University of Southampton

MONO-AND BI-DENTATE
GROUP 15 AND 16 LIGAND COMPLEXES
OF MAIN GROUP METAL HALIDES

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A Thesis Submitted for the Degree of Doctor of Philosophy
Department of Chemistry

October 1999
The synthesis and properties of tin(IV) and bismuth(III) halide complexes of mono- and bi-dentate ligands of groups 15 and 16 are described.

The complexes of SnX₄ (X = Cl, Br) with group 16 ligands of type R₂E (R = Me or Ph for E = S, Se; R = Me for E = Te), RE(CH₂)nER (E = S, Se or Te, R = Me or Ph, n = 1 - 3; n ≠ 1 or 2 for E = Te) and Ω-C₆H₄(EMe₂)₂ (E = S, Se or Te) have been synthesised and characterised by multinuclear NMR (^1H, ^119Sn, ^77Se, ^125Te) spectroscopy, IR spectroscopy and elemental analysis. Sn₄ adducts were also studied. Single crystal X-ray diffraction has been employed to structurally characterise [SnX₄{Me₂Se₂}] (X = Cl or Br), [SnCl₄{MeE(CH₂)₂EMe}] (E = S or Se), [SnCl₄{MeE(CH₂)nEMe}] (n = 2 for E = S, n = 3 for E = S or Se), [SnX₄{Ω-C₆H₄(EMe₂)}] (X = Cl for E = S; X = Cl or Br for E = Se or Te), [SnCl₄{PhE(CH₂)₂EPhe}] (n = 3 for E = S; n = 2 for E = Se) and [SnBr₄{MeS(CH₂)₃SMe}], and reveals a distorted octahedral geometry at the Sn IV centre. This is also observed for [SnCl₄{MeE(CH₂)₂EMe}] (E = S or Se), where a highly strained four-membered chelate ring is formed. Multinuclear NMR spectroscopy and X-ray diffraction proved highly complementary, and allow a number of trends with donor and acceptor to be derived. A structural analysis was also obtained for [SnI₄{η⁻¹-O-MeS(Ο)(CH₂)₃SMe}₂], exhibiting an octahedral Sn IV centre with two monodentate ligands bound through the sulfoxide donor.

An analogous series of complexes of phosphine and arsine ligands were also studied. The complexes of SnX₄ (X = Cl, Br or I) with the ligands Me₃P, RE(CH₂)₂ER (R = Me or Ph for E = P; R = Ph for E = As), Ω-C₆H₄(PPh₂)₂ and Ω-C₆H₄(AsMe₂)₂ were produced and characterised using multinuclear NMR (^1H, ^3¹P, ^1¹¹Sn) and IR spectroscopies, elemental analysis. The chemical shifts observed were consistent with an octahedral geometry at Sn IV and this was confirmed by the structural analysis of [SnI₄{Ω-C₆H₄(AsMe₂)}], showing the ligand to chelate forming six-coordinate Sn IV. The combination of techniques again allow trends with donor and acceptor to be identified. The oxidised complexes of Ω-C₆H₄(PCl₂)₂ were also studied for comparison and the structural analysis of solvated and unsolvated [SnI₄{Ω-C₆H₄(P(Ο)Ph₂)}] reveal an unusual seven-membered chelate ring.

Complexes were also formed by reaction of certain of these group 15 and 16 bidentate ligands and with BiX₃ (X = Cl, Br or I). Characterisation of a number of the complexes was achieved by single crystal X-ray diffraction studies which reveal a wide range highly unusual and unexpected structural motifs ranging from seven-coordinate chelate species ([BiBr₃{MeS(CH₂)₂SMe}₂]), Bi₂X₆ dimers with chelating ligands ([Bi₂I₆{Ω-C₆H₄(AsMe₂)}₂]), or bridging ligands forming polymeric sheets with 1:1 ([BiBr₃{MeE(CH₂)₃EMe}]ₙ (E = S or Se)), or 1:2 Bi : donor atom stoichiometries, ([Bi₂Br₆{PhS(CH₂)₂SPh}]ₙ), and the highly unusual complex [Bi₄Cl₄{MeS(CH₂)₃SMe}₄], consisting of Bi₄Cl₄ pseudo-cuboids linked in a three-dimensional network by bridging ligands.
Acknowledgements

First and foremost, I should like to thank Professor Bill Levason and Dr Gill Reid for their help, support and enthusiasm during the years of this research, particularly for dedicating many an hour of their time to the collection of NMR spectra. Thanks are also due to Bill for the elemental analyses of the more sensitive materials within this report.

Special mention is due for Dr Mike Webster in particular, but also Gill for all their help in teaching me the mystical art of single crystal X-ray diffraction. Mike deserves special credit for introducing me to the wonders of the Hamilton R-factor statistical test for absolute configuration (wet towel and stiff drink obligatory!). Thanks also to Dr Sandra Dann for collecting MASNMR data.

Thanks to Nick Holmes for surviving two years in a lab with me, I’ll make sure I get you next time! Prior to that Jeff Quirk is deserving of mention for spending hours on topics of little importance and providing me with the ideal role model.

Thanks to all other members of the Levason/Reid collective, from the 7th floor of the old department to the shiny new building, including Simon Pope, Julie Connolly, Andy Barton, Bhavesh Patel (has he broken the diffractometer yet?) and, prior to his defection, Doug Booth, all of whom have been the source of chemicals and distractions.

Everyone at the Church Lane residence; Adam Healy, Rich ‘Tommy’ Needs, Jon (Electrochemist!) Amphlett and Nic (Stato) Gibbard (and Kenny!). I’m grateful to the lads for hours of tedious footballing televisual entertainment, and Nic for replacing this with Coronation Street!

