

Unusual structural variations within a family of thioether macrocyclic complexes. Tin(IV) halide adducts of [12]-, [14]- and [16]-aneS₄

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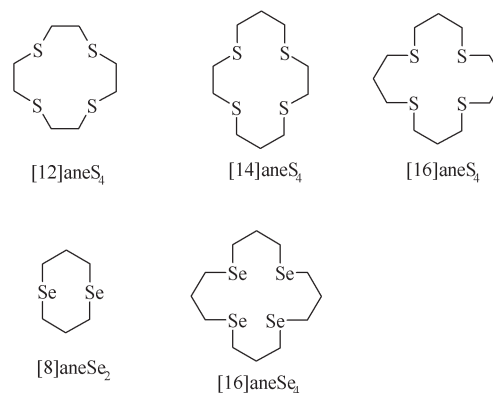
The hydrolytically sensitive compounds $[(\text{SnCl}_4)_2([n]\text{aneS}_4)]$ ($n = 12, 14, 16$) and $[\text{SnBr}_4([n]\text{aneS}_4)]$ are obtained in good yield upon reaction of 2 mol. equiv. of the parent tin tetrahalide with 1 mol. equiv. of macrocycle in rigorously anhydrous CH_2Cl_2 solution. Reactions of [16]aneSe₄ with SnX_4 ($\text{X} = \text{Cl}$ or Br) affords $[\text{SnX}_4([16]\text{aneSe}_4)]$, while reaction of [8]aneSe₂ gives $[\text{SnCl}_4([8]\text{aneSe}_2)]$. The crystal structures of the three closely related complexes $[\text{SnBr}_4([12]\text{aneS}_4)]$, $[\text{SnBr}_4([14]\text{aneS}_4)] \cdot 2/3\text{CH}_2\text{Cl}_2$ and $[\text{SnBr}_4([16]\text{aneS}_4)]$ have been determined. These species represent the first examples of Sn(IV) halide adducts with neutral Group 16 ligands which adopt polymeric structures. The complexes are all chain polymers, although there is unexpected structural dependence upon the macrocycle ring-size, giving each a distinct structural form. Unusually, the coordinated S atoms in both $[\text{SnBr}_4([14]\text{aneS}_4)] \cdot 2/3\text{CH}_2\text{Cl}_2$ and $[\text{SnBr}_4([16]\text{aneS}_4)]$ adopt a mutually *trans* arrangement. Far-IR spectra indicate that the chloro complexes all exist as *cis* octahedral tin(IV) species. Solution NMR spectroscopy shows that the tetrathia and tetraselena macrocyclic complexes are extensively dissociated at 295 K.

Introduction

We are examining the ligating characteristics of thio-, seleno- and telluro-ether ligands with p-block metals and metalloids. In comparison to the transition metal chemistry of these ligands, their main group coordination chemistry has developed much more slowly, and their properties are less well understood.^{1,2} In recent work we have shown that the heavy p-block trihalide Lewis acids of Group 15, arsenic(III), antimony(III) and bismuth(III), readily form complexes with polydentate and macrocyclic thio- and selenoether ligands to give new structural motifs based on a combination of primary M–X ($\text{X} = \text{Cl}, \text{Br}$ or I) interactions, secondary $\text{M} \cdots \text{E}$ ($\text{E} = \text{S}$ or Se) and, in some cases, $\text{M} \cdots \text{X}$ interactions.^{3–8}

Previous work on bidentate dithio-, diseleno- and ditelluro-ether ligands with tin(IV) tetrahalide Lewis acids has produced a series of discrete *pseudo*-octahedral compounds,^{9–11} and multinuclear NMR spectroscopic and X-ray crystallographic studies allowed identification of solution and solid state structures. The only reported (macro)cyclic thioether complexes with Sn(IV) are those involving [9]aneS₃, [18]aneS₆ (1,4,7,10,13,16-hexathiacyclooctadecane) and 1,5-dithiacyclooctane. The discrete dinuclear complex $[(\text{SnCl}_4)_2([18]\text{aneS}_6)]$ involves neutral SnCl_4 fragments coordinated in an *exo* fashion to two adjacent S-donor atoms of the macrocycle with *pseudo*-octahedral coordination at tin, $\text{Sn}–\text{S} = 2.535(10)–2.689(13)$ Å.¹² 1,5-Dithiacyclooctane (L) gives the centrosymmetric *trans*- $[\text{SnCl}_4(\eta^1\text{-L})_2]$ molecule, $d(\text{Sn}–\text{S}) = 2.602(1)$ Å,¹³ whereas SnCl_4 reacts with [9]aneS₃ in MeCN to give the cation–anion species $[\text{SnCl}_3([9]\text{aneS}_3)]_2[\text{SnCl}_6]$. The cation is six-coordinate with a facially coordinated [9]aneS₃ ligand, $\text{Sn}–\text{S} = 2.618(3)–2.657(4)$ Å.¹² In the same paper, the authors commented that SnCl_4 does not react with the macrocyclic thioethers [12]aneS₄ (1,4,7,10-tetrathiacyclododecane) or [15]aneS₅ (1,4,7,10,13-pentathiacyclopentadecane) in anhydrous MeCN solution.

