DALTON
FULL PAPER

Synthesis and structures of one-dimensional co-ordination polymers derived from bismuth(III) selenoether macrocyclic complexes

Andrew J. Barton, Anthony R. J. Genge, William Levason and Gillian Reid

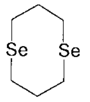
Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ

Received 22nd March 2000, Accepted 9th May 2000
Published on the Web 12th June 2000

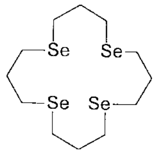
Treatment of BiX_3 (X = Cl or Br) with [8]aneSe_2 (1,5-diselenacyclooctane), [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane), [24]aneSe_6 (1,5,9,13,17,21-hexaselenacyclotetracosane) yielded species of formula $[BiX_3(L)]$ in moderate to high yield as intensely coloured powdered solids. The crystal structures of $[BiCl_3([8]aneSe_2)]$ and $[BiBr_3([16]aneSe_4)]$ each reveal infinite one-dimensional ladder structures derived from almost planar Bi_2X_6 dimer units linked by μ-bridging cyclic selenoethers. Each Bi is co-ordinated to a Se_2X_4 donor set, with the Se donor atoms occupying mutually *trans* co-ordination sites. The selenoether ligands adopt exocyclic arrangements and, in $[BiBr_3([16]aneSe_4)]$, it is two *trans* Se atoms which co-ordinate to Bi^{III}, leaving the other two Se atoms non-co-ordinating. The structures of these species are contrasted with related complexes involving acyclic selenoether ligands and with the few structurally characterised bismuth(III) halide complexes with macrocyclic thioether ligands.

Introduction

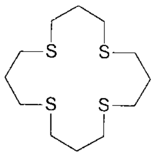
We have been interested for some time in the synthesis and properties of thio-, seleno- and telluro-ether ligands and the co-ordination chemistry of these with a wide range of d-block elements has now been investigated by ourselves and others.[1] More recently we have extended these studies to include the heavier p-block elements such as Sn^{IV} and Bi^{III}.[2,3] Compared to transition metal chemistry, main group co-ordination chemistry has in general received less attention, possibly due to the fact that the compounds often lack some of the features usually required for their characterisation *via* conventional spectroscopic methods, *e.g.* they are often colourless and/or labile in solution. Furthermore, complexes of the p-block elements may adopt a very wide range of geometries. This point is clearly demonstrated by our recent work on bismuth(III) halide complexes with acyclic thio- and seleno-ether ligands, which has revealed an extremely diverse range of structures ranging from discrete mononuclear species with chelating dithioethers, *e.g.* $[BiCl_3\{MeS(CH_2)_2SMe\}_2]$, through infinite one-, two- or three-dimensional networks, *e.g.* $[BiCl_3\{MeSe(CH_2)_3SeMe\}]$ and $[Bi_4Cl_{12}\{MeS(CH_2)_3SMe\}_4]\cdot 4H_2O$.[3] In order to investigate this chemistry further and to establish the range of structures and co-ordination modes possible for these systems, we have now extended this work to investigate the chemistry of Bi^{III} with macrocyclic selenoether ligands. Here we report the preparation and structures of a series of bismuth(III) selenoether macrocyclic complexes, $[BiX_3(L)]$ [X = Cl or Br; L = [8]aneSe_2 (1,5-diselenacyclooctane), [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane) or [24]aneSe_6 (1,5,9,13,17,21-hexaselenacyclotetracosane)]. The directly analogous thioether macrocyclic species $[BiX_3([16]aneS_4)]$ ([16]aneS_4 = 1,5,9,13-tetrathiacyclohexadecane) were also prepared for comparison.



