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Recent Developments in Thio-, Seleno-, and Telluro-ether Ligand Chemistry

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ABSTRACT: *New routes developed recently to overcome the difficulties usually associated with the sequential introduction of Te centers into polytelluroethers and the introduction of tellurium into macrocyclic compounds are described, including the synthesis of the first facultative telluro-ethers, $RTe(CH_2)_3Te(CH_2)_3TeR$, $R = Me$ or Ph, and the first tridentate S_2Te-donor macrocycles and a tetradentate S_3Te-donor macrocycle.*

The first systematic investigations into the preparation and characterization of coordination complexes of MX_3 ($M = As, Sb, Bi$; $X = Cl, Br, I$) involving polydentate and macrocyclic thio- and seleno-ether ligands are then discussed. The structures of examples of each class of compound are described, including the first examples of seleno-ether adducts of the group 15 acceptors. A more limited range of telluroether derivatives has been identified and the structure of the first example of this type is included. These species serve to demonstrate the wide structural diversity exhibited by these systems and the factors directing the assembly of these structures are highlighted. Heteroatom Chem 13:550–560, 2002; DOI 10.1002/hc.10100

INTRODUCTION

A considerable volume of literature concerning the coordination chemistry of macrocyclic thioether ligands has appeared over the last two decades. When contained within a macrocyclic framework, thio-ethers function as very effective ligands for a wide range of transition-metal ions, and many of the complexes show unexpected and unusual physical and chemical properties [1,2]. The ability of ligands, such as [9]aneS_3 (1,4,7-trithiacyclononane) and [18]aneS_6(1,4,7,10,13,16-hexathiacyclooctadecane), to enable discrete, reversible, one-electron redox processes at the coordinated metal center and to stabilize very rare radical species, such as Au(II) [3], Pd(III) [4], and Rh(II) [5], is particularly notable and this has provided the impetus for further studies on macrocyclic thio-ethers and studies on the heavier seleno- and telluro-ether analogues [6,7].

The group 16 chalcogenoether ligands ER_2 ($E =$ S, Se, or Te) are usually regarded as modest σ-donors to transition-metal centers, with little evidence for significant π-effects, except in a small number of specific complexes [8]. However, as group 16 is descended the electronegativity of the chalcogen reduces, and this is manifested in increased $E \rightarrow M$ σ-donation. Thus, theoretical and experimental data support the conclusion that $E \rightarrow M$ σ-donation increases from $S \rightarrow Se \rightarrow Te$ in low valent transition-metal systems [9,10]. Our earlier work was focused on comparable series of complexes involving Mn(I), Re(I), Rh(I), Ir(I), Cr(0), Mo(0), and W(0) [10–12],

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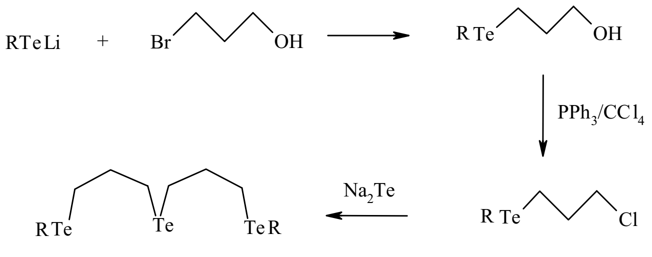
and these studies provide convincing evidence (from ^{55}Mn (or ^{95}Mo), ^{77}Se and ^{125}Te NMR spectroscopic studies, force constant analyses on the CO stretching vibrations and, to a lesser extent, X-ray structural studies) for seleno-ethers, and especially telluro-ethers, being superior σ-donor ligands compared to the analogous thio-ether ligands in these low valent systems. The results also prompted us to develop synthetic routes to polydentate and macrocyclic Te-containing ligands.

The first series of ditelluro-ethers was prepared ca. 14 years ago [13]. While telluro-ether ligand chemistry has grown over the last decade, the still very limited range of ligands reflects the considerably greater problems in the synthesis of other than the simplest types, compared to the thio-ether analogues. For example, the instability of the Te—H bond in tellurols (RTeH) means that these are not useful synthons, while the weak Te—C bond means that bi- or polydentates with $-TeCH_2CH_2Te-$ or *cis*-TeCH=CHTe-linkages are very unstable to elimination and cannot be isolated [13]. These problems are particularly pronounced in the synthesis of polydentate telluro-ethers and Te-containing macrocycles, where sequential generation of new Te—C bonds often competes with facile Te—C bond cleavage in precursors [13]. As a result of these problems, until recently only two tritelluro-ethers, the tripodal $MeC(CH_2TeR)_3$ (R = Me [13] or Ph [10]), the spirocyclic $C(CH_2TePh)_4$ [13], and one macrocycle 1,5,9-tritelluracyclododecane [14] have been described. We have also reported the preparation and characterization of the first linear tritelluro-ethers $Te(CH_2CH_2CH_2TeR)_2$ (R = Me, L^1, or Ph, L^2) [15]. Their synthesis depends upon the chlorination of $RTe(CH_2)_3OH$ with PPh_3/CCl_4 [16] to $RTe(CH_2)_3Cl$, which then reacts with Na_2Te in liquid ammonia to give $Te(CH_2CH_2CH_2TeR)_2$ (Scheme 1). Attempts to halogenate the alcohol function in this compound by using $SOCl_2$ or PBr_3 leads to halogenation of the tellurium, while attempts to introduce alternative leaving groups such as tosylate failed, yielding large amounts of elemental tellurium. However, the mild chlorination reaction using PPh_3/CCl_4 means that the new tritelluro-ether ligands can be obtained in good yield as orange oils after purification by flash column chromatography [15]. The new tritelluro-ethers do not have the steric limitations of the tripodal type and, therefore, support a wider range of metal center geometries, including both *fac* and *mer* coordination [15]. Importantly, the synthetic route developed to $RTe(CH_2)_3Cl$ should be extendable to allow preparation of tetradentate and macrocyclic telluro-ethers and this work is currently under investigation.