We wished to investigate the reaction of tin(IV) halides with various tetrathia and tetraselena crowns to establish the ligating modes and how variation of the ring size and donor type influences the species produced. We report here on the complexes formed between SnX_4 ($\text{X} = \text{Cl}$ or Br) and L ($\text{L} = [12]\text{aneS}_4$, [14]aneS₄, 1,4,8,11-tetrathiacyclotetradecane, or [16]aneS₄, 1,5,9,13-tetrathiacyclohexadecane, [8]aneSe₂, 1,5-diselenacyclooctane, and [16]aneSe₄, 1,5,9,13-tetraselenacyclohexadecane), including the crystal structures of the closely related series of compounds $[\text{SnBr}_4([12]\text{aneS}_4)]$, $[\text{SnBr}_4([14]\text{aneS}_4)] \cdot 2/3\text{CH}_2\text{Cl}_2$ and $[\text{SnBr}_4([16]\text{aneS}_4)]$, which exhibit surprisingly different structures as the ring-size of the macrocycle is changed.



Results and discussion

Reaction of 2 mol. equiv. of SnX_4 ($\text{X} = \text{Cl}$ or Br) with one mol. equiv. of L ($\text{L} = [12]\text{aneS}_4$, [14]aneS₄ or [16]aneS₄) in rigorously anhydrous CH_2Cl_2 solution affords colourless ($\text{X} = \text{Cl}$) or

yellow ($X = \text{Br}$) solids of composition $[(\text{SnCl}_4)_2\text{L}]$ or $[\text{SnBr}_4\text{L}]$, which were isolated in good yield by filtration, washing with CH_2Cl_2 and drying *in vacuo*. Similar reaction of SnCl_4 with one mol. equiv. of $[\text{8}]_{\text{ane}}\text{Se}_2$ affords the orange $[\text{SnCl}_4([\text{8}]_{\text{ane}}\text{Se}_2)]$ in good yield. Reaction of $[\text{16}]_{\text{ane}}\text{Se}_4$ with two mol. equiv. of SnX_4 affords the 1:1 adducts, $[\text{SnX}_4([\text{16}]_{\text{ane}}\text{Se}_4)]$. Both the SnX_4 precursors and the products are moisture sensitive, hence all manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques and the complexes were stored in a dinitrogen purged dry-box ($\text{H}_2\text{O} < 5 \text{ ppm}$). Attempts to react SnI_4 with $[\text{12}]_{\text{ane}}\text{S}_4$ under similar conditions resulted in isolation of the parent macrocycle, consistent with the poorer Lewis acidity of SnI_4 . However, treatment of SnI_4 with $[\text{9}]_{\text{ane}}\text{S}_3$ in anhydrous CH_2Cl_2 solution gave a dark purple solid which analyses as $[\text{SnI}_4([\text{9}]_{\text{ane}}\text{S}_3)]$ and shows evidence for $[\text{9}]_{\text{ane}}\text{S}_3$ in the IR spectrum. EDX analysis of this product also confirms the presence of Sn, I and S approximately in the expected ratios. This product was too poorly soluble for NMR studies.

The formation of species with a 2:1 SnCl_4 :tetrathiamacrocycle ratio is in accord with the product obtained from reaction of SnCl_4 with $[\text{18}]_{\text{ane}}\text{S}_6$ ¹² and may indicate a similar *cis*-chelate species, with distorted octahedral coordination at $\text{Sn}(\text{IV})$. However, we were surprised to obtain the 1:1 SnBr_4 :tetrathiamacrocycle species as the sole products even when using two molar equivalents of SnBr_4 per macrocycle. We have therefore sought single crystal X-ray structural information on a series of these derivatives – see below.

Infrared spectroscopy on the chloro and bromo complexes reveals up to four features in the range $332\text{--}300 \text{ cm}^{-1}$ ($X = \text{Cl}$), which are assigned to Sn--Cl stretching modes, consistent with a *cis*-disubstituted octahedral geometry.^{9–11} As expected the Sn--Br stretching modes occur at much lower frequency. However, these bands were ill defined and so it is difficult to establish with certainty how many Sn--Br bands are present in the spectra, hence preventing conclusive assignment of stereochemistry.

The crystal structures of the three closely related compounds $[\text{SnBr}_4([\text{12}]_{\text{ane}}\text{S}_4)]$, $[\text{SnBr}_4([\text{14}]_{\text{ane}}\text{S}_4)] \cdot 2/3\text{CH}_2\text{Cl}_2$ and $[\text{SnBr}_4([\text{16}]_{\text{ane}}\text{S}_4)]$ were determined to establish the consequences of varying the macrocycle ring size. These species turn out to display some rather unexpected structural features and they present the first examples of $\text{Sn}(\text{IV})$ complexes involving neutral Group 16 donor ligands that adopt extended structures.