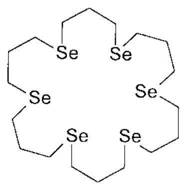
[8]aneSe_2



[16]aneSe_4



[16]aneS_4



[24]aneSe_6

Results and discussion

Reaction of BiX_3 (X = Cl or Br) with one molar equivalent of [8]aneSe_2 in anhydrous MeCN solution yields yellow solutions from which microcrystalline, air-stable, red powders with stoichiometry $[BiX_3([8]aneSe_2)]$ were obtained. Similarly, reaction of BiX_3 with one molar equivalent of [16]aneSe_4, [16]aneS_4 or [24]aneSe_6 in anhydrous MeCN yields deep orange $[BiX_3([16]aneSe_4)]$, bright yellow $[BiX_3([16]aneS_4)]$ or yellow–orange $[BiX_3([24]aneSe_6)]$. The IR spectra of the chloro derivatives show several features in the range 230–280 cm^{-1} which are probably associated with ν(Bi–Cl). Owing to the poor solubilities of the compounds in non-co-ordinating solvents, UV–visible spectra were recorded by diffuse reflectance. The spectra reveal only ill defined absorptions tailing from the UV into the visible region. Similarly, we were unable to obtain useful NMR spectroscopic data (^1H or ^{77}Se) due to the poor solubilities. Attempts to heat these solutions to increase the solubility results in decomposition, while dissolution in co-ordinating solvents readily displaces the selenoether ligand. Similar problems were encountered in our previous work on dithioether and diselenoether complexes of Bi^{III}.[3] A crystal structure determination was undertaken on $[BiCl_3([8]aneSe_2)]$ in order to determine the structural arrangement present and to provide a comparison with the closest acyclic selenoether analogue $[BiCl_3\{MeSe(CH_2)_3SeMe\}]$, the structure of which we have already reported.[3] Crystals of $[BiCl_3([8]aneSe_2)]$ were obtained by slow evaporation from a solution of the complex in

Table 1 Selected bond lengths (Å) and angles (°) for $[BiCl_3([8]aneSe_2)]$

Bi(1)–Se(1)	2.988(4)	Bi(2)–Se(3)	2.977(4)
Bi(1)–Se(2)	3.044(4)	Bi(2)–Se(4)	3.067(4)
Bi(1)–Cl(1)	2.61(1)	Bi(2)–Cl(3)	2.836(8)
Bi(1)–Cl(2)	2.522(8)	Bi(2)–Cl(4)	2.95(1)
Bi(1)–Cl(3)	2.77(1)	Bi(2)–Cl(5)	2.50(1)
Bi(1)–Cl(4)	2.832(8)	Bi(2)–Cl(6)	2.573(8)
Se(1)–Bi(1)–Se(2)	171.4(1)	Cl(3)–Bi(2)–Cl(4)	81.3(2)
Se(3)–Bi(2)–Se(4)	168.9(1)	Cl(5)–Bi(2)–Cl(6)	94.8(3)
Cl(1)–Bi(1)–Cl(2)	93.9(3)	Bi(1)–Cl(3)–Bi(2)	99.0(3)
Cl(3)–Bi(1)–Cl(4)	84.5(3)	Bi(1)–Cl(4)–Bi(2)	95.2(3)

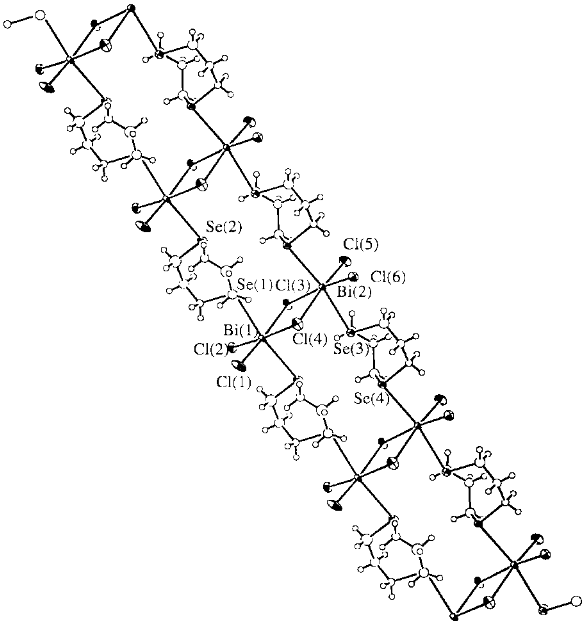


Fig. 1 View of the structure of a portion of the infinite 1-dimensional ladder adopted by $[BiCl_3([8]aneSe_2)]$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