All the other reprobates who have, at one time or other, frequented the inorganic department; Adam, Tommy, Geoff, Kenny, Radar, Eric, Paul, Arran, Ant, Durrell, Steve, Julia, Sandra and Chris Rudkin. Particular thanks should go to all who have managed to avoid me on the mountains in France or Southampton; Kenny, Nick, Chris Rudkin, Eric and Doug.

Finally, I must acknowledge the Department of Chemistry for four years of funding as X-ray technician and PhD research student.
"If we knew what we were doing, it wouldn't be called research, would it?"

Albert Einstein (1879-1955)
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Figure 6.1. View of the molecular structure of [Bi$_2$Br$_6$(dmpe)$_2$]

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Figure 6.10. View of [BiBr₃{MeS(CH₂)₂SMe}₂] with numbering scheme adopted. Ellipsoids are drawn at 40 % probability, hydrogen atoms have been omitted for clarity.

Figure 6.11. View of the [Bi₂Br₆{PhS(CH₂)₂SPh}]ₙ asymmetric unit with numbering scheme adopted. Ellipsoids are drawn at 40 % probability. Neighbouring atoms are included marked with an asterisk (*) (related by a crystallographic inversion centre).

Figure 6.12. View of a portion of [Bi₂Br₆{PhS(CH₂)₂SPh}]ₙ structure (phenyl rings at C(2) and C(2*) are omitted for clarity. Ellipsoids are drawn at 40 % probability. Atoms marked with an asterisk (*) are related by a crystallographic inversion centre.

Figure 6.13. View of the [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄] asymmetric unit with numbering scheme adopted. Ellipsoids are drawn at 40 % probability. Neighbouring atoms are included marked with an asterisk (*) (related by a crystallographic 4 symmetry).

Figure 6.14. View of a portion of the [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₙ structure with numbering scheme adopted showing the tetramer unit (H atoms are omitted for clarity and atoms marked with an asterisk are related by a crystallographic 4 operation. Ellipsoids are drawn at 40 % probability.

Figure 6.15. View of a portion of the [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₙ structure viewed down the c-axis of the three-dimensional polymer, illustrating the channels running through the structure (H atoms are omitted for clarity). Ellipsoids are drawn at 40 % probability.

Figure 6.16. View of the Bi₄Cl₄ core, illustrating the open cradle conformation. The dashed lines indicate secondary Bi---Cl interactions.

Figure 6.17. View of the asymmetric unit for [BiBr₃{MeS(CH₂)₂SMe}]ₙ with numbering scheme adopted. Ellipsoids are drawn at 40 %
probability. Neighbouring atoms are included marked with an asterisk (related by a crystallographic inversion centre). C(5) is disordered across two sites, C(5) and C(5b), in a 6:4 ratio.

Figure 6.18. View of a portion of the meso form of [BiBr₃{MeS(CH₂)₃SMe}]ₙ structure with the numbering scheme adopted (ellipsoids are drawn at 40% probability; H atoms are omitted for clarity and atoms marked with an asterisk (*) are related by a crystallographic inversion centre).

Figure 6.19. View of the asymmetric unit for [BiCl₃{MeSe(CH₂)₃SeMe}]ₙ with numbering scheme adopted. Ellipsoids are drawn at 40% probability. Neighbouring atoms are included marked with an asterisk (related by a crystallographic inversion centre).

Figure 6.20. View of a portion of the [BiBr₃([16]aneSe₄)]ₙ structure, illustrating the extended 'ladder' configuration. Ellipsoids are drawn at 40% probability. Atoms marked with an asterisk (*) are related by a crystallographic inversion centre.

Figure 6.21. View of the asymmetric unit for [BiBr₃{MeSe(CH₂)₃SeMe}]ₙ with numbering scheme adopted. Ellipsoids are drawn to 40% probability. Neighbouring atoms are included marked with an asterisk (*) (related by a crystallographic inversion centre).

Figure 6.22. View of the dimeric structure of [Bi₂I₆(diars)₂] with numbering scheme adopted. Ellipsoids are drawn at 40% probability. Atoms marked with an asterisk (*) are related by a crystallographic inversion centre. H atoms omitted for clarity.
ABBREVIATIONS

Techniques
- MASNMR: Magic Angle Spinning Nuclear Magnetic Resonance
- NMR: Nuclear Magnetic Resonance
- IR: Infra Red

Ligands - Acyclic
- L: Monodentate ligand
- L-L: Bidentate ligand
- R: Ligand substituent
- E: Donor atom
  - Ph: phenyl
  - Me: methyl
  - Pr: n-propyl
  - Bu: butyl
  - Et: ethyl
- dppe: 1,2-Bis(diphenylphosphino)ethane
- dmpe: 1,2-Bis(dimethylphosphino)ethane
- dppm: Bis(diphenylphosphino)methane
- dpae: Bis(diphenylarsino)ethane
- diars: α-C₆H₄(AsMe₂)₂
- triars: CH₂C(CH₂AsMe₂)₃

Ligands – Macrocyclic (general)
- y – crown – n: oxygen-donor macrocycle where:
  - y: number of atoms in ring
  - n: number of donor atoms
- [y]aneXₙ: y, n as for oxygen-donor macrocycle
  - X: donor heteroatom

Miscellaneous
- CH₂Cl₂: Dichloromethane
- CHCl₃: Chloroform
- thf: Tetrahydrofuran
- dmsO: Dimethylsulfoxide
- MeCN: Acetonitrile
- MeNO₂: Nitromethane
- Me₂CO: Acetone
- acac: Acetylacetonate
- TMS: Tetramethylsilane
Chapter 1

Introduction
1.1 Main Group Chemistry – Overview

It is difficult to compile an overview of the main group elements as no two elements are alike, even within the groups of the periodic table. The p-block is the only block to contain non-metals, and as well as these it also contains metalloids whose properties share characteristics of both metals and non-metals (Figure 1.1). In general the metallic elements (Al, Sn, Pb etc.) lie in the bottom left of the block with non-metals (C, N, O, halogens etc.) occupying the top right separated by the metalloid elements (Si, Ge, As etc.). While extensive reviews have been produced on the main group elements\(^1\) this study concentrates on the heavier p-block elements, whose coordination chemistry is the subject of this thesis. Previous, relevant studies on the coordination chemistry of their halides are discussed at the start of each chapter. The overview of the area and the properties of the starting halides are discussed here.

