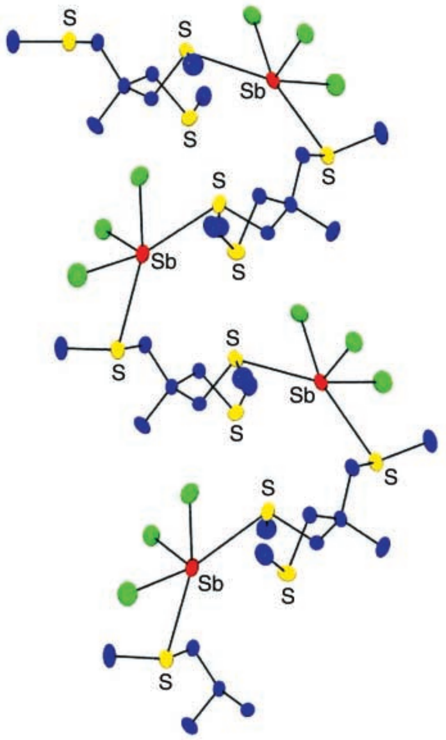

**Fig. 7** View of part of the infinite chain formed by [$SbCl_3\{MeC(CH_2SMe)_3\}$].

centre generating a two-dimensional network. The Sb–S bond distances are in the range 3.094(2)–3.294(2) Å, indicating secondary interactions, while the Sb–Cl distances are 2.384(2)–2.428(2) Å, similar to those in $SbCl_3$ itself. The structure of [$SbBr_3\{MeS(CH_2)_3SMe)\}$] is very similar.[34] The selenoether analogue [$SbCl_3\{MeSe(CH_2)_3SeMe\}$] is markedly different, adopting an infinite one-dimensional chain structure.[34] The Sb centres exhibit a distorted octahedral coordination environment comprising two *cis* terminal Cl's, two μ-Cl's and two mutually *cis* Se atoms from different diselenoethers. Thus, the chains are derived from weakly associated, asymmetric $Sb_2Cl_6$ units linked by bridging diselenoether ligands. The Sb–Se distances of *ca.* 3.2 Å are very similar to the Sb–S distances in the dithioether species above, again suggesting rather weak, secondary interactions. Crystal structures for [$SbCl_3$(1,4-dithiane)][35] and [$SbCl_3$(1,4-dithiacycloheptane)][36] have also been reported and both adopt polymeric structures with similar patterns of bond lengths to those above.

The structures obtained for the three compounds [$SbCl_3\{MeC(CH_2SMe)_3\}$], [$SbBr_3\{MeC(CH_2SeMe)_3\}$] and [$SbI_3\{MeC(CH_2SMe)_3\}$] exhibit a variety of different motifs for relatively small alterations in tripod donor type and halide. The structure of [$SbCl_3\{MeC(CH_2SMe)_3\}$] shows (Fig. 7) five-coordinate Sb(III) centres forming an infinite one-dimensional 'helical' structure derived from linking of these units by bridging $MeC(CH_2SMe)_3$ ligands. Coordination is *via* one S-donor to each Sb(III), *i.e.* each metal centre coordinates to sulfur atoms from two different thioether ligands, which function as bidentates. The weak secondary Sb···S bond lengths are 3.172(2), 3.106(2) Å.[33] In contrast, [$SbI_3\{MeC(CH_2SMe)_3\}$] involves six-coordinate antimony. Within this one-dimensional polymer each antimony atom is in a distorted octahedral environment, coordinated to two sulfur donor atoms, two terminal iodine ligands and two μ-bridging iodine atoms. The bridging unit is asymmetric, with bond lengths indicative of both primary Sb–I bonds (2.861(2) Å) and secondary Sb···I bonds (3.516(2) Å).[33] The Sb–S distances are 3.021(6) and 2.973(6) Å. The contrast between the chloro- and iodo-species is consistent with reduced lone pair activity in the heavier halogen system, as has been observed previously in other systems.[11]

