Inorg. Chem. **2002**, *41*, 2070–2076

Inorganic Chemistry
Article

Arsenic(III) Halide Complexes with Acyclic and Macrocyclic Thio- and Selenoether Coligands: Synthesis and Structural Properties

Nicholas J. Hill, William Levason, and Gillian Reid*

Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, U.K.

Received November 6, 2001

The preparations of the new complexes [$AsBr_3\{MeS(CH_2)_2SMe\}$], [AsX_3([9]aneS_3)] (X = Cl, Br or I; [9]aneS_3 = 1,4,7-trithiacyclononane), [$AsCl_3$([14]aneS_4)] ([14]aneS_4 = 1,4,8,11-tetrathiacyclotetradecane), [AsX_3([8]aneSe_2)] ([8]aneSe_2 = 1,5-diselenacyclooctane), [$(AsX_3)_2$([16]aneSe_4)] ([16]aneSe_4 = 1,5,9,13-tetraselenacyclohexadecane), and [$(AsBr_3)_2$([24]aneSe_6)] ([24]aneSe_6 = 1,5,9,13,17,21-hexaselenacyclotetracosane) are described. These are obtained from direct reaction of the appropriate AsX_3 and 1 mol equiv of the thio- or selenoether ligand in anhydrous CH_2Cl_2 (or thf for X = I) solution. The products have been characterized by microanalysis and IR and ^{1}H NMR spectroscopy. In solution they are extensively dissociated, reflecting the weak Lewis acidity of AsX_3. Reaction of AsX_3 with $MeSe(CH_2)_2SeMe$ or $MeC(CH_2EMe)_3$ (E = S or Se) gave only oils. Treatment of PCl_3 or PBr_3 with Me_2S, $MeE(CH_2)_2EMe$, or [9]aneS_3 failed to give solid complexes, and there was no evidence from NMR spectroscopy for any adduct formation in solution. The crystal structures of the first series of thioether and selenoether complexes of As(III) are described: [$AsBr_3\{MeS(CH_2)_2SMe\}$], $C_4H_{10}AsBr_3S_2$, $a = 10.2818(6)$ Å, $b = 7.8014(5)$ Å, $c = 14.503(1)$ Å, $\beta = 102.9330(2)°$, monoclinic, $P2_1/c$, $Z = 4$; [$AsI_3\{MeS(CH_2)_2SMe\}$], $C_4H_{10}AsI_3S_2$, $a = 9.1528(1)$ Å, $b = 11.5622(2)$ Å, $c = 12.0939(2)$ Å, $\beta = 93.863(1)°$, monoclinic, $P2_1/n$, $Z = 4$; [$AsCl_3$([9]aneS_3)], $C_6H_{12}AsCl_3S_3$, $a = 17.520(4)$ Å, $b = 17.520(4)$ Å, $c = 16.790(7)$ Å, tetragonal, $I4_1cd$, $Z = 16$; [$AsCl_3$([14]aneS_4)], $C_{10}H_{20}AsCl_3S_4$, $a = 13.5942(2)$ Å, $b = 7.7007(1)$ Å, $c = 18.1270(3)$ Å, $\beta = 111.1662(5)°$, monoclinic, $P2_1/n$, $Z = 4$; [$(AsCl_3)_2$([16]aneSe_4)], $C_{12}H_{24}As_2Cl_6Se_4$, $a = 9.764(3)$ Å, $b = 13.164(1)$ Å, $c = 10.627(2)$ Å, $\beta = 114.90(1)°$, monoclinic, $P2_1/n$, $Z = 2$; [$(AsBr_3)_2$([16]aneSe_4)], $C_{12}H_{24}As_2Br_6Se_4$, $a = 10.1220(1)$ Å, $b = 13.4494(2)$ Å, $c = 10.5125(2)$ Å, $\beta = 113.49(2)°$, monoclinic, $P2_1/n$, $Z = 2$. [$AsBr_3\{MeS(CH_2)_2SMe\}$] and [$AsI_3\{MeS(CH_2)_2SMe\}$] reveal discrete μ^2-halo As_2X_6 dimeric structures involving distorted octahedral As(III), with the dithioether ligand chelating. [$AsCl_3$([9]aneS_3)] adopts a discrete molecular distorted octahedral geometry with the thioether behaving as a weakly coordinated *fac*-capping ligand. [$AsCl_3$([14]aneS_4)] forms an infinite sheet involving two μ^2-chloro ligands on each As but bridging to two distinct As centers. Each macrocycle coordinates to two adjacent As centers via one S atom, giving a *cis*-octahedral Cl_4S_2 donor set at As(III). The structures of [$(AsCl_3)_2$([16]aneSe_4)] and [$(AsBr_3)_2$([16]aneSe_4)] adopt 2-dimensional sheet structures with μ^2-dihalo As_2X_6 dimers cross-linked by μ^4-tetraselenoether macrocycles, giving a disorted *cis*-X_4Se_2 donor set at each As center. These species are compared with their antimony(III) and bismuth(III) analogues where appropriate.

Introduction

We have been investigating the coordination chemistry of polydentate and macrocyclic thio- and selenoether ligands with a series of main group elements, including the heavy p-block ions of group 15, bismuth(III) and antimony(III). While the group 15 elements (P, As, Sb, Bi) are frequently incorporated in organic molecules as ligands, and hence their donor properties are well understood, much less effort has been devoted to studies of the group 15 elements as Lewis acids.[1]

In particular, we are interested in establishing the properties of complexes involving thio- and selenoether ligands and have shown that Bi(III) and Sb(III) readily form complexes with polydentate and macrocyclic thio- and selenoether ligands to give a diverse range of unusual, and

---

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

[1] Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2953.