Figure 1.1. P-Block elements illustrating metals (white), metalloids (circled) and non-metals (grey). (taken from ref. 1)
1.1.1. Group 14 Elements – Si, Ge and Sn

Nowhere is this enormous discontinuity in general properties between the first- and second-row elements as obvious as group 14, and this is followed by a transition through metalloids to metallic elements at the bottom of the group. This is well illustrated by their varying physical properties (Table 1.1). There is very little that can be taken from the chemistry of carbon and applied in detail to the chemistry of silicon. Carbon is a non-metallic element, silicon is essentially non-metallic, germanium is classed a metalloid and tin and lead are metallic in nature.

Table 1.1. Some properties of the Group 14 elements.\textsuperscript{2a}

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic structure</th>
<th>mp (°C)</th>
<th>bp (°C)</th>
<th>1st (kJ mol\textsuperscript{-1})</th>
<th>2nd (kJ mol\textsuperscript{-1})</th>
<th>3rd (kJ mol\textsuperscript{-1})</th>
<th>4th (kJ mol\textsuperscript{-1})</th>
<th>Electro-Negativity</th>
<th>Covalent radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>[He]2s\textsuperscript{2}2p\textsuperscript{2}</td>
<td>&gt;3550\textsuperscript{b}</td>
<td>4827</td>
<td>1086</td>
<td>2353</td>
<td>4618</td>
<td>6512</td>
<td>2.5 – 2.6</td>
<td>0.77</td>
</tr>
<tr>
<td>Si</td>
<td>[Ne]3s\textsuperscript{2}3p\textsuperscript{2}</td>
<td>1410</td>
<td>2355</td>
<td>786.3</td>
<td>1577</td>
<td>3228</td>
<td>4355</td>
<td>1.8 – 1.9</td>
<td>1.17</td>
</tr>
<tr>
<td>Ge</td>
<td>[Ar]3d\textsuperscript{10}4s\textsuperscript{2}4p\textsuperscript{2}</td>
<td>937</td>
<td>2830</td>
<td>760</td>
<td>1537</td>
<td>3301</td>
<td>4410</td>
<td>1.8 – 1.9</td>
<td>1.22</td>
</tr>
<tr>
<td>Sn</td>
<td>[Kr]4d\textsuperscript{10}5s\textsuperscript{2}5p\textsuperscript{2}</td>
<td>231.9</td>
<td>2260</td>
<td>708.2</td>
<td>1411</td>
<td>2942</td>
<td>3928</td>
<td>1.8 – 1.9</td>
<td>1.40\textsuperscript{c}</td>
</tr>
<tr>
<td>Pb</td>
<td>[Xe]6s\textsuperscript{2}6p\textsuperscript{2}</td>
<td>327.5</td>
<td>1744</td>
<td>715.3</td>
<td>1450</td>
<td>3080</td>
<td>4082</td>
<td>1.8</td>
<td>1.44\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Tetrahedral (i.e., sp\textsuperscript{3} radii).
\textsuperscript{b} Diamond.
\textsuperscript{c} Covalent radius of Sn\textsuperscript{II}, 1.63 Å.
\textsuperscript{d} Ionic radius of Pb\textsuperscript{II}, 1.33 (CN 6); of Pb\textsuperscript{IV}, 0.775 Å.

The group 14 elements form two series of halides, MX\textsubscript{2} and MX\textsubscript{4}. The stability of MX\textsubscript{2} increases down group 14; SiX\textsubscript{2} < GeX\textsubscript{2} < SnX\textsubscript{2} < PbX\textsubscript{2}, with the trend reversed for MX\textsubscript{4}; SiX\textsubscript{4} > GeX\textsubscript{4} > SnX\textsubscript{4} > PbX\textsubscript{4}. Silicon(IV) halides are formed as colourless, volatile liquids by reaction of silicon or silicon carbide with any halogen. Germanium(IV) halides are easily produced by reaction of GeO\textsubscript{2} with aqueous HX. The fluorides, SiF\textsubscript{4} and GeF\textsubscript{4} (produced by the thermal decomposition of BaGeF\textsubscript{6}), are gaseous. All these halides consist of discrete tetrahedral units. SnF\textsubscript{4}, which is produced by reaction of fluorine with tin, is different from the other group 14
tetrafluorides in being a white crystalline compound. The structure is polymeric (Figure 1.2) with octahedral coordination about the tin with SnF$_6$ units joined into planar layers by edge-sharing of four equatorial F atoms (Sn-F, 2.02 Å) with two further terminal F atoms mutually trans (Sn-F, 1.88 Å). The other tin(IV) halides are produced by reaction of elemental tin with the halogen under anhydrous conditions. These other tin(IV) halides follow the observed trend of discrete tetrahedral molecules with SnCl$_4$ a colourless liquid, while SnBr$_4$ is a colourless, crystalline solid and SnI$_4$ is an orange crystalline solid. All the group 14 tetrahalides are hygroscopic, and are immediately and completely hydrolysed by water. Controlled hydrolysis is possible with SiX$_4$ forming X$_2$SiOSiX$_3$ and (X$_2$SiO)$_2$SiX$_2$, GeX$_4$ is partially hydrolysed to give equilibria involving species of the type [Ge(OH)$_n$Cl$_{6-n}$]$^-$, and in the case of the tin(IV) halides, a number of hydrates of varying stoichiometries have been identified.