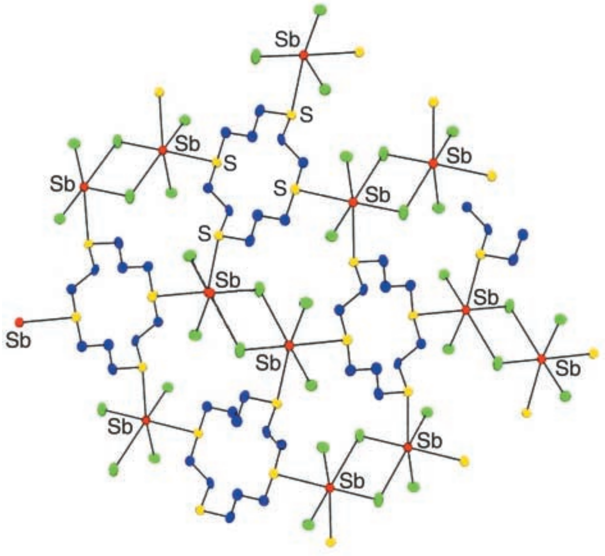

**Fig. 8** View of part of the infinite three-dimensional network formed by [$(SbBr_3)_2([14]aneS_4)$].

The structure of [$SbBr_3\{MeC(CH_2SeMe)_3\}$] is also a chain polymer, with six-coordinate, distorted octahedral Sb(III). The coordination set comprises three terminal Br and a *fac*-coordinated set of three Se-donors, from one bidentate selenoether and one monodentate selenoether.[33] This may be contrasted with the seven-coordinate Bi(III) in [$BiCl_3\{MeC(CH_2SeMe)_3\}$]—below.

[$SbCl_3([9]aneS_3)$] is a chain structure with seven-coordinate Sb, derived from tridentate ligation to one $[9]aneS_3$ and a further S-atom from an adjacent macrocycle, together with three terminal Cl's. The Sb–S bond distances span a considerable range, from 3.156(3)–3.409(3) Å, possibly suggesting that the Sb-based lone pair points between two of the S atoms of the tridentate thioether ring.[37] In contrast, [$SbI_3([9]aneS_3)$] is a discrete molecular compound with distorted octahedral $S_3I_3$ coordination at Sb, with no real evidence for stereochemical activity of the lone pair on Sb and significantly shorter Sb–S bond lengths, 2.840(2)–2.895(2) Å, probably reflecting both the decreased coordination number and the inactivity of the Sb lone pair.[38] Using the tetrathioether, $[14]aneS_4$, the complex [$(SbBr_3)_2([14]aneS_4)$] is formed,[33] which adopts an infinite coordination network, the repeat unit being an asymmetric $Sb_2Br_6S_4$ edge-shared bioctahedron (Fig. 8), The Sb atoms are coordinated to two terminal Br atoms and two μ-bridging Br atoms, with two terminal, mutually *cis* S atoms from different macrocycles completing the octahedron. Each $[14]aneS_4$ unit contributes one sulfur donor atom per antimony, bridging four antimony atoms in total. The only other macrocyclic thioether complex of Sb(III) reported is [$(SbCl_3)_2([18]aneS_6)$] which is molecular with two *fac* six-coordinate antimony centres disposed on opposite sides of the mean plane of the macrocycle.[37]

The cyclic selenoethers $[8]aneSe_2$, $[16]aneSe_4$ and $[24]aneSe_6$ form 1 : 1 (usually) or 1 : 2 (occasionally) macrocycle : $SbX_3$ complexes. The crystal structure of [$(SbBr_3)_2([16]aneSe_4)$] (Fig. 9) shows a two-dimensional sheet structure with $SbBr_3$ units coordinated weakly to two Se atoms from different selenoethers, giving distorted square pyramidal Sb(III). The macrocycles therefore function as exocyclic ligands bridging four Sb centres.[34]

A substantial range of thio- and seleno-ether complexes of Bi(III) halides and involving bi- and tri-dentate acyclic ligands and macrocycles has been reported and their structures established. These exhibit a surprising structural diversity from