10.1021/ic011139t CCC: $22.00
© 2002 American Chemical Society
Published on Web 03/22/2002

often polymeric, structural motifs based on a combination of primary M−X (X = Cl, Br or I) interactions and a series of secondary M···E (E = S or Se) and, in some cases, M···X interactions.[2−6] The motifs observed depend on a subtle balance between between donor type, ligand architecture, and complex solubility among other factors. The extent of the stereochemical activity of the lone pair based on the group 15 element also has a significant influence on the structures. In general, one would expect that the stereochemical activity would decrease down the group from P to Bi as the element gets larger.

The Lewis acidity of these heavier group 15 trihalides is considerably greater than for the nonmetal trihalides, PX_3 and AsX_3. This is reflected in the fact that coordination complexes in which these fragments function as Lewis acids are rare. For PX_3, coordination complexes are limited to species such as haloanions (PCl_4^- and PBr_4^-)[7,8] and PMe_3 and $AsMe_3$ adducts.[9] For AsX_3, structurally characterized examples include the haloanions,[10,11] $[AsCl_3(NMe_3)]$,[12] and a limited series of phosphine and arsine complexes, e.g. $[AsX_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$.[13−15] With this in mind, we have extended our studies to explore the coordination chemistry of arsenic trihalides with thio- and selenoether ligands. We very recently communicated the preparation and molecular structure of the first such complex, $[(AsCl_3)_4([24]aneSe_6)]$ ($[24]aneSe_6$ = 1,5,9,13,16,19,22-hexaselenacyclotetracosane).[16] This is a very unusual species involving four $AsCl_3$ units per hexaselenoether macrocycle, with two coordinated *exo* to the ring in a distorted sawhorse geometry via a single Se atom and the other two forming a weakly associated asymmetric dinuclear μ^2-dichloro unit *endo* to the ring with distorted octahedral coordination at each As center. Other than this species, the only well characterized example of an arsenic(III) thioether or selenoether complex is AsI_3(tetramethylhexathiaadamantane).[17]

We report here the synthesis and spectroscopic characterization of a series of As(III) thio- and selenoether complexes including $[AsBr_3\{MeS(CH_2)_2SMe\}]$, $[AsX_3([9]aneS_3)]$ (X = Cl, Br or I; $[9]aneS_3$ = 1,4,7-trithiacyclononane), $[AsCl_3([14]aneS_4)]$ ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane), $[AsX_3([8]aneSe_2)]$ ($[8]aneSe_2$ = 1,5-diselenacyclooctane), $[(AsX_3)_2([16]aneSe_4)]$ ($[16]aneSe_4$ = 1,5,9,13-tetraselenacyclohexadecane), and $[(AsBr_3)_2([24]aneSe_6)]$. Crystal structures of $[AsBr_3\{MeS(CH_2)_2SMe\}]$, $[AsI_3\{MeS(CH_2)_2SMe\}]$, $[AsCl_3([9]aneS_3)]$, $[AsCl_3([14]aneS_4)]$, $[(AsCl_3)_2([16]aneSe_4)]$, and $[(AsBr_3)_2([16]aneSe_4)]$ are also reported and compared with their Bi(III) and Sb(III) analogues where appropriate.

Results and Discussion

Reaction of AsX_3 (X = Cl and in some cases Br or I) with 1 mol equiv of L (L = $MeS(CH_2)_2SMe$, $[9]aneS_3$, $[12]aneS_4$, $[14]aneS_4$, $[8]aneSe_2$, $[16]aneSe_4$, and $[24]aneSe_6$) in anhydrous CH_2Cl_2 (or thf for X = I) affords, following workup, solid complexes of 1:1 As:L stoichiometry (except for L = $[16]aneSe_4$, which give 2:1 As:$[16]aneSe_4$ ratios, and $[24]aneSe_6$, where the 4:1 $[(AsCl_3)_4([24]aneSe_6)]$ and the 2:1 $[(AsBr_3)_2([24]aneSe_6)]$ were obtained) in good yields. The isolated solids are hydrolytically unstable and were therefore stored in a dry, N_2 flushed glovebox. Attempts to isolate complexes with $MeSe(CH_2)_2SeMe$ and $MeC(CH_2EMe)_3$ (E = S or Se) under similar conditions 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.[1−6] Even for $MeS(CH_2)_2SMe$, for which a solid of stoichiometry $[AsBr_3\{MeS(CH_2)_2SMe\}]$ was obtained, we have only been able to isolate extremely low yields (in the form of a few very small single crystals) of the iodo analogue, $[AsI_3\{MeS(CH_2)_2SMe\}]$, even after several attempts. Thus, while we report the crystal structure of this species (which serves as a useful comparison with that of $[AsBr_3\{MeS(CH_2)_2SMe\}]$), we have been unable to obtain sufficient sample to permit characterization of the bulk.

Solids could not be obtained from treatment of PCl_3 or PBr_3 with Me_2S, $MeE(CH_2)_2EMe$ (E = S or Se), or $[9]aneS_3$ under similar conditions, and ^{31}P NMR spectra in CH_2Cl_2 show no evidence for any interaction. This is also consistent with the very poor Lewis acidity of PX_3 compared to the heavier group 15 analogues.