The structure of $[\text{SnBr}_4([\text{12}]_{\text{ane}}\text{S}_4)]$ reveals (Fig. 1, Table 1) an infinite chain polymer involving distorted octahedral $\text{Sn}(\text{IV})$, coordinated *via* two S atoms from different (centrosymmetric) macrocycle units which occupy mutually *cis* coordination sites, and four terminal Br atoms. Each macrocycle utilises every alternate S atom to bridge the Sn centres, with the other two S atoms remaining uncoordinated. The Sn atom occupies a 4c atom site of symmetry *mm*. The Sn--S bond distance of $2.7697(17) \text{ \AA}$ is significantly longer than $d(\text{Sn--S}_{\text{trans}})$ in related complexes, *e.g.* *cis*- $[\text{SnBr}_4(\text{Me}_2\text{S})_2]$ $d(\text{Sn--S}) = 2.692(9)$, $2.692(8)$,¹⁴ *cis*- $[\text{SnBr}_4\{\text{MeS}(\text{CH}_2)\text{SMe}\}]$ $d(\text{Sn--S}) = 2.700(7) \text{ \AA}$.⁹ The Sn--Br distances are $2.5582(7)$ (Br *trans* Br) and $2.5407(7) \text{ \AA}$ (Br *trans* S). The distribution of angles subtended at Sn is large, with the S--Sn--S angle of $77.05(7)^\circ$ being particularly acute. The distribution of Sn--S and Sn--Br bond distances in this species parallels that observed in *cis*- $[\text{SnX}_4(\text{L--L})]$ ($\text{L--L} = \text{dithio-}, \text{deseleno-}$ or *ditelluro-ether*).^{9–11}

Unusually, the structure of $[\text{SnBr}_4([\text{14}]_{\text{ane}}\text{S}_4)] \cdot 2/3\text{CH}_2\text{Cl}_2$ (Fig. 2, Table 2) reveals three independent Sn-containing molecules in the asymmetric unit (in all of which the tin atoms occupy crystallographic inversion centres and there is a further inversion centre at the centre of the macrocyclic rings), together with a CH_2Cl_2 solvent molecule. Symmetry expansion of the macrocyclic species generates infinite chain polymers in each case, with distorted octahedral coordination at Sn through four Br atoms in a plane and two mutually *trans* S

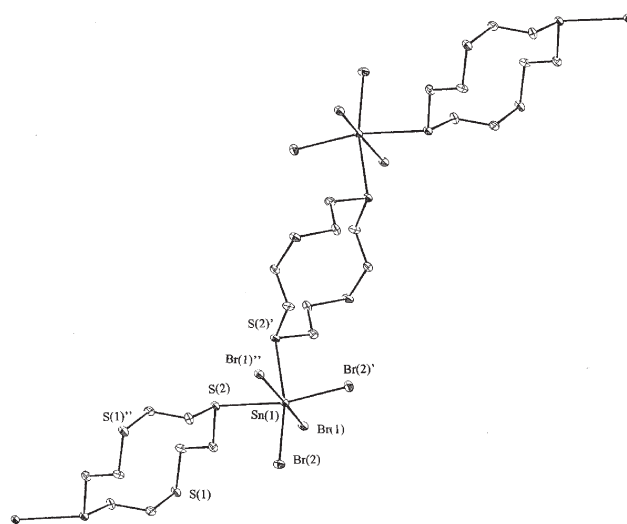


Fig. 1 View of a portion of the structure of $[\text{SnBr}_4([\text{12}]_{\text{ane}}\text{S}_4)]$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity. Atoms marked ' are related by the symmetry operation $x, y, \frac{1}{2}-z$, while those marked '' are related by the symmetry operation $-x, y, z$.

atoms from different thioether ligands. Like the $[\text{SnBr}_4([\text{12}]_{\text{ane}}\text{S}_4)]$ above, in this case the macrocycle uses every alternate S atom to bridge the tin centres. The *trans* configuration at tin is rather unusual for $\text{Sn}(\text{IV})$ -thioether complexes, the only other examples being $[\text{SnCl}_4(\eta^1\text{-L})_2]$ ($\text{L} = 1,5\text{-dithiacyclooctane}$), $d(\text{Sn--S}) = 2.602(1) \text{ \AA}$,¹³ and $[\text{SnX}_4(\text{Me}_2\text{S})_2]$ (of which the bromo derivative has been structurally characterised, $d(\text{Sn--S}) = 2.65(1) \text{ \AA}$)¹⁴ and contrasts with the *cis* arrangement seen for the 12-membered ring analogue, $[\text{SnBr}_4([\text{12}]_{\text{ane}}\text{S}_4)]$, above. The Sn--Br bond distances lie in the range $2.5614(7)\text{--}2.5887(6) \text{ \AA}$, while the Sn--S distances are $2.605(2)$, $2.637(2)$ and $2.656(2) \text{ \AA}$.