MeCN. The structure shows (Fig. 1, Table 1) an infinite one-dimensional ladder structure derived from almost coplanar Bi_2Cl_6 'rungs' which are linked by four bridging $[8]aneSe_2$ 'uprights'. The Se-donor atoms adopt mutually *trans* co-ordination sites on each Bi ion, giving Bi–Se 2.977(4)–3.067(4) Å. We have noted previously[3] that the introduction of mutually *cis* neutral ligands (*e.g.* phosphines[4]) is much more common than *trans* in bismuth(III) co-ordination chemistry. The Bi–$Cl_{terminal}$ bond distances of *ca.* 2.5 Å and Bi–$Cl_{bridging}$ distances of *ca.* 2.8 Å are similar to those observed in other related chlorobismuth species. The structure adopted by this $[8]aneSe_2$ complex may be compared with that of $[BiCl_3\{MeSe(CH_2)_3SeMe\}]$. Rather than the one-dimensional network seen for $[BiCl_3([8]aneSe_2)]$, $[BiCl_3\{MeSe(CH_2)_3SeMe\}]$ adopts an infinite two-dimensional sheet structure in which staggered Bi_2Cl_6 units are linked *via* four different bridging diselenoether ligands; the Se donors are mutually *trans*.[3]

Table 2 Selected bond lengths (Å) and angles (°) for $[BiBr_3([16]aneSe_4)]$

Bi(1)–Se(1)	2.952(2)	Bi(1)–Br(2)	2.711(2)
Bi(1)–Se(3)	3.095(2)	Bi(1)–Br(3)	3.002(2)
Bi(1)–Br(1)	2.693(2)	Bi(1)–Br(3*)	3.058(2)
Se(1)–Bi(1)–Se(3*)	162.86(4)	Br(3)–Bi(1)–Br(3*)	86.04(5)
Br(1)–Bi(1)–Br(2)	91.16(6)	Bi(1)–Br(3)–Bi(1*)	93.96(5)

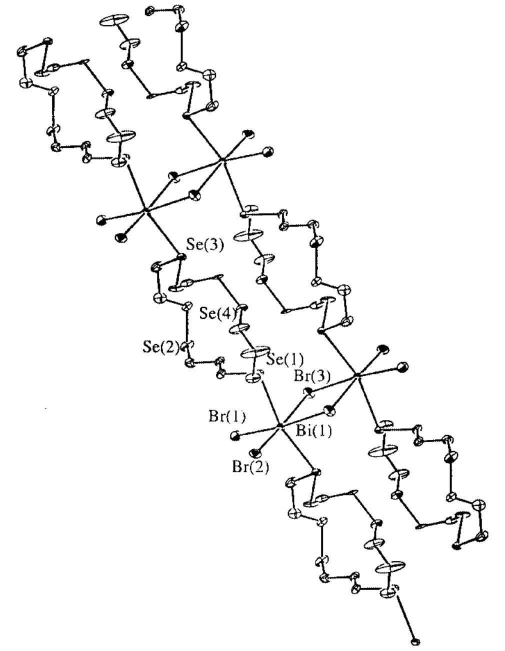


Fig. 2 View of the structure of a portion of the infinite 1-dimensional ladder adopted by $[BiBr_3([16]aneSe_4)]$ with the numbering scheme adopted. Hydrogen atoms are omitted for clarity and ellipsoids are drawn at the 40% probability level.