Infrared spectra of the complexes which we were able to isolate as solids show evidence for ligand and features in the range 380−420 or 260−300 cm^{-1} for X = Cl or Br, respectively, tentatively assigned to ν(As−Cl) and ν(As−Br).[18]

The compounds were sufficiently soluble in $CDCl_3$ or CD_2Cl_2 to permit ^1H NMR spectroscopic studies. However, in all cases the spectra show resonances very little shifted from those for the corresponding uncoordinated thio- or selenoether ligand, indicating either extensive dissociation or fast ligand exchange. Consistent with these conclusions, the $^{77}Se\{^1H\}$ NMR spectrum of $[(AsCl_3)_4([24]aneSe_6)]$ shows a singlet at 153 ppm, unshifted from free $[24]aneSe_6$.[16] These studies therefore reveal no structural information on the complexes.

---

[2] Genge, A. R. J.; Levason, W.; Reid, G. *Chem. Commun.* **1998**, 2159.
[3] Barton, A. J.; Genge, A. R. J.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2000**, 859.
[4] Barton, A. J.; Genge, A. R. J.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2000**, 2163.
[5] Barton, A. J.; Hill, N. J.; Levason, W.; Patel, B.; Reid, G. *Chem. Commun.* **2001**, 95.
[6] Barton, A. J.; Hill, N. J.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1621.
[7] Dillon, K. B.; Platt, A. W. G.; Schmidpeter, A.; Zwaschka, F.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1982**, *488*, 7.
[8] Sheldrick, W. S.; Keifer, J. *Z. Naturforsch.* **1989**, *B44*, 609.
[9] Summers, J. C.; Sisler, H. H. *Inorg. Chem.* **1970**, *9*, 862.
[10] E.g.: Sheldrick, W. S.; Kaub, J.; Hausler, H. J. *Z. Naturforsch.* **1986**, *43B*, 789.
[11] *Chemistry of Arsenic, Antimony and Bismuth*; Norman, N. C., Ed.; Blackie: New York, 1998.
[12] Webster, M.; Keats, S. *J. Chem. Soc., Dalton Trans.* **1971**, 836.
[13] Baum, G.; Greiling, A.; Massa, W.; Hiu, B. C.; Lorberth, J. *Z. Naturforsch* **1989**, *44b*, 560.
[14] Hill, N. J.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.*, in press.
[15] Sutton, G. J. *Aust. J. Chem.* **1958**, *11*, 416. Sutton, G. J. *Aust. J. Chem.* **1958**, *11*, 420.
[16] Barton, A. J.; Hill, N. J.; Levason, W.; Reid, G. *J. Am. Chem. Soc.* **2001**, *123*, 11801.
[17] Kniep, R.; Reski, H. D. *Inorg. Chim. Acta* **1982**, *64*, L83.
[18] Klapotke, T. *Main Group Met. Chem.* **1997**, *2*, 81.

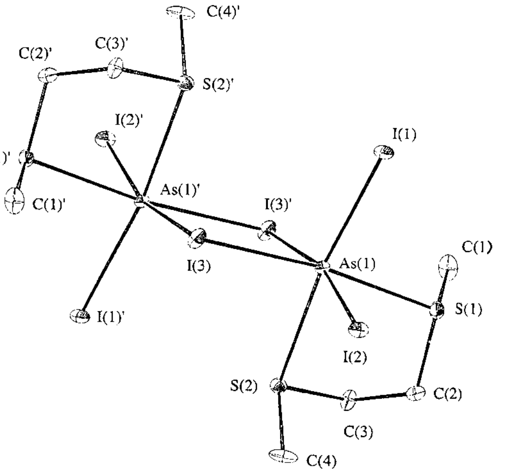

Figure 1. View of the structure of [$AsI_3\{MeS(CH_2)_2SMe\}$] with numbering scheme adopted. Symmetry-related neighbors are marked with primes. Ellipsoids are drawn at the 40% probability level, and H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [$AsI_3\{MeS(CH_2)_2SMe\}$]

As(1)−I(1)	2.723(1)	As(1)−I(2)	2.6202(9)
As(1)−I(3)	2.774(1)	As(1)−I(3′)	3.3357(9)
As(1)−S(1)	2.697(2)	As(1)−S(2)	2.792(2)

I(1)−As(1)−I(2)	95.93(3)	I(1)−As(1)−I(3)	99.40(3)
I(1)−As(1)−I(3′)	99.22(3)	I(1)−As(1)−S(1)	88.00(5)
I(1)−As(1)−S(2)	166.69(6)	I(2)−As(1)−I(3)	95.59(3)
I(2)−As(1)−I(3′)	164.21(4)	I(2)−As(1)−S(1)	84.48(5)
I(2)−As(1)−S(2)	90.35(5)	I(3)−As(1)−I(3′)	86.31(3)
I(3)−As(1)−S(1)	172.54(6)	I(3)−As(1)−S(2)	91.62(5)
I(3′)−As(1)−S(1)	91.61(5)	I(3′)−As(1)−S(2)	73.91(5)
S(1)−As(1)−S(2)	80.91(7)	As(1)−I(3)−As(1′)	93.69(3)

X-ray Crystallography. Given the poorer Lewis acidity of AsX_3 compared to SbX_3 and BiX_3, it is probably not very surprising that a much more limited range of complexes has been isolated in this work for AsX_3 with group 16 donor ligands (which are modest σ-donors compared to for example phosphines). This is also reflected in the ease of ligand dissociation/exchange indicated by the solution NMR studies above. Furthermore, even the isolated materials are in some cases rather waxy solids, and it has proved difficult to obtain good quality crystals from these rather "soft" materials.