A *trans* disposition of the two bound thioether atoms is also evident in the crystal structure of $[\text{SnBr}_4([\text{16}]_{\text{ane}}\text{S}_4)]$ (Fig. 3, Table 3), which involves coordination to $\text{Sn}(\text{IV})$ *via* four Br atoms and two thioether S atoms from different macrocycles. These macrocycles then bridge to adjacent Sn centres, although surprisingly, and unlike the two structures described above, the $[\text{16}]_{\text{ane}}\text{S}_4$ uses adjacent S atoms in the ring, to generate a 1D 'staircase' coordination polymer. The Sn--Br bond distances are all similar, and in accord with those observed for other $\text{Sn--Br}_{\text{trans Br}}$ units, while the bond angles subtended at tin are similar to those in $[\text{SnBr}_4([\text{14}]_{\text{ane}}\text{S}_4)] \cdot 2/3\text{CH}_2\text{Cl}_2$.

The $\text{Sn--S}_{\text{trans S}}$ bond distances observed in these *trans* species ($2.605(2)\text{--}2.656(2) \text{ \AA}$ for $[\text{SnBr}_4([\text{14}]_{\text{ane}}\text{S}_4)] \cdot 2/3\text{CH}_2\text{Cl}_2$; $2.641(2)$ and $2.693(2) \text{ \AA}$ for $[\text{SnBr}_4([\text{16}]_{\text{ane}}\text{S}_4)]$) are slightly shorter than in for example *cis*- $[\text{SnBr}_4\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}]$ ($2.700(7) \text{ \AA}$)⁹ and significantly shorter than in

Table 1 Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{SnBr}_4([\text{12}]_{\text{ane}}\text{S}_4)]$

$\text{Sn}(1)\text{--Br}(1)$	2.5582(7)
$\text{Sn}(1)\text{--Br}(2)$	2.5407(7)
$\text{Sn}(1)\text{--S}(2)$	2.7697(17)
$\text{Br}(2)\text{--Sn}(1)\text{--Br}(2')$	102.09(4)
$\text{Br}(2)\text{--Sn}(1)\text{--Br}(1)$	92.69(1)
$\text{Br}(1)\text{--Sn}(1)\text{--Br}(1'')$	171.43(4)
$\text{Br}(2)\text{--Sn}(1)\text{--S}(2')$	167.48(4)
$\text{Br}(2)\text{--Sn}(1)\text{--S}(2)$	90.43(3)
$\text{Br}(1)\text{--Sn}(1)\text{--S}(2)$	86.65(2)
$\text{S}(2)\text{--Sn}(1)\text{--S}(2')$	77.05(7)

Symmetry operations: prime (') = $x, y, \frac{1}{2}-z$; double prime (')' = $-x, y, z$.

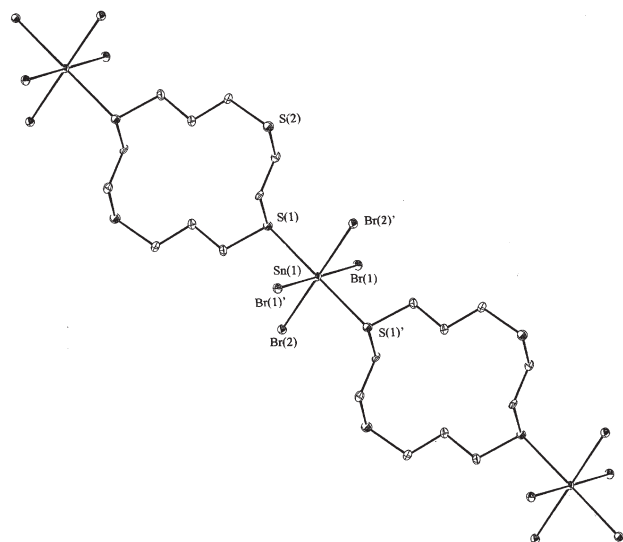


Fig. 2 View of a portion of one of the three crystallographically independent chains in the structure of $[\text{SnBr}_4([\text{14}] \text{aneS}_4)] \cdot 2/3 \text{CH}_2\text{Cl}_2$ with numbering scheme adopted. Atoms marked ' are related by the symmetry operation $-x, 1-y, 1-z$. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity.

$[\text{SnBr}_4([\text{12}] \text{aneS}_4)]$ above. However, in the latter two compounds the ligand *trans* to sulfur is bromide.