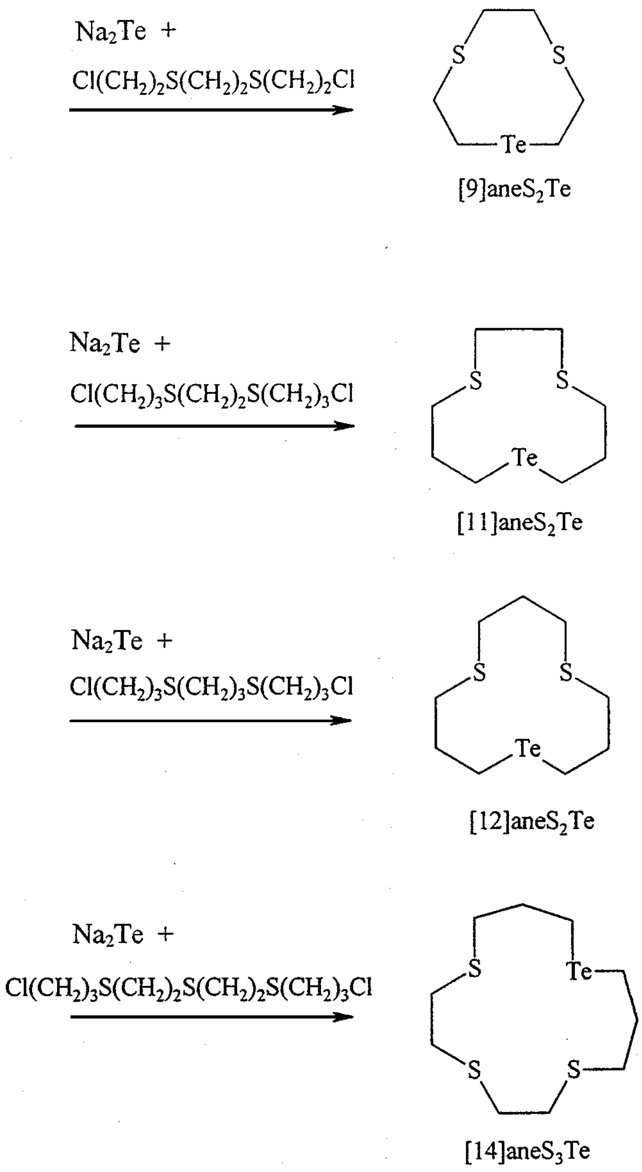
R = Me or Ph

SCHEME 1 Preparation of $RTe(CH_2)_3Te(CH_2)_3TeR$ (R = Me or Ph).

In view of the paucity of Te-containing macrocycles in the literature, we have also been trying to develop viable synthetic methods to allow Te atoms to be introduced into cyclic ligands. In our initial studies we developed a general synthesis for mixed donor Te-containing macrocycles, including the first series of mixed thia/tellura crowns, $[9]aneS_2Te$, $[11]aneS_2Te$, $[12]aneS_2Te$, and $[14]aneS_3Te$. These were prepared according to Scheme 2, in which Na_2Te in liquid NH_3 is treated with the appropriate α,ϖ-dichlorothioalkane. Following workup, the macrocyclic ligands are obtained as light yellow poorly soluble solids in moderate yields [17]. The coordination chemistry of these and other related Te-containing macrocycles are under investigation using a range of medium and low oxidation state transition-metal ions, including Pt(II), Rh(III), Ru(II), Mn(I), Mo(0), Cu(I), and Ag(I) [17,18]. We have structurally characterized the complex $[Ag([11]aneS_2Te)]BF_4$ which shows coordination to Ag(I) through all three donor atoms to give a cationic chain polymer with distorted trigonal planar coordination at silver via two S atoms from one macrocycle and the Te atom from another, Ag—S = 2.521(3), 2.634(3) and Ag—Te = 2.674(1) Å (Fig. 1) [17]. Further work towards the preparation of polytelluro-ether macrocycles is underway.

THIO-, SELENO-, AND TELLURO-ETHER COMPLEXES OF MX_3 (M = As, Sb, or Bi)

The coordination chemistry of macrocyclic and polydentate thio-ether and seleno-ether ligands has been studied in detail with elements from across the transition series, as described in several review articles [1,2,6,7]. In contrast, complexes of these ligands with elements from the p-block have been much less studied [19]. We have become interested in the Lewis acid chemistry of the group 15 species MX_3 (M = As, Sb, Bi) with thio-, seleno-, and telluro-ether ligands. In part this interest arises from the presence of an



Conditions: slow addition of a thf solution of the appropriate dichloro precursor to freshly prepared Na_2Te in liquid NH_3.

SCHEME 2 Preparation of [9]-, [11]-, and [12]-aneS_2Te and [14]aneS_3Te.

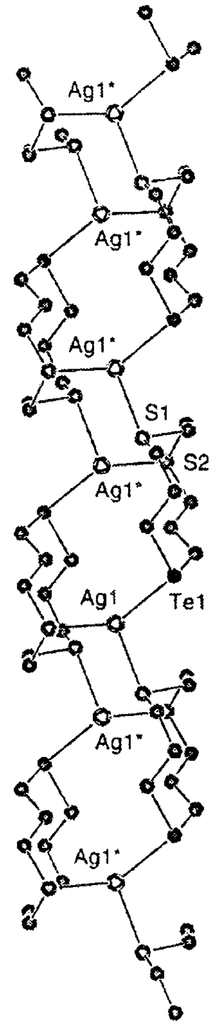


FIGURE 1 Crystal structure of the infinite 1-D cation in [Ag([11]aneS_2Te)]BF_4.

electron pair on the p-block element which may or may not be stereochemically active and the frequent occurrence of "secondary bonding interactions" [20], which make the structures much more difficult to predict reliably than for d-block complexes. However, as discussed later, the occurrence of one or both of these effects often leads to highly unusual and interesting structural motifs and polynuclear assemblies.