A very similar structural motif is observed for the tetraselenoether species $[BiBr_3([16]aneSe_4)]$ (Fig. 2, Table 2). In this case the one-dimensional arrangement is derived from almost planar Bi_2Br_6 units, with each Bi linked to the next Bi_2Br_6 units by bridging $[16]aneSe_4$ ligands. Co-ordination is *via* one Se-donor atom to each Bi, *i.e.* μ-bridging $[16]aneSe_4$. The macrocycles are bonded (and therefore bridge) *via* mutually *trans* selenium donors and adopt an exocyclic conformation. Within this centrosymmetric structure each Bi is co-ordinated *via* a *trans*-Se_2Br_4 donor set, Bi–Se(1) 2.952(2), Bi–Se(3) 3.095(2), Bi–Br(1) 2.693(2), Bi–Br(2) 2.711(2), Bi–Br(3) 3.002(2) and Bi–Br(3*) 3.058(2) Å. The other two mutually *trans* selenium atoms, Se(2) and Se(4), within each $[16]aneSe_4$ unit remain non-co-ordinating. The Bi–Se distances in these two bismuth(III) halogeno compounds incorporating cyclic selenoethers are very similar to those observed in the other structurally characterised bismuth selenoether species, *e.g.* $[BiX_3\{MeSe(CH_2)_3SeMe\}]$ (X = Cl or Br, *d*(Bi–Se) = 2.978(2)–3.036(2) Å) and $[BiCl_3\{MeC(CH_2SeMe)_3\}]$ (*d*(Bi–Se) = 2.962–3.156(4) Å).[3] The stereochemical activity of the Bi-based lone pair appears to be minimal in the new compounds. It is also noteworthy that while the compounds reported here are the first structurally characterised (macro)cyclic selenoether complexes involving bismuth, there is also only one other structurally characterised species which involves exocyclic $[16]aneSe_4$, that is $[Cu_n([16]aneSe_4)_n]^{n+}$ reported by Pinto and co-workers.[5]

In view of the potential availability of the two remaining Se atoms, Se(2) and Se(4), in $[BiBr_3([16]aneSe_4)]$ for co-ordination, we were interested to establish whether it might be possible to cross-link the chains of $[BiBr_3([16]aneSe_4)]$ through co-ordination of additional Bi to these atoms. However, treatment of $[BiBr_3([16]aneSe_4)]$ with one molar equivalent of $BiBr_3$ in MeCN solution gave no apparent reaction. Similarly, treatment of $[24]aneSe_6$ with two molar equivalents of BiX_3 yields only the 1 : 1 species $[BiX_3([24]aneSe_6)]$, although this may simply reflect the lower solubility of the 1 : 1 species.

Several macrocyclic thioether complexes of $BiCl_3$ have been reported previously, including $[BiCl_3([12]aneS_4)]$, $[BiCl_3([15]aneS_5)]$, $[BiCl_3([18]aneS_6)]$ and $[(BiCl_3)_2([24]aneS_8)]$ ($[12]aneS_4$ = 1,4,7,10-tetrathiacyclododecane, $[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane, $[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane, $[24]aneS_8$ = 1,4,7,10,13,16,19,22-octathiacyclotetracosane). Without exception, these adopt discrete molecular structures. In fact, all of the structurally characterised bismuth(III) halogeno complexes involving crown ethers and crown thioethers reflect the dominance of the pyramidal BiX_3 unit on the structures adopted, with weak $Bi\cdots O$ or $Bi\cdots S$ interactions replacing the secondary $Bi\cdots X$ interactions in the parent trihalides, generating 7-, 8- or 9-co-ordinate compounds.[6,7] A stereochemically active lone pair on the Bi, directed towards the weakly interacting S- or O-donors, is implied for these species. The selenoether macrocyclic complexes reported here are therefore markedly different in their co-ordination modes and geometries from those of the lighter Group 16 analogues, generating infinite chain structures. In view of these results we wished to investigate the factors which influence the structures adopted. We have noted previously that while ligands of the form $MeE(CH_2)_2EMe$ (E = S or Se) typically yield chelate complexes, introduction of an additional CH_2 unit (in $MeE(CH_2)_3EMe$) can lead to a tendency to bridge metal centres, *e.g.* in $[Ag_n\{MeE(CH_2)_3EMe\}_{2n}]^{n+}$[8] and in the bismuth(III) species $[BiX_3\{MeE(CH_2)_3EMe\}]$.[3] Since macrocyclic selenoether ligands involving dimethylene linkages are unstable[9] (these would otherwise provide the direct analogues of the macrocyclic thioether complexes above), we adopted an alternative strategy, to investigate the co-ordination of [16]aneS_4 (the direct analogue of [16]aneSe_4) with BiX_3. The 1 : 1 complexes $[BiX_3([16]aneS_4)]$ were obtained in good yield, however despite considerable efforts to obtain crystals suitable for a structure analysis we have not yet been successful.