The crystal structure of [$AsI_3\{MeS(CH_2)_2SMe\}$] reveals (Figure 1, Table 1) a centrosymmetric, discrete asymmetric μ^2-diiodo As_2I_6 unit with a chelating dithioether on each distorted octahedral As center in the *meso* arrangement, and the molecule is in the *isomer A* form.[11] The As−S distances of 2.697(2) and 2.792(2) Å are of magnitude similar to that of the As−$I_{terminal}$ distances (2.7227(10), 2.6202(9) Å), although the iodine atoms are considerably larger than sulfur. Also, examination of the As−I distances reveal three bonds at ca. 2.7 Å (primary interactions), with the fourth at ca. 3.3 Å (secondary interaction), suggesting that this species may be considered as derived from weakly associated $AsI_3\{MeS(CH_2)_2SMe\}$ square pyramids. This asymmetry in the $As_2(\mu^2\text{-}I_2)$ core suggests that the As-based lone pair is partially stereochemically active and localized along the vector of the long As1−I3′ bond. We also obtained crystals of [$AsBr_3\{MeS(CH_2)_2SMe\}$], whose structural features are very similar to the iodo analogue above (Table 2), with As−S = 2.725(3) and 2.876(3) Å.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$AsBr_3\{MeS(CH_2)_2SMe\}$]

As(1)−Br(1)	2.391(1)	As(1)−Br(2)	2.453(1)
As(1)−Br(3)	2.550(1)	As(1)−Br(3′)	3.258(1)
As(1)−S(1)	2.725(3)	As(1)−S(2)	2.876(3)

As(1)−Br(3)−As(1′)	99.00(4)	Br(1)−As(1)−Br(2)	95.21(5)
Br(1)−As(1)−Br(3)	93.48(5)	Br(2)−As(1)−Br(3)	99.09(5)
Br(1)−As(1)−S(1)	87.97(7)	Br(2)−As(1)−S(1)	89.22(6)
Br(3)−As(1)−S(1)	171.38(7)	Br(1)−As(1)−S(2)	81.39(6)
Br(2)−As(1)−S(2)	166.90(7)	Br(3)−As(1)−S(2)	93.76(7)
S(1)−As(1)−S(2)	78.05(8)	Br(1)−As(1)−Br(3′)	170.59(5)
Br(2)−As(1)−Br(3′)	93.19(4)	Br(3)−As(1)−Br(3′)	81.00(4)
S(1)−As(1)−Br(3′)	96.37(7)	S(2)−As(1)−Br(3′)	91.32(6)

The dimeric arrangements observed for these AsX_3/$MeS(CH_2)_2SMe$ systems contrast with [$BiCl_3\{MeS(CH_2)_2SMe\}_2$], which is monomeric with two chelating dithioethers, giving a pentagonal bipyramidal structure,[3] and [$SbBr_3\{MeS(CH_2)_2SMe\}$], which adopts a 3-dimensional lattice structure with bridging dithioethers and distorted octahedral Sb(III).[6] The difference from the Bi(III) complex is probably mainly steric in origin, the much larger Bi center being more able to accommodate 7-coordination. The difference from the Sb(III) complex is less clear, and with only a very limited range of structures known, it is difficult to be certain of the principal factors responsible for the structures observed. [$SbBr_3\{MeS(CH_2)_2SMe\}$] is assembled differently from its As analogue, with each pyramidal $SbBr_3$ unit linked by three secondary Sb···S interactions (one thioether uses only one lone pair; the other two use both lone pairs to bond to Sb).

Crystals of [$AsCl_3([9]aneS_3)$] were obtained by slow evaporation from a solution of the complex in CH_2Cl_2. The structure shows (Figure 2, Table 3) a discrete monomeric compound in which the $[9]aneS_3$ ligand behaves as a weakly coordinated tridentate face-capping ligand to arsenic, with three mutually *fac* Cl ligands occupying the other coordination sites to give a distorted octahedron. The As−S distances of ca. 2.8 Å are much longer than the As−Cl bonds (ca. 2.3 Å) despite the very similar covalent radii of S and Cl, suggesting weak (secondary) As···S interactions. The long As···S bonds lead to rather acute S−As−S angles, 76.66(6)−77.62(7)°. It would appear that in this species the lone pair on the small As(III) center is essentially stereochemically inactive (although there are some irregularities in the As−S distances, these are small).

The crystal structures of [$SbCl_3([9]aneS_3)$] and [$SbI_3([9]aneS_3)$] have both been established previously.[19,20] The former is an infinite chain with 7-coordinate Sb from tridentate ligation to one $[9]aneS_3$ and a further S-atom from an adjacent macrocycle, together with three terminal Cl's, $d(Sb-S) = 3.156(3) - 3.409(3)$ Å.[19] In contrast, [$SbI_3([9]aneS_3)$] is a discrete molecular compound with distorted octahedral S_3I_3 coordination at Sb, very similar to the structure of [$AsCl_3([9]aneS_3)$] above and with Sb−S bond lengths in the range 2.840(2)−2.895(2) Å, very considerably

---

(19) Willey, G. R.; Lakin, M. T.; Ravindran, M.; Alcock, N. W. *Chem. Commun.* **1991**, 271.

(20) Pohl, S.; Haase, D.; Peters, M. *Z. Anorg. Allg. Chem.* **1993**, *619*, 727.