Prior to our work in this general area, the structures of the thio-ether macrocyclic complexes [$BiCl_3$([12]aneS_4)] ([12]aneS_4 = 1,4,7,10-tetrathiacyclododecane), [$BiCl_3$([15]aneS_5)] ([15]aneS_5 = 1, 4,7,10,13-pentathiacyclopentadecane), and [$BiCl_3$-([18]aneS_6)] had been reported by Willey and coworkers. All these species 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 replaced by up to six secondary Bi···S interactions [21,22]. The related [$(BiCl_3)_2$([24]aneS_8)] ([24]aneS_8 = 1,4, 7,10,13,16,19,22-octathiacyclotetracosane) involves two eight-coordinate Bi(III) centers from five macrocyclic S atoms (two of which bridge the Bi centers) and three Cl's. The $BiCl_3$ fragments are on opposite sides of the mean plane of the macrocycle [23]. Two Sb(III) complexes of [9]aneS_3 have been described. [$SbCl_3$([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) to 3.409(3) Å, possibly suggesting that the Sb-based lone pair points between two of the S atoms of the tridentate thio-ether ring [24]. 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-based lone pair [25]. The only structurally characterized coordination complex of As(III) involving thio-, seleno-, or telluro-ether ligation is AsI_3. 1,3,5,7-(tetramethyl)-2,4,6,8,9,10-(hexathia)adamantane [26]. There have been no structural reports of thio-, seleno-, or telluro-ether ligand complexes with PX_3 acting as a Lewis acid. Likewise, no examples of Sb(III) or Bi(III) telluro-ethers have appeared in the literature.

Herein we describe the results of our investigations into the coordination chemistry of thio-, seleno-, and telluro-ether ligands with the heavier group 15 acceptors MX_3 (M = As, Sb, Bi; X = Cl, Br, I). The following discussion is organized according to the chalcogenoether ligand type present in the complexes and in order of increasing atomic weight of the group 15 element (As then Sb then Bi).

Thioether Complexes

In the course of our investigations of the coordination chemistry of AsX_3 with acyclic and macrocyclic thio-ether ligands, we have isolated and characterized the first such adducts, including complexes with 2,5-dithiahexane, [9]aneS_3, and [14]aneS_4 ([14]aneS_4 = 1,4,8,11-tetrathiacyclotetradecane) [27]. The compounds were obtained as colorless solids by reaction of AsX_3 with 1 mole equiv. of the thio-ether in anhydrous CH_2Cl_2 solution. NMR spectroscopic studies show that the products are extensively dissociated in solution and no useful structural information is revealed. Hence, for the As(III) complexes (and for the very poorly soluble and often polymeric Sb(III) and Bi(III) complexes, see later) X-ray crystallographic studies have assumed great importance in their characterization. The only acyclic dithio-ether complexes of As(III) to be isolated were [AsX_3{$MeS(CH_2)_2SMe$}] (X = Br or I). No solids were isolated from reactions between AsX_3 and $MeS(CH_2)_3SMe$ or the tripodal $MeC(CH_2SMe)_3$ under the same reaction conditions. The two dithiahexane complexes are isostructural, each forming a discrete μ^2-dihalo As_2X_6 unit with a chelating dithioether on each As center in the *meso* arrangement, giving the isomer A form (Fig. 2). The As—S distances of 2.697(2) and 2.792(2) Å (X = I) and 2.725(3) and 2.876(3) Å (X = Br) are consistent with weak, secondary interactions and the As-based lone pair appears to lie in the direction of the vertex associated with the long $As\cdots X_{bridging}$ bond [27]. The crystal structure of [$AsCl_3$([9]aneS_3)] (Fig. 3) shows a discrete six-coordinate monomer involving distorted octahedral S_3X_3-coordination at As(III), with the lone pair apparently stereochemically inactive, As—S = 2.720(4)–2.861(4) Å [27]. The constraints imposed by the small nine-membered ring, together with the long As—S bond distances, lead to unusually acute S—As—S angles in this species.

Reaction of $AsCl_3$ with [14]aneS_4 gave only the 1:1 product, [$AsCl_3$([14]aneS_4)], even when excess $AsCl_3$ was used. This contrasts with the SbX_3/[14]aneS_4 system from which only the 2:1 [$(SbX_3)_2$([14]aneS_4)] was isolated (and the bromo derivative was structurally characterized, see later). The structure shows each As center adopting a distorted octahedral geometry through two terminal Cl's, two S atoms, and two μ^2-Cl's. However, unusually the μ^2-Cl's link to two different As centers to give an infinite sheet polymer. The bridging tetrathio ether ligands link to two different As centers through coordination via two adjacent S atoms. Thus, each As is linked to two mutually cis S atoms from different macrocycles, with the other two S

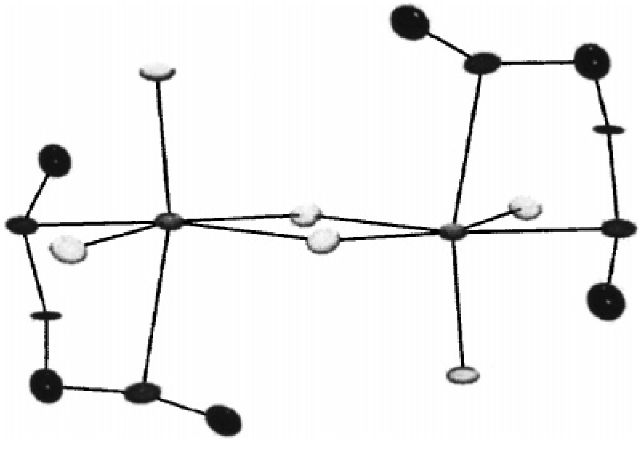


FIGURE 2 Crystal structure of [$AsBr_3${$MeS(CH_2)_2SMe$}].