The reasons for the occurrence of polymeric assemblies in these compounds may be a combination of the ability of the thioether macrocycles to function as bridging ligands *via exo* coordination, and the poor solubilities of the polymers, which result in them crystallising preferentially from solution. The structures reported here contrast with that of the discrete dinuclear $[(\text{SnCl}_4)_2([\text{18}] \text{aneS}_6)]$ containing the flexible hexathia macrocycle.¹²

Comparison of the structures of the related family of complexes $[\text{SnBr}_4([n] \text{aneS}_4)]$ ($n = 12, 14$ or 16) show that while they all adopt chain polymeric assemblies involving distorted octahedral Sn(IV) coordination in which the macrocycles function as bridging ligands between adjacent SnBr_4 units, there are marked differences in the coordination environment at tin and in the binding mode of the macrocycle as the ring-size is altered. In summary, the small 12-membered ring complex $\text{SnBr}_4([\text{12}] \text{aneS}_4)$ exists as the *cis* octahedral isomer at the tin, the macrocycle using alternating S atoms to bridge to neighbouring tin centres; the 14-membered ring complex $[\text{SnBr}_4([\text{14}] \text{aneS}_4)] \cdot 2/3 \text{CH}_2\text{Cl}_2$ gives a *trans* configuration at

Table 2 Selected bond lengths (Å) and angles (°) for $[\text{SnBr}_4([\text{14}] \text{aneS}_4)] \cdot 2/3 \text{CH}_2\text{Cl}_2$

Sn(1)–Br(1)	2.5660(6)
Sn(1)–Br(2)	2.5661(6)
Sn(1)–S(1)	2.6565(16)
Sn(2)–Br(3)	2.5614(7)
Sn(2)–Br(4)	2.5887(6)
Sn(2)–S(3)	2.6050(17)
Sn(3)–Br(6)	2.5625(7)
Sn(3)–Br(5)	2.5731(7)
Sn(3)–S(5)	2.6371(17)
Br(1)–Sn(1)–Br(2)	90.79(2)
Br(1)–Sn(1)–S(1)	89.31(4)
Br(2)–Sn(1)–S(1)	92.27(4)
Br(3)–Sn(2)–Br(4)	90.60(2)
Br(3)–Sn(2)–S(3)	84.53(4)
Br(4)–Sn(2)–S(3)	93.64(4)
Br(6)–Sn(3)–Br(5)	90.50(2)
Br(6)–Sn(3)–S(5)	96.70(4)
Br(5)–Sn(3)–S(5)	95.58(4)

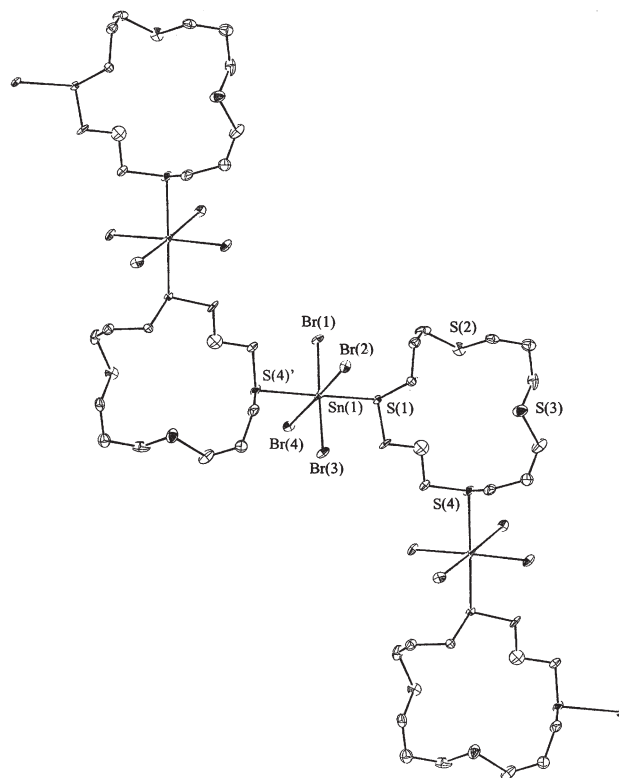


Fig. 3 View of a portion of the structure of $[\text{SnBr}_4([\text{16}] \text{aneS}_4)]$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity. Atoms marked ' are related by the symmetry operation $x + \frac{1}{2}, 2 - y, z$.

Sn, this macrocycle also using alternating S atoms to bridge the tin centres; the 16-membered ring analogue $[\text{SnBr}_4([\text{16}] \text{aneS}_4)]$ gives a *trans* geometry at tin, but uniquely uses adjacent S atoms in the ring to bridge the tin centers.