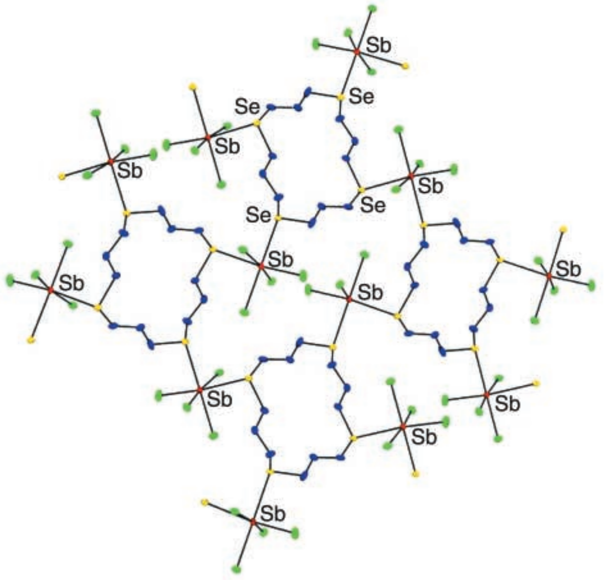

**Fig. 9** View of part of the infinite two-dimensional network formed by $[(SbBr_3)_2([16]aneSe_4)]$.

discrete monomers through oligomers to one-, two- and three-dimensional polymers.

With $MeS(CH_2)_2SMe$, the 1 : 2 chelate complex $[BiBr_3\{MeS(CH_2)_2SMe\}_2]$ is obtained. This species is a distorted pentagonal bipyramid with axial Br's, Bi–S = 2.918(5)–3.090(5), Bi–Br = 2.787(2)–2.826(2) Å. One dithioether ligand is in the meso form while the other is DL. This is only the second structurally authenticated example of both invertomers occurring in a single molecular complex.[39] The related $PhS(CH_2)_2SPh$ affords a 2 : 1 Bi : L complex, $[(BiBr_3)_2\{PhS(CH_2)_2SPh\}]$, even with excess L. The structure of this species is an infinite two-dimensional sheet composed of chains of orthogonal asymmetric μ-bridged $Bi_2Br_6$ units cross-linked by bridging dithioether ligands. The donor set at Bi comprises four bridging Br's (2.693(3)–3.274(3) Å), one terminal Br (2.596(2) Å) and one S atom (3.082(6) Å).[39] A very different species of formula $[(BiCl_3)_4\{MeS(CH_2)_3SMe\}_4]$ is obtained from $BiCl_3$ and ligand in $CH_2Cl_2$. In this case we observe (Fig. 10) a $Bi_4Cl_4$ 'open cradle' core which is cross-linked to other similar units by bridging dithioethers, to give a three-dimensional polymer. Each Bi is coordinated to two terminal Cl's (2.533(7), 2.538(7) Å), two μ-Cl's (2.913(7), 2.969(6) Å) and two S atoms (2.857(7), 2.977(7) Å). The geometry at Bi is therefore a severely distorted octahedron with an open triangular face which may accommodate the lone pair on bismuth. Additional long range Bi · · · Cl interactions (3.268(7) Å) link across the $Bi_4Cl_4$ units to form a pseudo-cubane core.[40]

The structures of $[BiBr_3\{MeS(CH_2)_3SMe\}]$ and $[BiX_3\{MeSe(CH_2)_3SeMe\}]$ (X = Cl or Br) are two-dimensional networks with co-planar $Bi_2X_6$ units bridged by thio- or seleno-ether ligands which occupy mutually *trans* coordination sites. The variation in Bi–Cl and Bi–Br distances are indicative of both primary and secondary interactions, while the Bi–S and Bi–Se distances are probably best regarded as weak, secondary bonds and in fact there is little difference between the latter, suggesting relatively stronger Bi–Se interactions.[39]

The structure of $[BiCl_3\{MeC(CH_2SeMe)_3\}]$ is also a two-dimensional sheet (Fig. 11), in this case incorporating seven-coordinate Bi(III) ions coordinated to two bridging Cl's, two terminal Cl's, two Se atoms from bidentate coordination by one tripod and one Se from the uncoordinated selenoether function on an adjacent molecule. The triselenoethers therefore cross-link these Bi units to give the infinite network. Similar Bi–Cl and Bi–Se bond length distributions are observed.[39] Surprisingly the iodo analogue, $[Bi_2I_6\{MeC(CH_2SeMe)_3\}_2]$ is quite different from the chloro species, comprising discrete dinuclear units derived from a twisted $Bi_2I_6$ rhomboidal core, with one bidentate triselenoether coordinated to each Bi centre, giving a distorted octahedral geometry.[39] Using the silicon-apex tripod, $MeSi(CH_2SMe)_3$, illustrates how very subtle changes in the ligand dramatically change the structure of the product. This gives the 1 : 1 polymer with $BiCl_3$ which contains single μ-Cl bridged $Cl_2Bi–Cl–BiCl_3$ units. There are therefore two different distorted octahedral Bi environments, one with bidentate coordination to one tripod and four Cl's, and the other with bidentate coordination to one tripod and monodentate coordination to another, and three Cl's.[41]