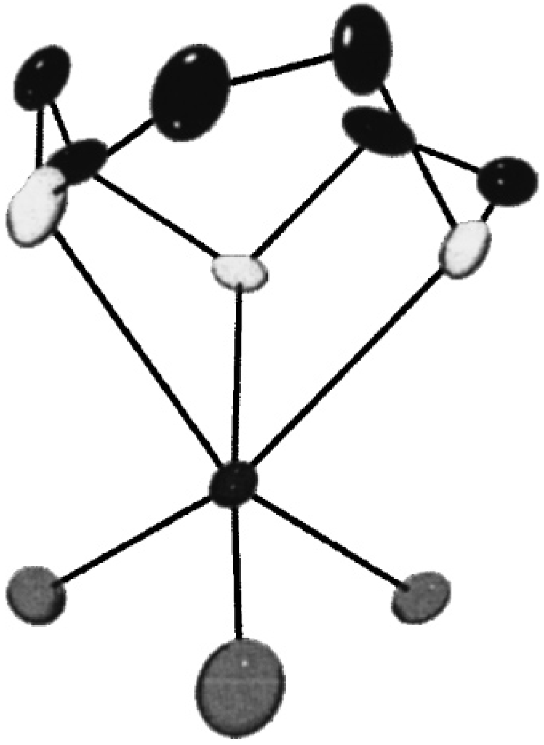


FIGURE 3 Crystal structure of [$AsCl_3$([9]aneS_3)].

atoms remaining uncoordinated, contrasting with [$(SbBr_3)_2$([14]aneS_4)] in which an Sb center is coordinated to each thio-ether S atom (hence the 2:1 stoichiometry). The very asymmetric As—$Cl_{bridging}$ distances suggest that the As-based lone pair is partially stereochemically active and in this case is probably oriented along the vector of the long As···Cl1′ bond [27].

Unlike in the arsenic systems (discussed earlier), SbX_3 (X = Cl, Br, or I) react readily with a wide range cyclic and acyclic bidentate and tripodal thio-ether ligands in anhydrous MeCN or THF to afford the 1:1 species [SbX_3(L)].

The dithio-ether compounds, [$SbCl_3${MeS-$(CH_2)_2$SMe}] and [$SbBr_3${MeS$(CH_2)_3$SMe}] exhibit unusual infinite 1- or 2-D structures derived from primary Sb—X bonding with weak, secondary Sb—S interactions to bridging thio-ethers [28,29]. The structure of [$SbCl_3${MeS$(CH_2)_2$SMe}] shows a distorted octahedral coordination environment at Sb derived from three terminal Cl's and three S atoms from different dithio-ethers, one terminal and two μ^2-bridging [28]. On each dithio-ether the second S atom coordinates to an adjacent Sb center generating a 2-D 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$(CH_2)_3$SMe)}] is very similar [29]. Crystal structures for [$SbCl_3$(1,4-dithiane)] [30] and [$SbCl_3$(1,4-dithiacycloheptane)] [31] have also been reported and both adopt polymeric structures with similar patterns of bond lengths to those given in the preceding text.

The structures obtained for compounds [$SbCl_3${MeC$(CH_2SMe)_3$}] and [SbI_3{MeC$(CH_2SMe)_3$}] exhibit surprisingly different motifs given the fact that only the halide is different. The structure of [$SbCl_3${MeC$(CH_2SMe)_3$}] shows (Fig. 4) five-coordinate Sb(III) centers forming an infinite 1-D "helical" structure derived from linking of the $SbCl_3$ units by bridging MeC$(CH_2SMe)_3$ ligands. The thio-ether ligand bridges adjacent $SbCl_3$ units via coordination to each through one S-donor, i.e., each metal center coordinates to sulfur atoms from two different thio-ether ligands, which function as bidentates. The weak secondary Sb···S bond lengths are 3.172(2) and 3.106(2) Å [29]. In contrast, [SbI_3{MeC$(CH_2SMe)_3$}]

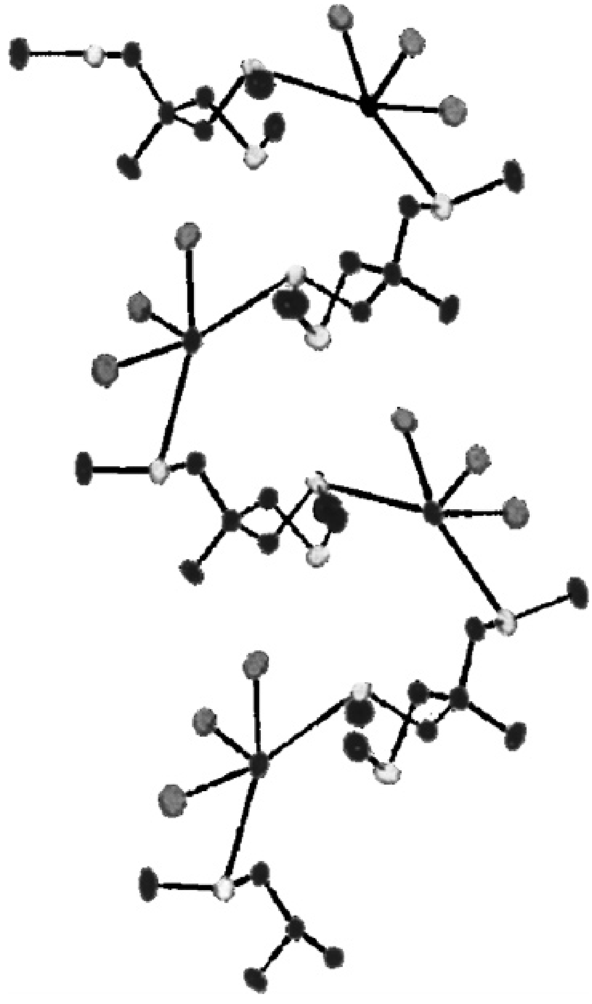


FIGURE 4 Crystal structure of [$SbCl_3${MeC$(CH_2SMe)_3$}].

involves six-coordinate antimony. Within this 1-D polymer each antimony atom is in a distorted octahedral environment, coordinated to two sulfur donor atoms, two terminal iodine ligands, and two μ^2-iodine atoms. The bridging within the Sb_2I_6 dimer 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) [29]. 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 observed in other systems [32].