¹H NMR spectra were recorded from solutions of the complexes in anhydrous CD_2Cl_2 solution to avoid competition from the solvent for coordination to tin. The $\text{SnX}_4/[n] \text{aneS}_4$ systems are extensively dissociated at 295 K, with ¹H NMR spectra little different from 'free' macrocycle. Upon cooling to 183 K the spectra still show broad, ill-defined resonances

Table 3 Selected bond lengths (Å) and angles (°) for $[\text{SnBr}_4([\text{16}] \text{aneS}_4)]$

Sn(1)–Br(1)	2.5625(13)
Sn(1)–Br(2)	2.5528(13)
Sn(1)–Br(3)	2.5774(12)
Sn(1)–Br(4)	2.5489(12)
Sn(1)–S(4')	2.641(2)
Sn(1)–S(1)	2.693(2)
Br(4)–Sn(1)–Br(2)	177.61(4)
Br(4)–Sn(1)–Br(1)	88.98(5)
Br(2)–Sn(1)–Br(1)	90.96(3)
Br(4)–Sn(1)–Br(3)	89.86(3)
Br(2)–Sn(1)–Br(3)	90.36(5)
Br(1)–Sn(1)–Br(3)	175.87(4)
Br(4)–Sn(1)–S(4')	92.88(5)
Br(2)–Sn(1)–S(4')	84.75(6)
Br(1)–Sn(1)–S(4')	96.53(6)
Br(3)–Sn(1)–S(4')	87.48(6)
Br(4)–Sn(1)–S(1)	91.56(7)
Br(2)–Sn(1)–S(1)	90.83(7)
Br(1)–Sn(1)–S(1)	89.61(7)
Br(3)–Sn(1)–S(1)	86.47(7)
S(4')–Sn(1)–S(1)	172.48(10)

Symmetry operation: prime (') = $x + \frac{1}{2}, 2 - y, z$.

and hence we conclude that these systems have still not reached the low temperature limit on the ^1H NMR time scale (see Experimental), hence structural information in solution cannot be obtained from these spectra. For the bromides, which are known to be polymeric in the solid state (see above), dissolution in non-coordinating solvent must involve dissociation/fragmentation. For the SnCl_4 /selenoether species however, the presence of a $\text{I} = \frac{1}{2}$ nucleus on the donor atoms (^{77}Se) of the ring provides a more direct probe of the coordination to tin and hence an opportunity to deduce some structural information. At 295 K $[\text{SnCl}_4(\text{[16]aneSe}_4)]$ is extensively dissociated, but cooling to 183 K leads to two sharp resonances of approximately equal intensity at $\delta(^{77}\text{Se})$ 290 and 157 ppm, consistent with both coordinated and uncoordinated Se atoms, and a 1:1 adduct involving a distorted octahedral Cl_4Se_2 donor set at tin. The ^{119}Sn NMR shift of -644 ppm (183 K) is also consistent with this assignment. The ^{77}Se NMR data on $[\text{SnCl}_4(\text{[8]aneSe}_2)]$ at 183 K ($\delta(^{77}\text{Se}) = 287$) are consistent with a chelating diselenoether, the coordination shift is similar to that observed in $[\text{SnCl}_4\{\text{MeSe}(\text{CH}_2)_3\text{SeMe}\}]$ which is a discrete monomer.¹⁰

The successful isolation of the new tetra-halo tin(IV) complexes involving tetrathia or tetraselena macrocycles described here is probably a consequence of using the non-coordinating (and rigorously anhydrous) CH_2Cl_2 solvent.

Experimental

Infrared spectra were measured as Nujol mulls between CsI plates using a Perkin-Elmer 983G spectrometer over the range 180–4000 cm^{-1} . ^1H NMR spectra were recorded in CDCl_3 or CD_2Cl_2 using a Bruker DPX400 spectrometer, while $^{77}\text{Se}\{^1\text{H}\}$ and ^{119}Sn NMR spectra used a Bruker DPX400 spectrometer operating at 76.33 or 149.02 MHz and are referenced to neat external Me_2Se and Me_4Sn respectively. Microanalyses were obtained from the University of Strathclyde Microanalytical Laboratory. Tin tetrahalides and the thioether macrocycles (Aldrich) were obtained commercially and used as received. The $[\text{8]aneSe}_2$ and $[\text{16]aneSe}_4$ were prepared by the literature method.¹⁵ Standard Schlenk techniques and anhydrous solvents were used for all preparations and the CH_2Cl_2 was freshly distilled from CaH_2 prior to use. Isolated yields were typically 60–70% in each case.

Preparations

$[(\text{SnCl}_4)_2(\text{[12]aneS}_4)]$

To a solution of $[\text{12]aneS}_4$ (0.05 g, 0.2 mmol) in anhydrous CH_2Cl_2 (20 cm^3) was added two molar equivalents of SnCl_4 (0.05 cm^3 , 0.4 mmol). The resulting mixture was stirred at room temperature for ca. 30 min. Concentration *in vacuo* to ca. 5 cm^3 gave a white solid. The solution was decanted from the solid which was subsequently washed with CH_2Cl_2 and dried *in vacuo*. Calc. for $\text{C}_8\text{H}_{16}\text{Cl}_8\text{S}_4\text{Sn}_2$: C, 12.6; H, 2.1. Found: C, 12.9; H, 2.1%. ^1H NMR (CD_2Cl_2 , 223 K): δ 3.50, 2.74 (1:1, both broad, coord. and uncoord. SCH_2). ^{119}Sn NMR (CD_2Cl_2 , 223 K): -564 . IR/ cm^{-1} : 334, 320, 312 (Sn–Cl).