There is also a clear trend of increasing Lewis acidity progressing down the group 14 elements. The MX$_4$ molecules are able to act as electron acceptors as they possess two vacant d-orbitals. Together with the s- and p-orbitals, these hybridise to form a set of six d$^2$sp$^3$ hybrids, adopting the octahedral geometry commonly found in adducts of these MX$_4$ compounds. There is also an observed decrease in Lewis acidity with halide type, F > Cl > Br > I as the M-X bond becomes less polar and the effective charge on the M centre increases. This has also dictated the types of ligands that have been studied for these systems. In the vast majority of cases the ligands have been those with O- or N-donor systems. In contrast, the number of systems involving the softer P- and S-donor systems are few, As- and Se-donor systems rarer still, and for Te, systems of this nature have not been studied at all. Those that have been studied are discussed in detail in the introductions of the relevant chapters (S, chapter 2; Se, chapter 3; P/As, chapter 5).

**Figure 1.2. View of the polymeric SnF$_4$ structure**

![Figure 1.2](image-url)
Industrial uses of the group 14 elements are widespread. The principal uses of silicon are within solid state electronics (silicon based transistor circuitry forms the basis for all modern electrical devices), ceramics, and polymers.\textsuperscript{14} Germanium is also a key constituent within the solid state electronics industry (transistor action was first discovered in germanium), but also within optics (germanium is transparent in the infrared region of the spectrum) and other smaller applications (alloys, strain gauges, and superconductors).\textsuperscript{15} Industrially, tin has a great deal of uses. Free radical reactions of organotin compounds are widespread and are reviewed briefly by A.G.Davies\textsuperscript{16} and in greater detail in other reviews.\textsuperscript{17} Tin(IV) oxide has interesting surface chemistry with a porous nature, which has been studied by Sharygin et al.,\textsuperscript{18} and this leads to uses in catalysis and gas sensing. Organotins of oxidation states +II and +IV have a wide variety of uses and effects in biological chemistry, these are reviewed for general aspects,\textsuperscript{19} environmental problems\textsuperscript{20} and biochemistry and toxicology.\textsuperscript{21}
1.1.2. Group 15 elements - Bi

As with the group 14 elements, the properties and characteristics of the group 15 elements vary greatly from top to bottom. This is again seen in the physical properties of the elements (Table 1.2). Nitrogen (which has the obvious distinction of being gaseous under normal conditions) is not included, as there is little resemblance between the characteristics it displays and the other group 15, elements except for the stoichiometries of some simple ionic compounds (e.g. NH₃, PH₃, NCl₃, BiCl₃). The elements of group 15 form two series of halides MX₃ and MX₅. In the case of bismuth the +3 oxidation state is far more stable than the +5 oxidation state.

In the gas phase the bismuth(III) halides studied here are pyramidal molecules. In the normal solid, crystalline state however, there are additional near neighbours and weak, secondary Bi···X interactions form. It is proposed that these interactions are formed about the site of the lone pair of electrons. In a review of SbX₅ complexes, Sawyer and Gillespie found the same weak interactions forming. They too postulate that these interactions are formed around the direction of maximum electron density of the lone pair, but not directly over it. Complexes of BiX₃ are discussed in Chapter 6. With no visible spectroscopy or nuclei suitable for study by NMR, the coordination chemistry of BiX₃ is very limited and most of what has been studied dates back to the 1960s, when characterisation techniques were limited. The vast majority of characterised complexes of BiX₃ adopt octahedral Bi⁺⁺ centres, suggesting the lone pair is not stereochemically active, but there are numerous examples of other stoichiometries where there is a clear void left within the coordination sphere, consistent with the lone pair being stereochemically active in these cases. It is difficult to predict when the lone pair of electrons will be stereochemically active though certain general trends for the group 15 elements are apparent. Stereochemical activity of the lone pair is found to decrease according to As > Sb > Bi²⁺ and also with increasing coordination number and increasing atomic number of the halogen.
Table 1.2. Physical properties of the Group 15 elements.\textsuperscript{2b}

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic structure</th>
<th>mp (°C)</th>
<th>Sum of 1\textsuperscript{st} three ionisation enthalpies (kJ mol\textsuperscript{-1})</th>
<th>Electronegativity</th>
<th>Covalent radius\textsuperscript{a} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>[Ne]3s\textsuperscript{2}3p\textsuperscript{3}</td>
<td>44.1</td>
<td>5.83</td>
<td>2.06</td>
<td>1.10</td>
</tr>
<tr>
<td>As</td>
<td>[Ar]3d\textsuperscript{10}4s\textsuperscript{2}4p\textsuperscript{3}</td>
<td>813 (36 atm)</td>
<td>5.60</td>
<td>2.20</td>
<td>1.21</td>
</tr>
<tr>
<td>Sb</td>
<td>[Kr]4d\textsuperscript{10}5s\textsuperscript{2}5p\textsuperscript{3}</td>
<td>630.5</td>
<td>5.05</td>
<td>1.82</td>
<td>1.41</td>
</tr>
<tr>
<td>Bi</td>
<td>[Xe]4f\textsuperscript{14}5d\textsuperscript{10}6s\textsuperscript{2}6p\textsuperscript{3}</td>
<td>271.3</td>
<td>5.02</td>
<td>1.67</td>
<td>1.52</td>
</tr>
</tbody>
</table>

a. For trivalent state.