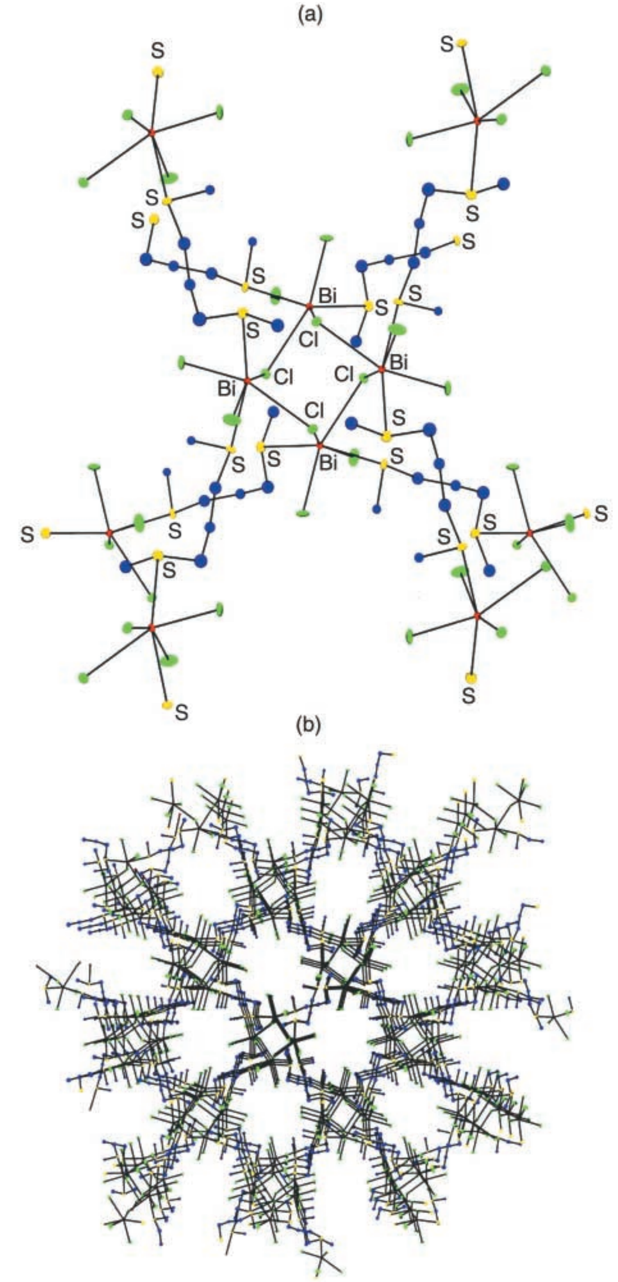

**Fig. 10** Two views of the infinite three-dimensional network formed by $[(BiCl_3)_4\{MeS(CH_2)_3SMe\}_4]$.

The $[BiCl_3([12]aneS_4)]$, $[BiCl_3([15]aneS_5)]$ and $[BiCl_3([18]aneS_6)]$ all adopt discrete monomeric structures based on a pyramidal $BiCl_3$ unit coordinated to four, five and six S atoms respectively from the macrocycle, giving coordination numbers from seven to nine. The Bi · · · S distances (2.987(3)–3.346(8) Å) are relatively long and the complexes may be regarded as derived from an essentially unperturbed $BiCl_3$ unit in which the secondary Bi · · · Cl interactions present in solid $BiCl_3$ are