These results show that cyclic selenoethers serve to add to the structural diversity seen in bismuth(III) halide co-ordination chemistry, revealing structural arrangements which contrast with those identified for the acyclic selenoether complex analogues and also markedly different from those seen for several thioether macrocyclic complexes of Bi^{III}. We are currently investigating the chemistry of these and related macrocyclic ligands with other p-block elements.

Experimental

Infrared spectra were measured as Nujol mulls between CsI plates using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}. All preparations used the same general method, which is detailed for one example below. Standard Schlenk methods were used. [8]aneSe_2, [16]aneSe_4 and [24]aneSe_6 were prepared by the literature method.[9]

Preparations

$[BiCl_3([8]aneSe_2)]$. A solution of $BiCl_3$ (0.16 g, 0.52 mmol) in dry, degassed MeCN (4 cm^3) was added to a stirred solution of [8]aneSe_2 (0.24 g, 1.04 mmol) in CH_2Cl_2 (2 cm^3) at room temperature. A yellow solution formed almost immediately. Concentrating the solution *in vacuo* gave a red solid which was filtered off, washed with CH_2Cl_2 and dried *in vacuo*. Yield 0.157 g, 55%. Required for $C_6H_{12}BiCl_3Se_2$ C 13.0, H 2.2%; found C 13.2, H 2.2%. IR (CsI): ν_{Bi-Cl} 244, 258 and 273 cm^{-1}.

$[BiBr_3([8]aneSe_2)]$. Red solid. Yield 66%. Required for $C_6H_{12}BiBr_3Se_2$ C 10.4, H 1.7%; found C 10.7, H 1.9%.

$[BiCl_3([16]aneSe_4)]$. Deep orange solid. Yield 35%. Required for $C_{12}H_{24}BiCl_3Se_4$ C 18.0, H 3.0%; found C 18.2, H 3.0%. IR (CsI): ν_{Bi-Cl} 247 and 256 cm^{-1}.

$[BiBr_3([16]aneSe_4)]$. Orange solid. Yield 60%. Required for $C_{12}H_{24}BiBr_3Se_4$ C 15.4, H 2.6%; found C 15.5, H 2.6%.

$[BiCl_3([24]aneSe_6)]$. Yellow solid. Yield 60%. Required for $C_{18}H_{36}BiCl_3Se_6$ C 20.8, H 3.5%; found C 20.5, H 3.2%. IR (CsI): ν_{Bi-Cl} 235 and 255 cm^{-1}.

$[BiBr_3([24]aneSe_6)]$. Orange solid. Yield 57%. Required for $C_{18}H_{36}BiBr_3Se_6$ C 18.4, H 3.1%; found C 18.0, H 2.8%.