Figure 1.3. View of the structure, with bond lengths, of SbF\textsubscript{3} (reproduced from ref. 23)

As a general rule the Lewis acidity for the BiX\textsubscript{3} compounds will decrease with increasing halide, F > Cl > Br > I, as the electron density is drawn closer to the Bi\textsuperscript{III} centre, reducing the attraction towards electron donors.
Chapter 1

Introduction

1.2. Ligands

1.2.1. Group 15 Ligands

Phosphines have been the centre of a great deal of research in recent years, mainly because of their importance in a number of key industrial processes such as hydrogenation of alkenes (Wilkinson’s complex\textsuperscript{27}) or hydroformylation of alkenes.\textsuperscript{28} In most cases the study of phosphine donors has involved mono- or bi-dentate tertiary phosphine ligands, and more recently interest has arisen in macrocyclic phosphines.\textsuperscript{29} In this research the tin(IV) halide complexes of the group 15 donors are studied. The study carries on previous research of tin(IV) halide-phosphine complexes,\textsuperscript{30} which warrants further studies as the results would appear to indicate the formation of phosphine-oxide complexes rather than the desired tin-diphosphine complexes.

1.2.2. M-P/As Bonding

In discussing group 15 ligand binding properties, the generally accepted description of phosphine bonding is that for transition metal complexes was first proposed by Chatt.\textsuperscript{31} While this model holds for middle to late transition metals, it should be noted that the binding in early transition metals and main group metals is different due to their lack of suitable, filled $n$ orbitals.

In transition metal-phosphine bonding the lone pair on the phosphine is donated into an empty metal $d$ orbital forming a $\sigma$ bond. The phosphine also possesses empty $3d$ orbitals into which $\pi$ backbonding can occur from electrons of filled metal $d$ orbitals of suitable symmetry, the effect being mutually reinforcing (synergic). While this model was applied extensively some workers suggested that a number of the properties observed in phosphine coordination could be explained purely in terms of $\sigma$ bonding. It was argued that the $3d$ orbitals of the phosphorus donor are too high in energy and too diffuse to contribute significantly to bonding. There do remain certain aspects, such as the stabilisation of zerovalent metal phosphine complexes and the high spectrochemical position of phosphines, which cannot be explained by $\sigma$ bonding alone. The general consensus, therefore, is that the bonding is dominated by $\sigma$ bonding, and may be supplemented by a small $\pi$ bonding component when the phosphine carries electronegative substituents.
The \( \sigma \)-donor power was traditionally quoted in terms of proton basicity \([pK_a(H_2O)]\), determined either experimentally or estimated from Hammett \( \sigma_p \) or Kabachnik \( \sigma^* \) constants.\(^\text{32}\) Since then, gas-phase photoelectron spectroscopy (PES) has been used to measure directly the binding energy of the phosphorus lone pair.\(^\text{33}\) The results of the PES studies show that electron binding energy decreases with more electronegative substituents such that \( \text{PPh}_3 > \text{PPh}_2\text{Me} > \text{PPhMe}_2 > \text{PMe}_3 \), opposite to the order expected and that obtained from \( pK_a \) measurements.\(^\text{34,34}\) The nature of the \( \pi \) bonding has also been questioned and consequently changed. Early work had assumed that the \( \pi \) bond was \( \text{M(d\( \pi \))}-\text{P(3d\( \pi \))} \), but subsequent molecular orbital calculations\(^\text{35}\) and PES experiments\(^\text{36}\) have shown that these phosphorus 3d orbitals are not involved in \( \pi \) bonding. With this and other data collected from X-ray crystallography, the \( \pi \) backbonding from the metal is now considered to be accepted by the \( \text{P-X (X = H or C)} \) \( \sigma^* \) orbital.\(^\text{37}\)

For main group metals, the lack of suitable, filled \( \pi \)-bonding orbitals means that the bonding between the phosphine and the metal centre is purely \( \sigma \)-donor in character.

From studies on \( \{\text{(C}_5\text{H}_5)\text{Fe(CO)}_2\}\)^+ complexes with monodentate group 15 ligands, \( \text{ER}_3 \) (where \( \text{E} = \text{N, P, As, Sb or Bi} \)), the \( \sigma \)-donor ability of the ligands, based on ligand exchange experiments, was found to decrease down group 15 in the order \( \text{E} = \text{P} > \text{As} > \text{Sb} > \text{N} > \text{Bi} \).\(^\text{38}\) Steric effects due to the donor atom increase down the group, \( \text{PR}_3 < \text{AsR}_3 < \text{SbR}_3 < \text{BiR}_3 \), while the steric effects due to the substituents, \( \text{R} \), decreases down the group, \( \text{PR}_3 > \text{AsR}_3 > \text{SbR}_3 > \text{BiR}_3 \).\(^2\)

Until ca. 1970 the trends in metal-phosphine bonding were almost entirely attributed to the electronic effects discussed previously. However, the steric effects of the substituents are also significant and the accepted model for this was proposed by Tolman.\(^\text{39}\) who described the cone angle (\( \Theta \)) created by the substituents. Changes in the M-P or P-C bond lengths have little effect on the value of the cone angle. The largest changes are seen where rotation about the P-C bonds is possible and marked variations in the cone angles are observed. Since the concept of a cone angle treats the entire ligand as a solid cone, intermeshing of neighbouring substituents is not allowed for, and the resulting steric effect of the ligand is usually overestimated. This has lead to considerably more sophisticated methods of describing the cone angle.\(^\text{40}\) What Tolman’s cone angle does allow, however, is a simple, semiquantitative way of discussing the relative steric effects of different ligands. The advent of X-ray crystallography has created a wealth of data with which to work. Oliver and Smith\(^\text{41}\)
have used these data to compare thirty platinum(II) complexes of PCy₃ to examine the steric effects. They showed that steric overcrowding in such molecules was accommodated in several ways, most importantly in lengthening the M-P bond.