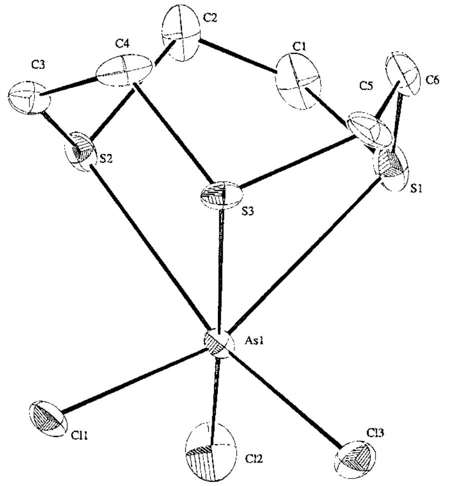

Figure 2. View of the structure of [$AsCl_3$([9]aneS_3)] with numbering scheme adopted. Ellipsoids are drawn at the 40% probability level, and H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [$AsCl_3$([9]aneS_3)]

As1−Cl1	2.304(2)	As1−Cl2	2.339(3)
As1−Cl3	2.361(2)	As1−S3	2.715(3)
As1−S2	2.776(2)	As1−S1	2.857(2)

Cl1−As1−Cl2	97.26(9)	Cl1−As1−Cl3	97.17(8)
Cl2−As1−Cl3	100.0(1)	Cl1−As1−S3	84.67(7)
Cl2−As1−S3	173.7(1)	Cl3−As1−S3	85.64(7)
Cl1−As1−S2	86.19(6)	Cl2−As1−S2	97.44(9)
Cl3−As1−S2	161.62(8)	S3−As1−S2	76.66(6)
Cl1−As1−S1	157.85(8)	Cl2−As1−S1	99.03(9)
Cl3−As1−S1	94.66(7)	S3−As1−S1	77.62(7)
S2−As1−S1	76.92(6)		

shorter than in [$SbCl_3$([9]aneS_3)].[20] The 6-coordinate geometry in [SbI_3([9]aneS_3)] probably arises due to the steric influence of the bulky iodo ligands at Sb(III), preventing further S-coordination (which does occur for the less sterically hindered $SbCl_3$ derivative, [$SbCl_3$([9]aneS_3)], but gives extremely long Sb−S bond distances). It is therefore not surprising that the smaller As(III) center can only accommodate 6-coordination even with the less bulky chloro ligands in [$AsCl_3$([9]aneS_3)]. The difference in the average Sb−S and As−S bond distances in the 6-coordinate species is ca. 0.08 Å, which is less than the difference in the formal ionic radii or covalent radii of As(III) and Sb(III) (ca. 0.20 Å), consistent with $AsCl_3$ being a poorer acceptor than SbI_3.

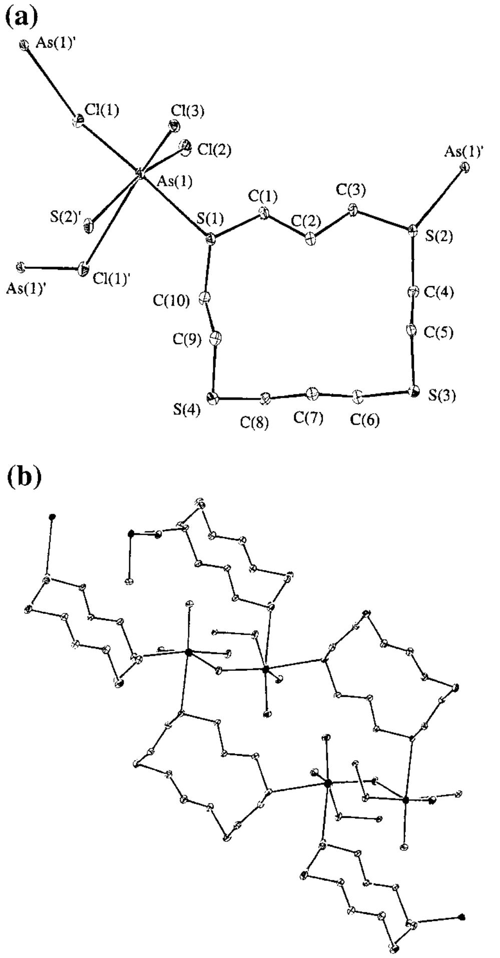

Figure 3. (a) View of the asymmetric unit of [$AsCl_3$([14]aneS_4)] together with nearest symmetry-related neighbors (marked with primes) and showing the atom-numbering scheme. Ellipsoids are drawn at the 40% probability level, and H atoms are omitted for clarity. (b) View of part of the 2-dimensional sheet structure of [$AsCl_3$([14]aneS_4)].

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [$AsCl_3$([14]aneS_4)]

As(1)−Cl(1)	2.2937(8)	As(1)−Cl(1′)	3.3731(8)
As(1)−Cl(2)	2.2821(9)	As(1)−Cl(3)	2.1889(8)
As(1)−S(1)	2.8709(9)	As(1)−S(2′)	2.9655(9)

As(1)−Cl(1)−As(1′)	127.77(3)	Cl(1)−As(1)−Cl(1′)	93.76(2)
Cl(1)−As(1)−Cl(2)	94.90(3)	Cl(1)−As(1)−Cl(3)	94.15(3)
Cl(1)−As(1)−S(1)	169.50(3)	Cl(1)−As(1)−S(2′)	94.29(3)
Cl(2)−As(1)−Cl(1′)	99.82(3)	Cl(2)−As(1)−Cl(3)	94.75(3)
Cl(2)−As(1)−S(1)	94.33(3)	Cl(2)−As(1)−S(2′)	169.01(3)
Cl(3)−As(1)−Cl(1′)	162.74(3)	Cl(3)−As(1)−S(1)	80.10(3)
Cl(3)−As(1)−S(2′)	90.58(3)	S(1)−As(1)−Cl(1′)	89.58(2)
S(1)−As(1)−S(2′)	77.10(2)	S(2′)−As(1)−Cl(1′)	73.55(2)