$[(\text{SnCl}_4)_2(\text{[14]aneS}_4)] \cdot \text{CH}_2\text{Cl}_2$

Method as for $[(\text{SnCl}_4)_2(\text{[12]aneS}_4)]$, but using $[\text{14]aneS}_4$. White solid. Calc. for $\text{C}_{10}\text{H}_{20}\text{Cl}_8\text{S}_4\text{Sn}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 15.1; H, 2.6. Found: C, 14.3; H, 3.1%. ^1H NMR (CD_2Cl_2 , 223 K): δ 3.74, 3.61, 3.53 (coord. SCH_2), 2.99, 2.85 (uncoord. SCH_2), 2.12, 2.03 (SCH_2CH_2). ^{119}Sn NMR (CD_2Cl_2 , 223 K): -603 . IR/ cm^{-1} : 332, 328, 323 (Sn–Cl).

$[(\text{SnCl}_4)_2(\text{[16]aneS}_4)]$

Method as for $[(\text{SnCl}_4)_2(\text{[12]aneS}_4)]$, but using $[\text{16]aneS}_4$. White solid. Calc. for $\text{C}_{12}\text{H}_{24}\text{Cl}_8\text{S}_4\text{Sn}_2$: C, 17.6; H, 3.0. Found: C, 17.4; H, 3.0%. ^1H NMR (CD_2Cl_2 , 193 K): δ 3.40, 3.03, 2.58, 2.05, 1.81 (coord. and uncoord. SCH_2 and CH_2). ^{119}Sn NMR (CD_2Cl_2 , 193 K): -543 . IR/ cm^{-1} : 332, 327, 316, 300 (Sn–Cl).

$[\text{SnBr}_4(\text{[12]aneS}_4)]$

To a solution of $[\text{12]aneS}_4$ (0.05 g, 0.2 mmol) in degassed CH_2Cl_2 (20 cm^3) was added SnBr_4 (0.175 g, 0.4 mmol) and the resulting solution was stirred for ca. 30 min. Concentration *in vacuo* afforded a yellow precipitate, which was filtered, washed with CH_2Cl_2 and dried *in vacuo*. Calc. for $\text{C}_8\text{H}_{16}\text{Br}_4\text{S}_4\text{Sn}$: C, 14.2; H, 2.4. Found: C, 14.5; H, 2.1%. ^1H NMR (CD_2Cl_2 , 300 K): δ 2.75 (s); (183 K): 3.0–4.3 (br *m*, coordinated SCH_2), 2.60 (br *s*, uncoordinated SCH_2). IR/ cm^{-1} : 221 (br, Sn–Br).

$[\text{SnBr}_4(\text{[14]aneS}_4)]$

Method as for $[\text{SnBr}_4(\text{[12]aneS}_4)]$, but using $[\text{14]aneS}_4$. Yellow solid. Calc. for $\text{C}_{10}\text{H}_{20}\text{Br}_4\text{S}_4\text{Sn}$: C, 17.0; H, 2.9. Found: C, 16.9; H, 2.6%. ^1H NMR (CD_2Cl_2 , 300 K): δ 2.79 (*s*, $\text{SCH}_2\text{CH}_2\text{S}$), 2.67 (*t*, $\text{SCH}_2\text{CH}_2\text{CH}_2$), 1.95 (*q*, $\text{CH}_2\text{CH}_2\text{CH}_2$); (183 K): 3.73, 3.33 (coord. SCH_2), 2.80 (br, uncoord. SCH_2), 2.15 (br, SCH_2CH_2). IR/ cm^{-1} : 223 (br, Sn–Br).

$[\text{SnBr}_4(\text{[16]aneS}_4)]$

Method as for $[\text{SnBr}_4(\text{[12]aneS}_4)]$, but using $[\text{16]aneS}_4$. Yellow solid. Calc. for $\text{C}_{12}\text{H}_{24}\text{Br}_4\text{S}_4\text{Sn}$: C, 19.6; H, 3.3. Found: C, 20.2; H, 3.2%. ^1H NMR (CD_2Cl_2 , 300 K): δ 2.66 (*t*, SCH_2), 1.95 (*q*, SCH_2CH_2); (183 K): 3.30, 2.77, 2.57, 2.12 (all broad). IR/ cm^{-1} : 223 (br, Sn–Br).