**Figure 1.4. Schematic diagram showing the cone angle, Θ.**

1.2.3. *Group 16 Ligands - M-S/Se/Te Bonding*

The general electronic configuration of the group 16 elements is ns², np⁴, nd⁰. Hence in the case of dialkylated species such as thioethers, selenoethers and telluroethers there are two of these valence electrons involved in bonding interactions with the alkyl groups, leaving four electrons in non-bonding orbitals on the heteroatom. In a review of thioether complexes of transition metals Murray and Hartley describe the orbitals on the group 16 elements as varying from sp³ hybridised on oxygen, to an s and three p orbitals on tellurium, with sulphur and selenium lying somewhere between these two extremes. In the case of thioethers they consider sulfur to be sp³ hybridised resulting in two lone pairs. One or both of these may be involved in a coordinate bond to an electron acceptor.

If only one lone pair is involved in bonding then the other may either remain non-bonding resulting in stereoelectronic repulsion, or take part in π donation by rehybridisation to sp² followed by π donation of the lone pair from a p orbital to the
electron acceptor. In theoretical studies, Schumann and Hoffmann\textsuperscript{43} predicted that the M-L (L = S, Se or Te) bond strengths increase as group 16 is descended. Within the same study\textsuperscript{43} on complexes of [C\textsubscript{5}H\textsubscript{5}Fe(CO)\textsubscript{2}]\textsuperscript{+}, ligand exchange experiments indicated that the M-E bond strengths increase as group 16 is descended. This is in contrast to group 15 where the opposite is found.\textsuperscript{43} In more recent studies,\textsuperscript{44} the same conclusions are drawn from observed ν(CO) force constants of low valent Mn(I), Re(I), Cr(0), Mo(0) and W(0) carbonyl complexes. The trend that arises from these is that the CO bond weakens in the order S → Se → Te, the suggested reasoning being that with decreasing electronegativity down group 16 an increase in π backdonation from the metal centre results in weakening CO bonds. For metal halide systems, there is evidence that Se offers stronger binding than S, but Te ligands appear to bond more weakly as the metal oxidation state increases.\textsuperscript{45} The rationale for this being that the overlap between the large Te σ-donor orbital and the contracted metal orbitals is poorer for Te than for Se.

As well as filled valence orbitals, all group 16 elements have empty nd orbitals, providing the possibility for π back-donation from metal to ligand, if the orbitals are of the correct symmetry and energy. The importance of this π back-donation is ill-defined but should increase down the group. However, in all cases, it is less important than for phosphines, arsines and stibines. For thioethers, as with group 15 ligands, suitably oriented S-C σ* orbitals are considered to be the most likely acceptors of π backbonding.\textsuperscript{46} In a review of structurally characterised examples of late transition metal complexes of [9]aneS\textsubscript{3} (1,4,7-trithiacyclononane), Blower et al.\textsuperscript{46} argue that they observe increasing S-C bond lengths consistent with π backbonding into these σ* orbitals. In the most extreme example, [Re([9]aneS\textsubscript{3})\textsubscript{2}]\textsuperscript{2+}, it was suggested that this effect was strong enough to break the S-C bonds, releasing ethene, forming [Re([9]aneS\textsubscript{3})(SCH\textsubscript{2}CH\textsubscript{2}SCH\textsubscript{2}CH\textsubscript{2}S)]\textsuperscript{+}.

With no strong π back-donation, modest σ donor abilities and any stereoelectronic effects arising from the non-bonding pair of electrons, group 16 ethers are considered poor ligands relative to group 15 ligands. As discussed for the group 15 donor ligands, the lack of suitable, filled π orbitals on the main group metals studied in this thesis means that π backbonding in these systems is not an option and bonding is restricted to σ donation.
1.2.4. Pyramidal Inversion

Since the thio-, seleno- and telluro-ethers used in this study can bind via one of two lone pairs, there are different invertomers that can be formed for [SnX₄(L-L)]. In solution the molecules are able to switch between invertomers, either by a dissociative route or via pyramidal inversion. Pyramidal inversion at sulfur atoms was first studied in 1966 by Abel et al.⁴⁷ using ¹H NMR spectroscopy with [PtCl₂{MeS(CH₂)₂SMe}]. It was found that the inversion process occurred slowly on the NMR timescale, such that the protons were nonequivalent and the meso and dl invertomers (Figure 1.5) could be identified.

Figure 1.5. meso and dl invertomers for [PtCl₂{MeS(CH₂)₂SMe}] (taken from ref. 47)

![Diagram of meso and dl invertomers for [PtCl₂{MeS(CH₂)₂SMe}]]

Typical activation energies are in the range 35 – 100 kJ mol⁻¹.⁴⁸ Since the activation energy for this process is low, and ¹⁹⁵Pt-¹H coupling is retained at higher temperatures, the mechanism proposed for this process is via a planar transition state (Figure 1.6) with both lone pairs bonded to the metal.⁴⁹,⁵⁰ The onset of pyramidal inversion in bidentate complexes occurs at significantly higher temperatures than for trans monodentate complexes. The trans effect on the inversion barriers seen for halide ions in these complexes is found to be in the order Cl > Br > I.⁴²

Figure 1.6. Proposed mechanism for pyramidal inversion in [PtCl₂{MeS(CH₂)₂SMe}]⁴⁹,⁵⁰

![Diagram of proposed mechanism for pyramidal inversion in [PtCl₂{MeS(CH₂)₂SMe}]]
1.3. Physical Measurements

The complexes formed in this study were all characterised using a combination of techniques. Microanalyses were collected for all solids isolated. The other means of characterisation were infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and single crystal X-ray diffraction. The following is a brief overview of these three techniques which, for the purposes of this study, prove highly complementary.