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).[6] Analysis of the bond length distribution in the crystal structure of [$AsCl_3$([14]aneS_4)] and comparison with [$(SbBr_3)_2$([14]aneS_4)] may shed some light on possible reasons for this difference. The structure shows (Figure 3, Table 4) some unusual features. In this case each As center adopts a distorted octahedral geometry through two terminal Cl's, two S atoms, and two μ^2-Cl's. However, unlike in the [AsX_3{MeS(CH$_2$)$_2$SMe}] dimers above (and the majority of Bi(III) and Sb(III) derivatives with thio- and selenoether ligands), the μ^2-Cl's link to two different As centers to give an infinite sheet polymer. The bridging tetrathioether 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. The other important differences between this species and [$(SbBr_3)_2$([14]aneS_4)] are that the latter has an Sb center (within μ^2-dibromo Sb_2Br_6 dimers) coordinated to each thioether S atom (hence the 2:1 stoichiometry), but one pair of symmetry related Sb−S bonds is significantly longer than the other pair (3.143(4) vs 2.965(4) Å). The very asymmetric As−Cl$_{\text{bridging}}$ distances

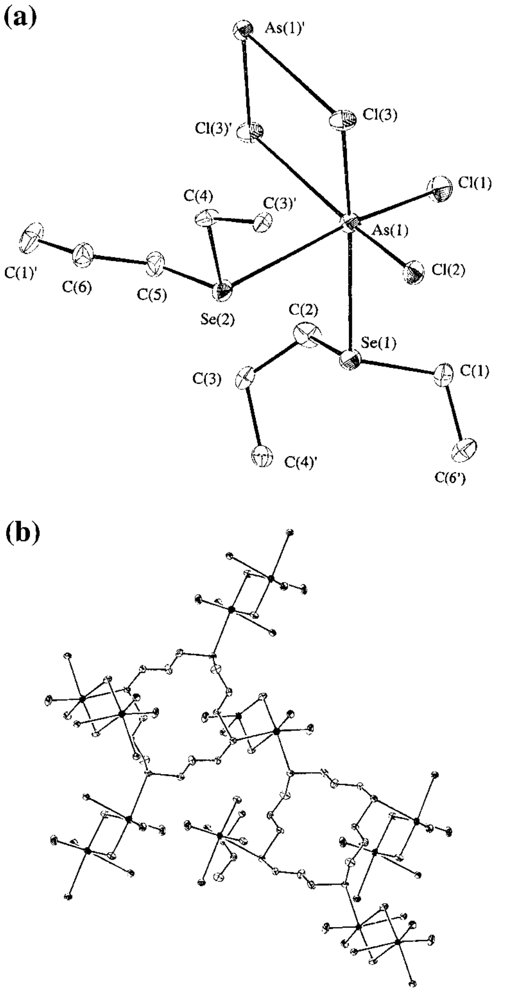

Figure 4. (a) View of the asymmetric unit for the structure of $[(AsCl_3)_2([16]aneSe_4)]$ with nearest symmetry-related neighbors (marked with primes) and showing the atom-numbering scheme. Ellipsoids are drawn at the 40% probability level, and H atoms are omitted for clarity. (b) View of part of the 2-dimensional sheet structure of $[(AsCl_3)_2([16]aneSe_4)]$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[(AsCl_3)_2([16]aneSe_4)]$

Se(1)−As(1)	2.922(1)	Se(2)−As(1)	3.163(2)
As(1)−Cl(2)	2.196(3)	As(1)−Cl(1)	2.243(3)
As(1)−Cl(3)	2.314(3)	As(1)−Cl(3′)	3.294(3)
Cl(2)−As(1)−Cl(1)	94.6(1)	Cl(2)−As(1)−Cl(3)	93.3(1)
Cl(1)−As(1)−Cl(3)	95.1(1)	Cl(2)−As(1)−Se(1)	83.08(8)
Cl(1)−As(1)−Se(1)	91.51(9)	Cl(3)−As(1)−Se(1)	172.67(9)
Cl(2)−As(1)−Se(2)	86.08(9)	Cl(1)−As(1)−Se(2)	171.03(9)
Cl(3)−As(1)−Se(2)	93.78(8)	Se(1)−As(1)−Se(2)	79.67(4)
Cl(2)−As(1)−Cl(3′)	172.7(1)	Cl(1)−As(1)−Cl(3′)	88.0(1)
Cl(3)−As(1)−Cl(3′)	79.7(1)	Se(1)−As(1)−Cl(3′)	103.72(6)
Se(2)−As(1)−Cl(3′)	92.43(6)	As(1)−Cl(3)−As(1′)	100.3(1)

suggest that the As-based lone pair is partially stereochemically active and in this case is oriented along the vector of the long As···Cl1′ bond.