By using the tetrathio-ether [14]aneS_4 the complex $[(SbBr_3)_2([14]aneS_4)]$ is formed [29], which adopts an infinite coordination network, the repeat unit being an asymmetric $Sb_2Br_6S_4$ edge-shared bioctahedron (Fig. 5). The Sb atoms are coordinated to two terminal Br atoms and two μ^2-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 thio-ether complex of Sb(III) reported is $[(SbCl_3)_2([18]aneS_6)]$, which is molecular with two *fac* six-coordinate antimony centers disposed on opposite sides of the mean plane of the macrocycle [24].

A substantial range of thio-ether complexes of Bi(III) halides and involving bi- and tri-dentate ligands was prepared and their structures established. These too exhibit a surprising structural diversity from discrete monomers through oligomers to 1-, 2-, and 3-D polymers.

With $MeS(CH_2)_2SMe$, the 1:2 chelate complex $[BiBr_3\{MeS(CH_2)_2SMe\}_2]$ was obtained. This species is a distorted pentagonal bipyramidal monomer with axial Br's, Bi—S = 2.918(5)–3.090(5), Bi—Br = 2.787(2)–2.826(2) Å. One dithio-ether ligand is in the *meso* form while the other is *DL* [33]. 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 2-D sheet composed of infinite chains of orthogonal asymmetric μ^2-bridged Bi_2Br_6 units cross-linked by bridging dithio-ether 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) [33]. A species of formula $[(BiCl_3)_4\{MeS(CH_2)_3SMe\}_4]$ was obtained from $BiCl_3$ and ligand in CH_2Cl_2. In this case we observe (Fig. 6) a very distorted cubane Bi_4Cl_4 core which is cross-linked to other similar units by bridging dithio-ethers, to give a 3-D polymer. Each Bi is coordinated to two terminal Cl's (2.533(7), 2.538(7) Å), two μ^2-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

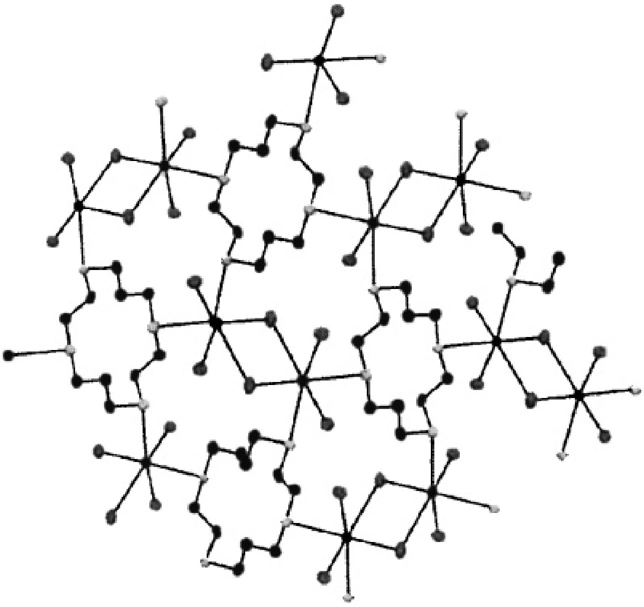


FIGURE 5 Crystal structure of $[(SbBr_3)_2([14]aneS_4)]$.

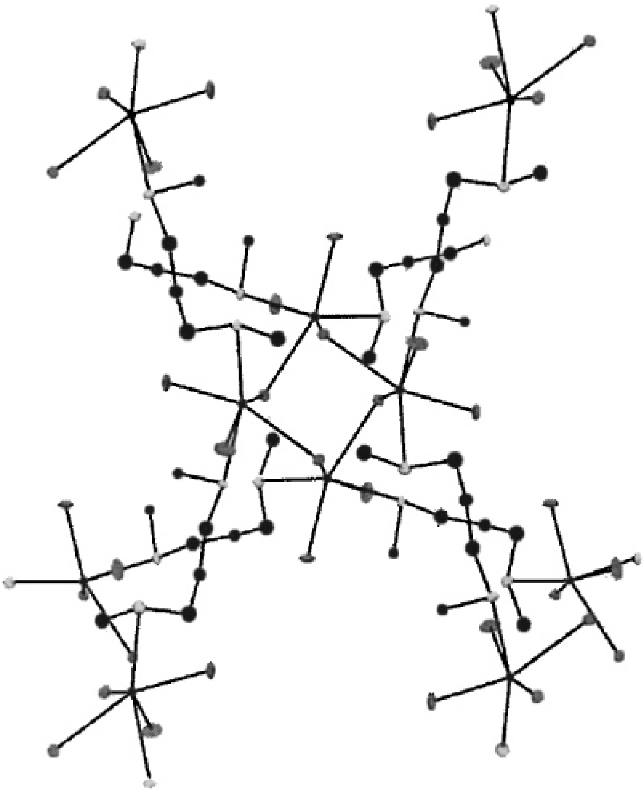


FIGURE 6 Crystal structure of $[(BiCl_3)_4\{MeS(CH_2)_3SMe\}_4]$.

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 [34].

The structure of the analogous $[BiBr_3\{MeS(CH_2)_3SMe\}]$, obtained from MeCN solution, is a 2-D network with co-planar Bi_2Br_6 units bridged by thioether ligands, which occupy mutually trans coordination sites. The variation in Bi—Br distances are indicative of both primary and secondary interactions, while the Bi—S distances are best regarded as weak, secondary bonds [33].

Selenoether Ligands

No solid products were obtained by reaction of AsX_3 with acyclic bidentate $MeSe(CH_2)_3SeMe$ or the tripodal $MeC(CH_2SeMe)_3$, probably reflecting the poor Lewis acidity of the As(III) ion. However, the macrocyclic seleno-ethers have proved much more effective ligands, although the resulting products are extensively dissociated in solution from NMR measurements. The 1:1 species $[AsX_3([8]aneSe_2)]$ ($[8]aneSe_2 = 1,5$-diselenacyclooctane) almost certainly adopt the same ladder-like structure seen for the Bi(III) analogue later. With the tetraselenoether ligand $[16]aneSe_4$ (1,6,9,13-tetraselenacyclohexadecane) we obtained the 2:1 $[(AsX_3)_2([16]aneSe_4)]$ compounds of which the $[(AsX_3)_2([16]aneSe_4)]$ 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 assumes is occupied by the As-based lone pair, As—Se = 2.922(3), 3.164(3) Å [27]. This species is similar to $[(SbBr_3)_2([16]aneSe_4)]$ (see later).