1.3.1. Single Crystal X-ray Diffraction

Figure 1.7. Rigaku AFC7S four circle diffractometer

The data for the X-ray structural analyses within this study were, in the majority of cases, collected on a Rigaku AFC7S four-circle diffractometer (Figure 1.7) using a sealed Mo-Kα X-ray tube with radiation of wavelength 0.71073 Å. However, in the case of [BiBr₃{MeS(CH₂)₃SMe}] the crystals obtained were smaller and the data were collected instead on an Enraf-Nonius KappaCCD diffractometer (Figure 1.8) that uses a
Nonius FR591 rotating anode X-ray generator. By rotating the anode within the X-ray source a more powerful beam is possible and the heat generated is dispersed across a much larger area relative to the anode found in a sealed tube. The increased power possible from a rotating anode source means that smaller, and less strongly diffracting, crystals may be analysed. The collection strategies are also very different for the four-circle and the KappaCCD diffractometer. The Rigaku AFC7S collects intensities of reflections using a scintillation counter. This contains a material, such as thallium-doped sodium iodide, which produces light when X-rays fall on it. This light is, in turn, detected and amplified by a photomultiplier, such that an electrical pulse is produced for every X-ray photon that is incident on the detector face, which is normally a few millimetres in diameter. In contrast the KappaCCD diffractometer uses an area detector. This uses a technology more commonly found in video cameras where a CCD (charge-coupled device) is used to measure the incident X-ray photons. Rather than direct recording of the X-ray photons, a phosphor is fibre-optically coupled to the CCD chip and the incident radiation produces an electron-hole pair on the semiconductor. The CCD has a detection area of a few centimetres in diameter and collects several reflections simultaneously as an image for computer analysis.

\[\text{Figure 1.8. Enraf-Nonius KappaCCD area detector diffractometer}\]
Data Collection

The crystal is mounted on a goniometer which allows adjustment of the position in three dimensions and is placed at the centre of the diffractometer. The different sizes of detector area employed by the diffractometers also leads to different collection strategies. The four-circle diffractometer needs four full rotation axes (\(\chi\), \(\phi\), \(\omega\) and \(\theta\); Figure 1.9a) in order to position the goniometer for all the necessary reflections. The KappaCCD, with a larger detector area does not need to use full circles. Instead \(\phi\), \(\omega\) and \(\theta\) are used along with a partial \(\kappa\) axis (Figure 1.9b). The principal advantages of using a CCD based diffractometer are the reduced time periods required to collect a full dataset (hours compared to days for the scintillation counter) and the ability to obtain structural analyses of much smaller, less strongly diffracting samples.

The most crucial part of data collection is, without doubt, selection of a suitable crystal. The morphology of the crystal (well defined faces/edges) is a good indicator of quality, but better still are the optical characteristic of the crystal when viewed under plane-polarized light. While viewed under polarized light, if the crystal is rotated the light should be extinguished in certain directions and allowed through at 90° to this direction. Once selected the crystal is mounted on the goniometer head. If the material is sensitive to moisture or air it can be mounted within a capillary tube, though usually a coating of an inert oil, followed by rapid cooling in a stream of cold N\(_2\) gas is sufficient. The crystal is then aligned in the centre of the X-ray beam. If the data is to be collected at room temperature the crystal needs to mounted with a glue to prevent movement, but more normally collection is at low temperature (e.g. 150 K), to reduce molecular vibrations, so a grease, which freezes solid, is sufficient.

Figure 1.9. Schematic diagrams of a) four-circle diffractometer and b) Enraf-Nonius KappaCCD diffractometer (taken from ref. 51)
Chapter 1

The first stage of collection is then to identify the unit cell. On the four circle diffractometers this is achieved by finding > 15 reflections by scanning randomly across the crystal. The ability of the CCD detector to collect several reflections simultaneously speeds this process up. From these the simplest unit cell that connects the reflections is calculated, together with an orientation matrix which relates the position of the crystal with the Miller indices, hkl. The initial pattern can also be used to identify symmetry elements present within the cell. The symmetry elements are checked by measuring independent reflections which would be expected to be equivalent due to the symmetry. From this a Laue group may be assigned which can reduce the amount of data that needs to be collected. At this point on the four-circle diffractometer a psi-scan is collected by measuring the intensity of one reflection while rotating the crystal about 360° in the diffraction vector (ψ). This can be used to correct for irregular absorption arising from the crystal morphology. Heavier atoms will absorb more radiation and, in some cases, the psi-scan does not provide an adequate correction. In these cases an empirical absorption correction may be applied during structure solution, e.g. DIFABS.\textsuperscript{52} For the KappaCCD the nature of the rotation axes prevent psi-scan measurements. Instead an empirical absorption correction is calculated based on symmetry equivalent reflection that have been collected (SORTAV\textsuperscript{53}). During collection on the four circle diffractometer standard reflections are collected every 150 reflections which may be compared to calculate the degree of decay which may arise from decomposition by the environment or, for heavily absorbing crystals, the X-ray radiation. The intensities (I(hkl)) and observed structure amplitudes (|F_o|) of the required reflections are measured.

Structure Solution

Once collected, the reflections are ordered according to hkl and from the characteristic systematic absences arising from the symmetry a space group can be assigned. At this point it is possible to gauge the quality of the data according to what percentage of the maximum possible data has been observed and, if equivalent reflections have been measured, a comparison of these can be calculated (R_{int}). Once sorted, the data are solved using one of two strategies, direct methods or Patterson synthesis. The phases of the reflections are unknown. In the Patterson synthesis this problem is avoided by calculating the Fourier transform of the squared amplitudes F_o^2 with all phases set equal to zero. The Patterson map produced by this represents a map.
of vectors between the atoms in the structure. Thus for two atoms at \((x_1, y_1, z_1)\) and \((x_2, y_2, z_2)\) there will be a peaks in the Patterson map at \((x_1-x_2, y_1-y_2, z_1-z_2)\) and \((x_2-x_1, y_2-y_1, z_2-z_1)\). From this it can be said that for a peak in the map at \((u, v, w)\) there must be two atoms whose \(x\) coordinates differ by \(u\), \(y\) coordinates differ by \(v\) and \(z\) coordinates differ by \(w\). A Patterson map contains a total of \(n^2 - n\) reflections and while these resemble electron density peaks they are more spread out and overlap. This means that Patterson synthesis is best suited to structures containing heavy atoms.