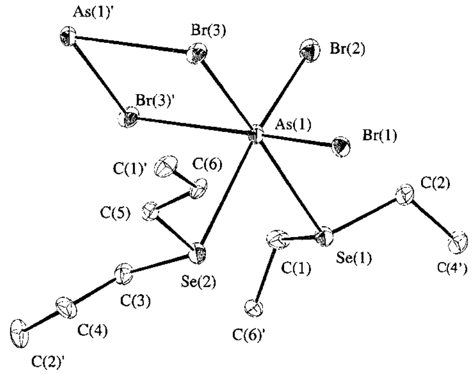

Figure 5. View of asymmetric unit for the structure of $[(AsBr_3)_2([16]aneSe_4)]$ with nearest symmetry-related neighbors (marked with primes) and showing the atom-numbering scheme. Ellipsoids are drawn at the 40% probability level, and H atoms are omitted for clarity. Note that the infinite structure is very similar to that in Figure 4b.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[(AsBr_3)([16]aneSe_4)]$

Br(1)−As(1)	2.3691(9)	Br(2)−As(1)	2.4452(9)
Br(3)−As(1)	2.5209(9)	Br(3′)−As(1)	3.279(1)
Se(1)−As(1)	2.8876(9)	Se(2)−As(1)	3.0854(9)
As(1)−Br(3)−As(1′)	97.48(3)	Br(1)−As(1)−Br(2)	95.69(3)
Br(1)−As(1)−Br(3)	93.71(3)	Br(2)−As(1)−Br(3)	94.49(3)
Br(1)−As(1)−Se(1)	82.01(3)	Br(2)−As(1)−Se(1)	91.43(3)
Br(3)−As(1)−Se(1)	173.02(4)	Br(1)−As(1)−Se(2)	84.30(3)
Br(2)−As(1)−Se(2)	171.72(3)	Br(3)−As(1)−Se(2)	93.76(3)
Se(1)−As(1)−Se(2)	80.37(2)	Br(1)−As(1)−Br(3′)	174.82(3)
Br(2)−As(1)−Br(3′)	88.17(3)	Br(3)−As(1)−Br(3′)	82.52(3)
Se(1)−As(1)−Br(3′)	101.38(2)	Se(2)−As(1)−Br(3′)	92.37(2)

Crystals of the tetraselenoether macrocyclic species $[(AsCl_3)_2([16]aneSe_4)]$ (Figure 4, Table 5) and $[(AsBr_3)_2([16]aneSe_4)]$ (Figure 5, Table 6) show very similar 3-dimensional polymer structures assembled from asymmetric (weakly associated) dinuclear μ^2-dihalo As_2X_6 dimers cross-linked by coordination to $[16]aneSe_4$ molecules, with each Se atom linked to a different As center. In these species, the considerable asymmetry in the As−X bond lengths within the dinuclear core suggests partial stereochemical activity for the lone pair on each As along the long As1−Cl3′ or As1−Br3′ axis. As in the cases above, the As−Se bond distances in these two compounds (2.9217(15), 3.1633(19) and 2.8876(9), 3.0854(9) Å) are only shorter by ca. 0.1 Å than *d*(Sb−Se) in the closely related $[(SbBr_3)_2([16]aneSe_4)]$, less than the difference in the covalent radii of As(III) vs Sb(III), reflecting the poorer Lewis acidity of the former.[5]

We have now crystallographically characterized the related series of complexes of the selenoether macrocycle $[16]aneSe_4$, $[(AsBr_3)_2([16]aneSe_4)]$, $[(SbBr_3)_2([16]aneSe_4)]$, and the 1:1 species $[BiBr_3([16]aneSe_4)]$. We note, although without an adequate explanation, that while the Sb(III) and As(III) species are structurally very similar (with the same space group and similar unit cell dimensions), and show coordination through two mutually cis Se atoms from different macrocycles, unusually the Bi(III) species shows mutually trans Se coordination.

Conclusions

The first series of thioether and selenoether complexes involving AsX_3 as a Lewis acid has been synthesized, and crystal structures of six of the new complexes have been obtained. The structures show some significant differences from their Bi(III) and Sb(III) analogues (where known). With the very limited range of examples structurally characterized and the possibility of isomers occurring under different reaction conditions, at this stage one cannot draw too many conclusions regarding the reasons for the structural differences. However, consideration of the Bi/Sb/As to S/Se bond length distributions in a series of complexes with a given ligand suggests that the much poorer Lewis acidity of AsX_3 compared to either BiX_3 or SbX_3 plays a significant role. Also, the much smaller radius of As(III) has steric implications, and while 7-coordination is observed in thio- and selenoether derivatives of Bi(III) and Sb(III), the maximum coordination number observed by us for As is 6 (although a small number of cases involving 7-coordinate As(III) are known[21]). In general in the complexes reported here the As-based lone pair does seem to have significant stereochemical activity. However, $[AsCl_3([9]aneS_3)]$ appears to be the exception, with little or no stereochemical activity. This may in part be a consequence of the constraints imposed by the ring on the small As(III) center.

Finally, similar reactions using PCl_3 or PBr_3 and Me_2S, $MeS(CH_2)_2SMe$, $MeSe(CH_2)_2SeMe$, or $[9]aneS_3$ failed to give any solid products and ^{31}P NMR spectra of the reaction mixtures show no shift from free PX_3, consistent with the very poor Lewis acidity of the PX_3.

Experimental Section

Infrared spectra were measured as Nujol mulls between CsI plates using a Perkin-Elmer 1710 spectrometer over the range 220−4000 cm^{-1}. ^1H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 using a Bruker AM300 spectrometer. Microanalyses were obtained from the University of Strathclyde Microanalytical Laboratory. Arsenic trihalides (Aldrich or Alfa) were obtained commercially and used as received. The selenoether macrocycles were prepared by the literature method,[22] while $[9]aneS_3$ and $[14]aneS_4$ were purchased from Aldrich. Standard Schlenk techniques and anhydrous solvents were used for all preparations and manipulations.