Although complexes of $[24]aneSe_6$ (1,5,9,13,17,21-hexaselenacyclotetracosane) 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 discrete $[(AsCl_3)_4([24]aneSe_6)]$ is very unusual, displaying a new structural type with both endo and exo coordination of the As(III) centers [35]. A very unusual feature is the occurrence of an asymmetric As_2Cl_6 μ^2-chloro bridged dinuclear unit coordinated within the macrocyclic ring, giving a distorted octahedral Se_2Cl_4 coordination environment at these As atoms. The two remaining, mutually trans Se atoms each coordinate in an exo fashion to further As centers. The exo-bound $AsCl_3$ units therefore form four-coordinate distorted sawhorse units through coordination to the 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 hexaseleno-ether macrocycle therefore uses all six Se donor atoms to bind to the As centers (Fig. 7), As—Se(endo) = 2.994(2), 3.005(2); As—Se(exo) = 3.091(2) Å.

Compounds of formula $[SbX_3(L)]$ ($L = MeSe(CH_2)_nSeMe$ ($n = 2$ or 3) and $MeC(CH_2SeMe)_3$) are obtained in good yield from reaction of SbX_3 with L in anhydrous MeCN (or THF for X = I) [28,29]. The structure of the seleno-ether complex $[SbCl_3\{MeSe(CH_2)_3SeMe\}]$ is an infinite 1-D chain [29]. The Sb centers adopt distorted octahedral coordination comprising two cis terminal Cl's, two μ^2-Cl's, and two mutually cis Se atoms from different diseleno-ethers. Thus, the chains are derived from weakly associated, asymmetric Sb_2Cl_6 units linked by bridging diseleno-ether ligands. The Sb—Se distances of ca. 3.2 Å are very similar to the Sb—S distances in the dithio-ether species (discussed earlier), again suggesting rather weak, secondary interactions.

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 seleno-ether and one monodentate seleno-ether [29].

The cyclic seleno-ethers $[8]aneSe_2$, $[16]aneSe_4$, and $[24]aneSe_6$ form 1:1 (usually) or 2:1 (occasionally) macrocycle:SbX_3 complexes. The crystal structure of $[(SbBr_3)_2([16]aneSe_4)]$ (Fig. 8) shows a 2-D sheet structure with $SbBr_3$ units coordinated

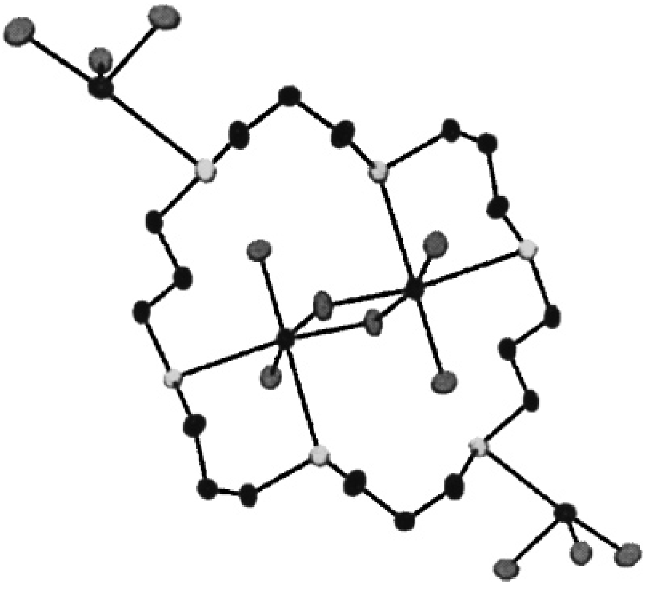


FIGURE 7 Crystal structure of $[(AsCl_3)_4([24]aneSe_6)]$.

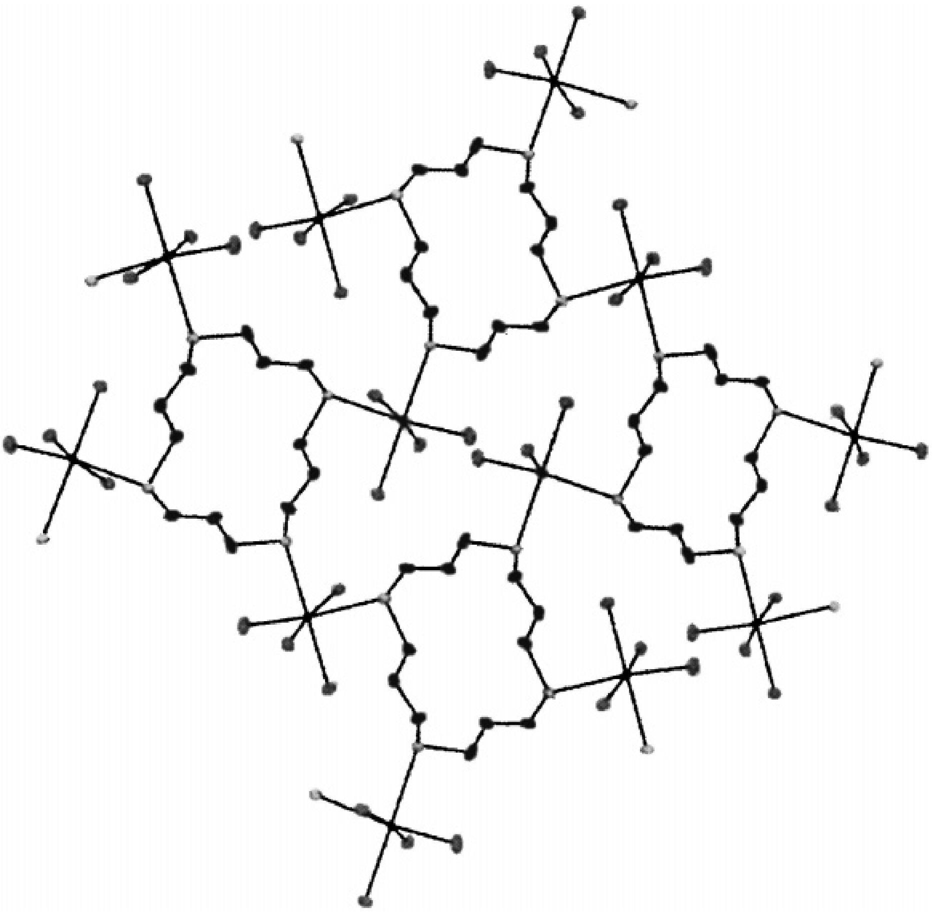


FIGURE 8 Crystal structure of [$(SbBr_3)_2$([16]aneSe_4)].