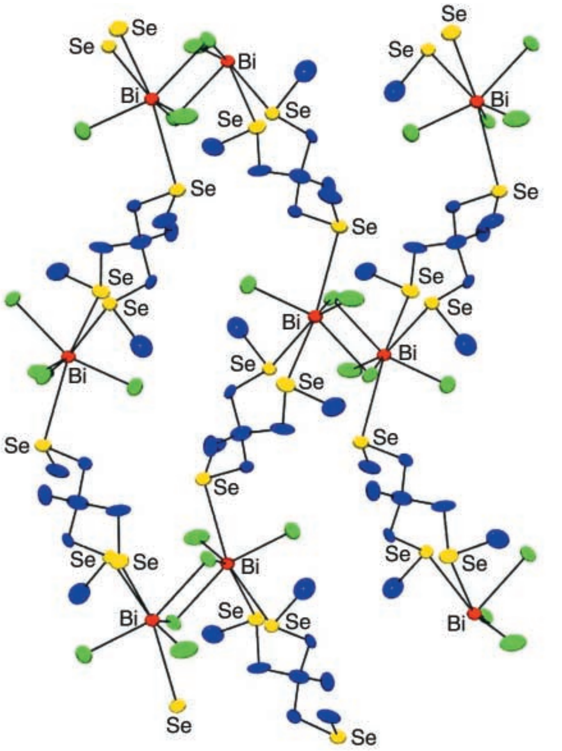

**Fig. 11** View of part of the two-dimensional network formed by $[BiCl_3\{MeC(CH_2SeMe)_3\}]$.

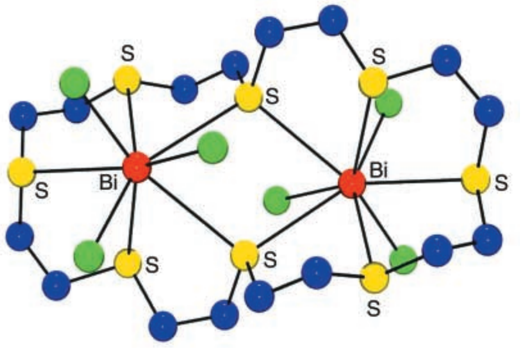

**Fig. 12** View of the crystal structure of $[(BiCl_3)_2([24]aneS_8)]$, redrawn from ref. 19.

replaced by up to six secondary Bi···S interactions.[42,43] The related $[(BiCl_3)_2([24]aneS_8)]$ involves two eight-coordinate Bi(III) centres with five macrocyclic S atoms (two of which bridge the Bi centres) and three Cl's. The $BiCl_3$ fragments are on opposite sides of the mean plane of the macrocycle (Fig. 12).[19]

The selenoether macrocyclic complexes $[BiX_3(L)]$ (L = $[8]aneSe_2$, $[16]aneSe_4$ and $[24]aneSe_6$) are obtained as intensely coloured yellow to red solids in moderate yield by treatment of the parent $BiX_3$ with L in anhydrous MeCN. The crystal structures of $[BiCl_3([8]aneSe_2)]$ and $[BiBr_3([16]aneSe_4)]$ (Fig. 13) each reveal infinite one-dimensional ladder structures assembled from nearly coplanar $Bi_2X_6$ 'rungs' linked by bridging L 'uprights', the Se atoms occupying mutually *trans* coordination sites. The selenoether macrocycles adopt exocyclic arrangements and in $[BiBr_3([16]aneSe_4)]$ it is alternate Se atoms which coordinate to the Bi centres, leaving the other two Se atoms non-coordinating. These species contrast with molecular structures of the thioether macrocyclic complexes above.[44]

### Group 16 and 17

There are no complexes of polydentate or macrocyclic thioether complexes with selenium or tellurium halides. A number of diiodine charge transfer complexes involving thioether macrocycles are known, including for example $[n]aneS_4{\cdot}I_2$ ($n$ = 12, 14 or 16), $[18]aneS_6{\cdot}I_2$ and $2[9]aneS_3{\cdot}4I_2$, which mostly adopt extended structures with iodine–sulfur interactions linking them into various polymeric networks.[45,46]

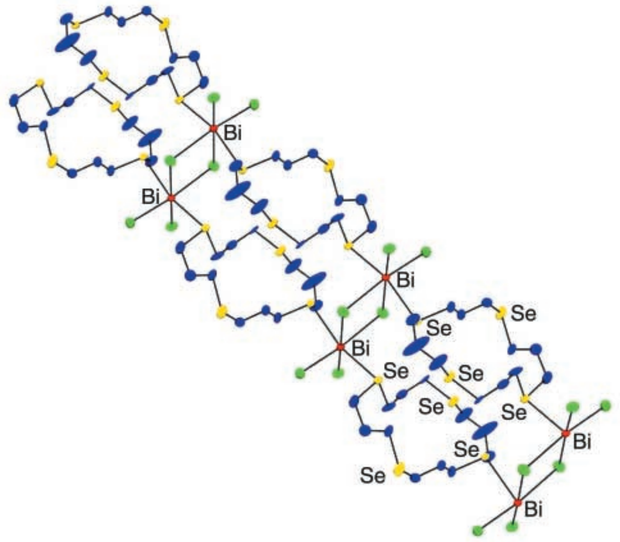

**Fig. 13** Crystal structure of $[BiBr_3([16]aneSe_4)]$.

## Conclusions

In attempting to draw together some themes from the structures described above, we would begin with three *caveats*:

(1) the field is relatively new with the majority of the results being obtained in the mid–late 1990s;

(2) the structures described reflect (obviously!) those which have yielded X-ray quality crystals and since the structures in many cases contain weak secondary interactions, different conditions/solvents may lead to quite different building blocks;

(3) the depth of coverage across the p-block is very uneven at present.

Thus, while we may predict six-coordination for new Sn(IV) complexes with some confidence, the range of ligands used with Tl(I) or Pb(II) is currently too small to predict structural motifs for new complexes, although high coordination numbers and irregular geometries are to be expected. For Sb(III), Bi(III) and less clearly (due to the more limited number of examples) for As(III), the bewildering range of coordination numbers, highly distorted geometries, stereochemical activity or inactivity of the lone pair, and range of polymeric networks, defies any simple rationalisation. This probably indicates that the energy differences between several possible structures are small, and small changes in ligand architecture, co-ligands or crystallisation conditions, may produce dramatic changes in complex structure. It would also suggest that some of the above complexes may be obtainable in more than one structural form, although no examples are known at present. The structural variety exhibited even for bidentate thio- or seleno-ether complexes seems far greater than that in for example, diphosphine analogues. We attribute this to the Group 16 donor atoms in the ligands having two lone pairs, greater flexibility and lower steric demands, and hence are able to link pyramidal $MX_n$ or dimer $M_2X_n$ units into a variety of polymeric motifs, in some cases using both lone pairs on the Group 16 atom. Main group complexes with phosphorus or arsenic macrocycles remain a completely unexplored area, so comparison with the thia- or selena-crown complexes is not possible.

Areas requiring further study include complexes with most of the Group 13 Lewis acids (both halides and alkyls), Sn(II), possibly $TeX_4$ and Ge(II). Thio- or seleno-ether complexes of

Group 13–15 fluorides are also currently absent. Whilst the strong M–F σ bonds which are highly polarised toward F, may make the M–F σ* orbitals very poor acceptors towards soft S or Se donors, $SbF_3$, $AsF_3$ and $SbF_5$ are worthy of examination. In this review we have also not mentioned the pentahalides of Group 15; whilst $AsCl_5$ is too unstable, $SbCl_5$ and even $PCl_5$ may form adducts. We have very recently obtained some compounds containing $SbCl_5$, although structural data are not yet available.[30] Telluroether complexes are fully characterised only with Sn(IV), although we have species with Sb(III) and Bi(III) of unknown structures. The presently limited telluroether chemistry, reflects both the smaller range of ligand types known and their relatively recent availability.[4] However, since our studies of d-block telluroether complexes,[4] have shown that these often differ significantly from those of their lighter analogues, further studies of the p-block compounds should be rewarding.

In summary, this Perspective has provided an overview of an area little explored until recently—we hope it has illustrated some highly unusual structures, which may also be compared and contrasted with the supramolecular architectures and networks formed by transition metal systems, *e.g.* Cu(I) and Ag(I), currently a very active research area. We aimed to show that substantial progress has been made of late, but much remains to be explored, and if this Perspective stimulates new work in the area, it will have more than fulfilled its purpose.

## Acknowledgements

The authors would like to thank the EPSRC, the University of Southampton for supporting this work and the Cambridge Crystallographic Data Centre for access to the facilities. We also thank Mr N. J. Hill for assistance in preparing the figures. Many of the compounds discussed in this article which come from our own laboratories are mainly from the efforts of three postgraduate students, Anthony R. J. Genge, Andrew J. Barton and Nicholas J. Hill.