Preparations. $[AsCl_3([9]aneS_3)]$. Addition of a CH_2Cl_2 solution (5 cm^3) of $[9]aneS_3$ (0.045 g, 0.25 mmol) to a CH_2Cl_2 solution (5 cm^3) of $AsCl_3$ (0.045 g, 0.25 mmol) produced a clear pale yellow solution. Concentration of the solution in vacuo produced a yellow solid which was filtered, washed with CH_2Cl_2, and dried in vacuo. Yield: 54%. Anal. Calcd for $C_6H_{12}AsCl_3S_3$: C, 19.9; H, 3.3. Found: C, 20.3; H, 3.5. ^1H NMR: δ 3.1 (s, CH_2). IR/cm^{-1}: 418 br (As−Cl).

The other compounds were prepared similarly—see Supporting Information.

X-ray Crystallography. Details of the crystallographic data collection and refinement parameters are given in Table 7. Crystals of $[AsCl_3([9]aneS_3)]$, $[AsCl_3([14]aneS_4)]$, $[(AsCl_3)_2([16]aneSe_4)]$, $[(AsBr_3)_2([16]aneSe_4)]$, $[AsBr_3\{MeS(CH_2)_2SMe\}]$, and $[AsI_3\{MeS(CH_2)_2SMe\}]$ were obtained by slow evaporation from layered solutions of the individual reactants in CH_2Cl_2 in an N_2-purged drybox. Data collection used a Rigaku AFC7S four-circle diffractometer ($[AsCl_3([9]aneS_3)]$ and $[(AsCl_3)_2([16]aneSe_4)]$) ($T$ = 150 K) or an Enraf Nonius Kappa CCD diffractometer ($[AsBr_3\{MeS(CH_2)_2SMe\}]$,

Table 7. Crystallographic Data

	$[AsI_3\{MeS(CH_2)_2SMe\}]$	$[AsBr_3\{MeS(CH_2)_2SMe\}]$	$[AsCl_3([9]aneS_3)]$	$[AsCl_3([14]aneS_4)]$	$[(AsCl_3)_2([16]aneSe_4)]$	$[(AsBr_3)_2([16]aneSe_4)]$
formula	$C_4H_{10}AsI_3S_2$	$C_4H_{10}AsBr_3S_2$	$C_6H_{12}AsCl_3S_3$	$C_{10}H_{20}AsCl_3S_4$	$C_{12}H_{24}As_2Cl_6Se_4$	$C_{12}H_{24}As_2Br_6Se_4$
MW	577.88	436.88	361.62	449.49	846.71	1113.45
cryst system	monoclinic	monoclinic	tetragonal	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$I4_1cd$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	9.1528(1)	10.2818(6)	17.520(4)	13.5942(2)	9.764(3)	10.1220(1)
b/Å	11.5622(2)	7.8014(5)	17.520(4)	7.7007(1)	13.164(1)	13.4494(2)
c/Å	12.0939(2)	14.503(1)	16.790(7)	18.1270(3)	10.627(2)	10.5125(2)
β/deg	93.863(1)	102.9330(2)	90	111.1662(5)	114.90(1)	113.49(2)
V/Å^3	1276.95(3)	1133.8(1)	5153(2)	1769.60(4)	1239.0(4)	1312.48(3)
Z	4	4	16	4	2	2
μ(Mo Kα)/cm^{-1}	101.93	139.11	37.03	28.27	92.17	172.24
no. of unique obsd reflcns	3035	2435	1322	4282	2297	2994
no. of obsd reflcns with $I > 2\sigma(I)$	2560	1689	1080	3246	1653	2598
R	0.046	0.061^a	0.036^a	0.039	0.075^a	0.066^a
R_w	0.061	0.146^a	0.095^a	0.043	0.201^a	0.173^a

[a] R_1 (based on F) and wR_2 (based on F^2) for $F > 4\sigma(F)$ from SHELXL-97.

---

(21) Alcock, N. W.; Ravindran, M.; Willey, G. R. *Acta Crystallogr., Sect. B* **1993**, *49*, 507.

(22) Batchelor, R. J.; Einstein, F. W. B.; Gay, I.. D.; Gu, J.-H.; Johnston, B. D.; Pinto, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 6582.

$[AsI_3\{MeS(CH_2)_2SMe\}]$, $[(AsBr_3)_2([16]aneSe_4)]$) ($T = 120$ K) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Structure solution and refinement were routine.[23−28] Selected bond lengths and angles are presented in Tables 1−6.

Acknowledgment. We thank the EPSRC for support and Professor M. B. Hursthouse for access to the Nonius Kappa CCD diffractometer.

Supporting Information Available: IR and ^1H NMR spectroscopic data and analyses for all compounds and X-ray crystallographic files, in CIF format, for the structures of $[AsBr_3\{MeS(CH_2)_2SMe\}]$, $[AsI_3\{MeS(CH_2)_2SMe\}]$, $[AsCl_3([9]aneS_3)]$, $[AsCl_3([14]aneS_4)]$, $[(AsCl_3)_2([16]aneSe_4)]$, and $[(AsBr_3)_2([16]aneSe_4)]$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011139T

---

(23) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATTY, The DIRDIF Program System*; Technical Report of the Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1992.

(24) *TeXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1995.

(25) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(26) Blessing, R. H. *Acta Crystallogr*., *Sect*. *A* **1995**, *51*, 33.

(27) Walker, N.; Stuart, D. *Acta Crystallogr*., *Sect*. *A* **1983**, *39*, 158.

(28) Flack, H. D. *Acta Crystallogr*., *Sect*. *A* **1983**, *39*, 876.