weakly to two Se atoms from different seleno-ethers, giving distorted square pyramidal Sb(III). The macrocycles therefore function as *exocyclic* ligands bridging four Sb centers [28].

The Bi-diseleno-ethers [BiX_3{MeSe$(CH_2)_3$SeMe}] are structurally very similar to the thio-ether analogue (discussed earlier). The tripodal seleno-ether complex [$BiCl_3${MeC$(CH_2SeMe)_3$}] is a 2-D sheet (Fig. 9), 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 seleno-ether function on an adjacent tripod. The triseleno-ethers therefore cross-link these Bi units to give the infinite network. Similar Bi—Cl and Bi—Se bond length distributions are observed [33]. Surprisingly the iodo analogue, [Bi_2I_6{MeC$(CH_2SeMe)_3$}$_2$] is quite different, comprising discrete dinuclear units derived from a twisted Bi_2I_6 rhomboidal core, with one bidentate triseleno-ether coordinated to each Bi center, giving a distorted octahedral geometry [33]. Rabinovich and co-workers have

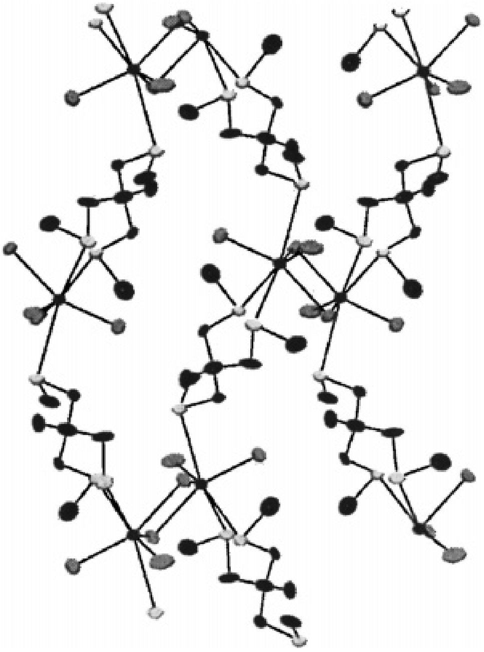


FIGURE 9 Crystal structure of [$BiCl_3${MeC$(CH_2SeMe)_3$}].

reported the structure of the Bi(III) complex obtained on coordination to the silicon-apex tripod thio-ether, $MeSi(CH_2SMe)_3$. This illustrates how very subtle changes in the ligand dramatically change the structure of the product. The product is a 1:1 polymer containing single μ^2-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 another, and three Cl's [36].

The seleno-ether macrocyclic complexes $[BiX_3(L)]$ (L = [8]aneSe_2, [16]aneSe_4, and [24]aneSe_6) are obtained as intensely colored 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. 10) each reveal infinite 1-D ladder structures assembled from nearly coplanar Bi_2X_6 "rungs" linked by bridging L "uprights," the Se atoms occupying mutually trans coordination sites. The seleno-ether macrocycles adopt *exocyclic* arrangements and in $[BiBr_3([16]aneSe_4)]$ it is alternate Se atoms which coordinate to the Bi centers, leaving the other two Se atoms non-coordinating. These species contrast with molecular structures of the thio-ether macrocyclic complexes discussed earlier [37].

Telluroether Ligands

No AsX_3 adducts with telluro-ether ligands have been isolated and only a much more limited range of telluro-ether complexes of Sb(III) and Bi(III) has been obtained. Reaction of $MeTe(CH_2)_3TeMe$ or $MeC(CH_2TeMe)_3$ (L) with 1 mole equiv. of SbX_3 in anhydrous CH_2Cl_2 yields orange/brown powdered solids of stoichiometry $[SbX_3L]$, although no structural data have been obtained for these species todate [38].

The only structurally characterized Bi(III) telluro-ether complex is $[BiBr_3(PhTeMe)]$ which adopts a chain polymer structure involving $[(PhTeMe)Br_3Bi(\mu^2\text{-}Br_2)BiBr_3(PhTeMe)]$ dimers, based upon five-coordinate Bi, with the telluro-ethers occupying *anti* coordination sites and the stereochemically active lone pair on each Bi leading to pseudo-octahedral Bi(III). These dimers are then weakly associated into infinite chains via long range intermolecular Bi···Cl interactions (Fig. 11) [38].