$[\text{SnCl}_4(\text{[8]aneSe}_2)]$

Method as for $[(\text{SnCl}_4)_2(\text{[12]aneS}_4)]$, but using a 1:1 mol. ratio of SnCl_4 : $[\text{8]aneSe}_2$. Yellow solid. Calc. for $\text{C}_6\text{H}_{12}\text{Cl}_4\text{Se}_2\text{Sn}$: C, 14.3; H, 2.4. Found: C, 14.1; H, 2.2%. ^1H NMR (CD_2Cl_2 , 300 K): δ 3.42, 3.27, 1.71 (br). $^{77}\text{Se}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): 287. ^{119}Sn NMR (CD_2Cl_2 , 183 K): -656 . IR/ cm^{-1} : 333, 320, 314, 300 (Sn–Cl).

$[\text{SnCl}_4(\text{[16]aneSe}_4)]$

Method as for $[(\text{SnCl}_4)_2(\text{[12]aneS}_4)]$, but using $[\text{16]aneSe}_4$. Yellow solid. Calc. for $\text{C}_{12}\text{H}_{24}\text{Cl}_4\text{Se}_4\text{Sn}$: C, 19.4; H, 3.3. Found: C, 19.2; H, 3.7%. ^1H NMR (CD_2Cl_2 , 183 K): δ 3.0–3.5 (br *m*, coord. SeCH_2), 2.65 (br *s*, uncoord. SeCH_2), 1.7–2.1 (br *m*, coord. SeCH_2CH_2), 1.86 (br *s*, uncoord. SeCH_2CH_2). $^{77}\text{Se}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 183 K): 290, 157 (1:1 ratio of coord. and uncoord. Se). ^{119}Sn NMR (CD_2Cl_2 , 183 K): -644 . IR/ cm^{-1} : 332, 327, 316, 305 (Sn–Cl).

$[\text{SnBr}_4(\text{[16]aneSe}_4)]$

Method as for $[\text{SnBr}_4(\text{[12]aneS}_4)]$, but using $[\text{16]aneSe}_4$. Yellow solid. Calc. for $\text{C}_{12}\text{H}_{24}\text{Br}_4\text{Se}_4\text{Sn}$: C, 15.6; H, 2.6. Found: C, 14.4; H, 2.6%. ^1H NMR (CD_2Cl_2 , 183 K): see text. IR/ cm^{-1} : 223 (br, Sn–Br).

X-ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 4. Pale yellow crystals of $[\text{SnBr}_4(\text{[12]aneS}_4)]$ and $[\text{SnBr}_4(\text{[16]aneS}_4)]$ were obtained by slow evaporation of the filtrate left after removal of the bulk material from the reaction mixture in the glove box. Crystals

Table 4 Crystallographic data

	[SnBr ₄ ([12]aneS ₄)]	[SnBr ₄ ([14]aneS ₄)]·2/3CH ₂ Cl ₂	[SnBr ₄ ([16]aneS ₄)]
Formula	C ₈ H ₁₆ Br ₄ S ₄ Sn	C _{10.67} H _{21.33} Br ₄ Cl _{1.33} S ₄ Sn	C ₁₂ H ₂₄ Br ₄ S ₄ Sn
<i>M</i>	678.78	763.45	734.88
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	<i>Cmcm</i> (no. 63)	<i>P</i> $\bar{1}$ (no. 2)	<i>Pca</i> 2 ₁ (no. 29)
<i>a</i> /Å	10.5135(3)	11.2865(3)	19.4987(7)
<i>b</i> /Å	8.3306(3)	11.5634(3)	10.0624(3)
<i>c</i> /Å	19.6638(7)	13.3067(4)	10.9104(3)
α /°	90	104.8650(10)	90
β /°	90	103.4750(10)	90
γ /°	90	92.8590(10)	90
<i>U</i> /Å ³	1722.23(10)	1621.19(8)	2140.66(12)
<i>Z</i>	4	3	4
μ (Mo-K α)/mm ⁻¹	11.227	9.119	9.042
Unique reflections	1069	7125	4590
Obs. reflections with [<i>I</i> > 2 σ (<i>I</i>)]	991	5762	4105
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0412	0.0467	0.0535
<i>R</i> 1 (all data)	0.0447	0.0635	0.0626
<i>wR</i> 2 (all data)	0.1072	0.1077	0.1380

Common data: *T* = 120 K; λ (Mo-K α) = 0.71073 Å; *R*1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$; *wR*2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

of [SnBr₄([14]aneS₄)]·2/3CH₂Cl₂ were obtained by careful layering of a CH₂Cl₂ solution of SnBr₄ with a CH₂Cl₂ solution of the tetrathia-macrocyclic. Data collection used a Nonius Kappa CCD diffractometer (*T* = 120 K) with graphite monochromated Mo-K α radiation (λ = 0.71073 Å). Structure solution and refinement were routine.^{16–19} For [SnBr₄([16]aneS₄)] the Flack parameter indicated possible twinning, and refinement with a TWIN command led to a modest improvement to the fit. Selected bond lengths and angles are presented in Tables 1–3. CCDC reference numbers 208975 [12], 208976 [14] and 208977 [16]. See <http://www.rsc.org/suppdata/nj/b3/b307863a/> for crystallographic data in .cif or other electronic format.

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