## References

1 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1.
2 S. R. Cooper and S. C. Rawle, *Struct. Bonding (Berlin)*, 1990, **72**, 1.
3 E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109.
4 W. Levason, S. D. Orchard and G. Reid, *Coord. Chem. Rev.*, 2001, in the press.
5 A. E. Reed and P. V. R. Schleyer, *J. Am. Chem. Soc.*, 1990, **112**, 1434.
6 R. E. Rundle, *J. Am. Chem. Soc.*, 1963, **85**, 112.
7 P. Pyykko, *Chem. Rev.*, 1997, **97**, 597.
8 C. K. Prout and J. D. Wright, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 659.
9 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.
10 G. A. Landrum and R. Hoffmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 1887; G. A. Landrum, N. Goldberg and R. Hoffmann, *J. Chem. Soc., Dalton Trans.*, 1997, 3605.
11 C. J. Carmalt and N. C. Norman, in *The Chemistry of Arsenic, Antimony and Bismuth*, N. C. Norman, ed., Blackie, London, 1998, ch. 1.
12 R. J. Gillespie and I. Hagittai, *The VSEPR Model of Molecular Geometry*, Allyn and Bacon, Boston, 1991.
13 G. H. Robinson and S. A. Sangokoya, *J. Am. Chem. Soc.*, 1988, **110**, 1494.
14 G. H. Robinson, H. Zhang and J. L. Atwood, *Organometallics*, 1987, **6**, 887.
15 K. Wieghardt, M. Kleine-Boynann, B. Nuber and J. Weiss, *Inorg. Chem.*, 1986, **25**, 1654.
16 J. Blank, H.-D. Hausen, W. Schwarz and J. Weidlein, *J. Organomet. Chem.*, 1993, **443**, 154.
17 A. J. Blake, J. A. Greig and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1991, 529.
18 A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1992, 2987.
19 A. J. Blake, D. Fenske, W.-S. Li, V. Lippolis and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 3961.
20 A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 4549.
21 C. T. G. Knight and A. E. Merbach, *Inorg. Chem.*, 1985, **24**, 576.
22 S. E. Dann, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1996, 4471.
23 S. E. Dann, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 2207.
24 A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 4479.
25 N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1994, 695.
26 G. R. Willey, A. Jarvis, J. Palin and W. Errington, *J. Chem. Soc., Dalton Trans.*, 1994, 255.
27 M. M. Olmstead, K. A. Williams and K. Musker, *J. Am. Chem. Soc.*, 1982, **104**, 5567.
28 H.-J. Küppers, K. Wieghardt, B. Nuber and J. Weiss, *Z. Anorg. Allg. Chem.*, 1989, **577**, 155.
29 See A. Balshall, M. McPartlin, B. P. Murphy, H. R. Powell and S. Walker, *J. Chem. Soc., Dalton Trans.*, 1994, 1383 and references therein.
30 N. J. Hill, W. Levason and G. Reid, unpublished work.
31 A. J. Barton, N. J. Hill, W. Levason and G. Reid, *J. Am. Chem. Soc.*, in the press.
32 A. J. Barton, N. J. Hill, W. Levason and G. Reid, unpublished work.
33 A. J. Barton, N. J. Hill, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 2001, 1621.
34 A. J. Barton, N. J. Hill, W. Levason, B. Patel and G. Reid, *Chem. Commun.*, 2001, 95.
35 G. Kiel and R. Engler, *Chem. Ber.*, 1974, **107**, 3444.
36 M. Schmidt, R. Bender and C. Burschka, *Z. Anorg. Allg. Chem.*, 1979, **454**, 160.
37 G. R. Willey, M. T. Lakin, M. Ravindran and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1991, 271.
38 S. Pohl, D. Haase and M. Peters, *Z. Anorg. Allg. Chem.*, 1993, **619**, 727.
39 A. J. Barton, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 2000, 859.
40 A. R. J. Genge, W. Levason and G. Reid, *Chem. Commun.*, 1998, 2159.
41 H.-W. Yim, K. Lam, A. L. Rheingold and D. Rabinovich, *Polyhedron*, 2000, **19**, 849.
42 G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 591.
43 G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 1339.
44 A. J. Barton, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 2000, 2163.
45 A. J. Blake, F. Cristiani, F. A. Devillanova, A. Garau, L. M. Gilby, R. O. Gould, F. Isaia, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1997, 1337.
46 A. J. Blake, F. A. Devillanova, A. Garau, L. M. Gilby, R. O. Gould, F. Isaia, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 2037.