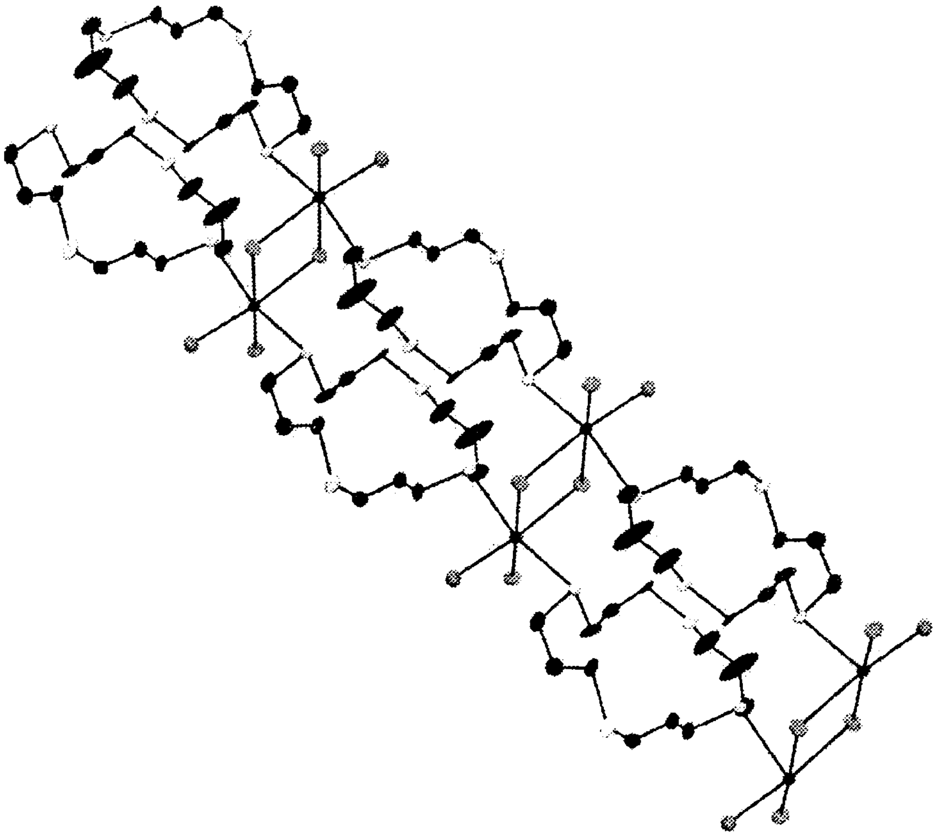


FIGURE 10 Crystal structure of $[BiBr_3([16]aneSe_4)]$.

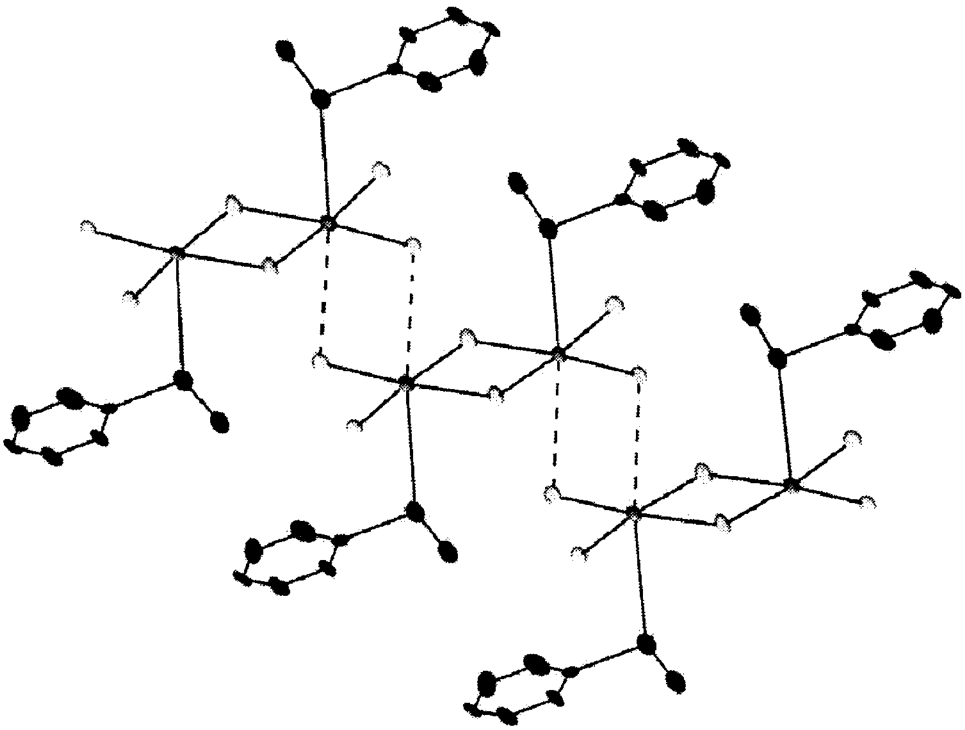


FIGURE 11 Crystal structure of [$BiBr_3$(PhTeMe)].

CONCLUSIONS

We have shown that the heavier chalcogenoethers function as superior σ-donors towards low valent transition-metal centers compared to the more widely studied thio-ethers. On the basis of these observations more effort is necessary to develop satisfactory syntheses for polydentate and macrocyclic telluro-ethers to allow their coordination chemistry to be examined in detail. We have recently identified successful new synthetic routes to facultative tritelluro-ether ligands (in which the Te atoms are introduced sequentially) and to a range of mixed S/Te macrocycles with different ring sizes.

Our work on the coordination chemistry of the group 15 acceptors MX_3 has generated the first complexes of these species with seleno-ether or telluro-ether coordination and revealed a surprising structural diversity depending upon the particular ligands employed, from monomers to 1-, 2-, and 3-D polymers. The structures identified are apparently dictated by several factors including the occurrence of both primary (M—X) and secondary (M—S/Se/Te) bonding interactions and the ligand denticity and architecture. The marked changes in structure resulting from subtle changes in the MX_3/L system suggest that the energy differences between several possible structures are small, and that other structural isomers may result from changes in crystallization procedures, reaction conditions, etc., although we have not yet identified more than one structural form for any particular system. The rather more limited range of arsenic(III) complexes isolated and their extensive dissociation in solution are consistent with the trend in Lewis acidity $AsX_3 < SbX_3 < BiX_3$. The size of the acceptor ion and the stereochemical activity of the M-based lone pair also play important roles. Thus, higher coordination numbers are evident for Bi and Sb complexes (5–7) compared to the complexes of the small As center (4–6). Finally, the presence of only two substituents on each chalcogen atom (compared to three in phosphines and arsines) and two lone pairs on each (compared to one in phosphines and arsines) lead to lower steric demands in the chalcogenoether systems, and the occasional occurrence of bridging chalcogen atoms where both lone pairs are involved in coordination. These factors also lead to significantly greater structural variety in the chalcogenoether complexes.

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