Table 3 Crystallographic data

	$[BiCl_3([8]aneSe_2)]$	$[BiBr_3([16]aneSe_4)]$
Formula	$C_6H_{12}BiCl_3Se_2$	$C_{12}H_{24}BiBr_3Se_4$
M	557.42	932.85
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$
a/Å	9.362(6)	11.963(3)
b/Å	12.142(9)	12.022(2)
c/Å	11.356(3)	9.509(2)
α/°		91.30(2)
β/°	99.67(3)	109.78(2)
γ/°		118.64(2)
U/Å^3	1272(1)	1100.7(6)
Z	4	2
μ(Mo-Kα)/cm^{-1}	201.53	200.62
Unique obs. reflections	2367	3867
Obs. reflections with $[I_o > 2\sigma(I_o)]$	1929	2902
R	0.043	0.044
R_w	0.055	0.056

$[BiCl_3([16]aneS_4)]$. Bright yellow solid. Yield 68%. Required for $C_{12}H_{24}BiCl_3S_4$ C 23.6, H 3.9%; found C 24.0, H 3.9%. IR (CsI): ν_{Bi-Cl} 264 and 271 cm^{-1}.

$[BiBr_3([16]aneS_4)]$. Bright yellow solid. Yield 92%. Required for $C_{12}H_{24}BiBr_3S_4$ C 19.3, H 3.2%; found C 19.6, H 3.0%.

X-Ray crystallography

Details of the crystallographic data collection and, refinement parameters are given in Table 3. Crystals of $[BiCl_3([8]aneSe_2)]$ and $[BiBr_3([16]aneSe_4)]$ were obtained by slow evaporation from solutions of the appropriate complexes in MeCN. Data collection used a Rigaku AFC7S four-circle diffractometer (T = 150 K) with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Structure solution and refinement were routine.[10,11] For $[BiCl_3([8]aneSe_2)]$ a Bi_2Cl_6 unit and two [8]aneSe_2 ligands were identified in the asymmetric unit. Attempts to refine these C atoms anisotropically led to non-positive definite thermal parameters, presumably since the scattering is dominated by the heavy Bi and Se atoms. The C atoms were therefore refined isotropically for the [8]aneSe_2 structure. The Flack parameter confirmed the correct choice of enantiomorph for this species.[12]

CCDC reference number 186/1975.

See http://www.rsc.org/suppdata/dt/b0/b002287j/ for crystallographic files in .cif format.

Acknowledgements

We thank the EPSRC and the University of Southampton for support.

References

1 For examples see E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109.

2 S. E. Dann, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1996, 4471; *J. Chem. Soc., Dalton Trans.*, 1997, 2207; A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 4549.

3 A. R. J. Genge, W. Levason and G. Reid, *Chem. Commun.*, 1998, 2159; A. J. Barton, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 2000, 859.

4 See for examples N. C. Norman and N. L. Pickett, *Coord. Chem. Rev.*, 1995, **145**, 27; W. Clegg, M. R. J. Elsegood, V. Graham, N. C. Norman, N. L. Pickett and K. Tavakkoli, *J. Chem. Soc., Dalton Trans.*, 1994, 1743.

5 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu and B. M. Pinto, *J. Organomet. Chem.*, 1991, **411**, 147.

6 G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 591; *J. Chem. Soc., Dalton Trans.*, 1992, 1339;

A. J. Blake, D. Fenske, W.-S. Li, V. Lippolis and M. Schroder, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3961.

7 R. D. Rogers, A. H. Bond, S. Aguinaga and A. Reyes, *J. Am. Chem. Soc.*, 1992, **114**, 2967.

8 J. R. Black, N. R. Champness, W. Levason and G. Reid, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3439; *Inorg. Chem.*, 1996, **35**, 1820; *Inorg. Chem.*, 1996, **35**, 4432.

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

10 SHELXS 86, G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.

11 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1995.

12 H. D. Flack, *Acta Crystallogr.*, *Sect. C*, 1983, **39**, 876.