Direct methods attempts to obtain approximate reflection phases from the measured intensities. Several factors help in this process. Firstly while the wave has half its value positive and half negative, the electron density within the structure must be positive or zero, it cannot be negative. Secondly the electron density is not evenly distributed, but localised at the sites of the atoms. This means that the waves must be added together in such a way as to maximise the positive regions and minimise the negative regions. Direct methods involve selecting the most important reflections which contribute most to the Fourier transform, working out the probable phase relationships between these, and then calculating the remaining relationships. The most promising solution is then used to calculate a Fourier transform from the observed amplitudes. If successful recognisable features of the molecules should be found in the electron density map calculated. Unlike the Patterson synthesis atom size is unimportant so this method is suitable for all structures.

**Structure Refinement**

Once a solution has been found the structure must be refined. This is done by least-squares analysis. From the parameters that have been defined during solution (these include \(x, y, z\), occupancy, and a description of the atoms thermal motion) the reverse procedure is carried out and a Fourier transform is calculated for the data to produce the amplitudes that would be observed for this structure \(|F_c|\). The refinement process defines the ‘best fit’ of the two sets of data (\(|F_o|\) and \(|F_c|\)) as that which minimises the least-squares sum:

\[ \sum w_i(|F_o| - |F_c|)^2 \]

Where \(w_i\) is a weighting factor applied to each reflection calculated according to its reliability, for the structures in this thesis this is based on the e.s.d.s, \(1/\sigma^2(F_o^2)\) is used.
From this, a comparison can be made between the calculated model and the observed data. This is normally done by calculating an \( R \)-factor (residual factor) defined as:

\[
R = \frac{\sum (|F_o|_i - |F_c|_i)}{\sum |F_o|_i}
\]

The same \( R \)-factor is calculated but with weighting. This weighted \( R \)-factor is defined as:

\[
R_w = \sqrt{\frac{\sum w_i (|F_o|_i - |F_c|_i)^2}{\sum w_i |F_o|_i^2}}
\]

Another commonly quoted comparison is the goodness of fit (GOF) which is calculated based on similar principles and is defined as:

\[
GOF = \frac{\sum (|F_o|_i - |F_c|_i) / \sigma_i}{(n - m)} \approx 1
\]

Where \( n = \) the number and reflections used
\( m = \) the number of variables refined

Iterative cycles of least-squares refinements are used until these values are minimised. Typically the \( R \)-factor has a value of 0.02 – 0.07 for a satisfactory solution. Once refinement is complete the residual peaks and troughs remaining in the Fourier difference map should be minimised such that they are close to zero.

### 1.3.2. Nuclear Magnetic Resonance (NMR) Spectroscopy

For all of these compounds a major characterisation technique has been NMR spectroscopy, both in solution and in the solid state. Using multinuclear NMR spectroscopy, with low temperature attachment, it is possible to probe the dynamic processes occurring in solution. There follows a brief discussion of the nuclei studied.
$^{31}$P NMR Spectroscopy\textsuperscript{54}

Phosphorus has a 100% abundance of $^{31}$P with spin $I = \frac{1}{2}$ and a relative receptivity to hydrogen of $6.6 \times 10^{-2}$ and is therefore an excellent nucleus for NMR spectroscopic studies of metal-phosphine complexes. Chemical shifts are normally referenced to an external 85% aqueous $\text{H}_3\text{PO}_4$ solution. The chemical shift of the phosphines is largely governed by the nature of the substituent. If the substituents are electron-rich a lower frequency shift is observed, while electron-poor substituents have the opposite effect and a high frequency shift is found. When a phosphine is coordinated to a metal centre the formation of a M-P $\sigma$ bond involves the movement of electrons away from the phosphine to the metal deshielding the $^{31}$P nucleus. The result is that a shift to higher frequency is usually observed for coordinated phosphines. In the case of the diphosphines the size of the chelate-ring formed is an important factor. Garrou\textsuperscript{55} has reviewed the chelate-ring parameter, $\Delta R$. This is defined as the difference between the coordination chemical shift, $\Delta$, of the cis-coordinated monodentate complex ($\text{cis} - \text{[SnX}_4\text{(Me}_3\text{P)}_2\text{]}$), and the observed coordination chemical shift of an equivalent cis-coordinated bidentate chelate complex (e.g. $\Delta(\text{cis} - \text{[SnX}_4\text{(Me}_3\text{P)}_2\text{]}$) $- \Delta(\text{SnX}_4\text{(dmpe)})$. Generally, for a five-membered chelate-ring $\Delta R$ is found to be positive while for four- and six-membered chelate-rings a negative $\Delta R$ is observed. This is best illustrated for the series $\text{[PtMe}_2\text{(Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\text{]}}$ where $\Delta R$ values of $-52.2$, $+24.1$, $-14.1$ and $-0.7$ are observed for $n = 1$ to 4, representing four- to seven-membered chelate rings.\textsuperscript{55} The reason for this effect is not clear and there are exceptions. One highly relevant example for this main group metal study is that of Siegl, Schier and Schmidbaur\textsuperscript{56} who see a coordination shift to low frequency in the $^{31}$P NMR spectrum of the $\text{C}_6\text{H}_4\text{(PPh}_2\text{)}_2$ complex of indium(III) chloride.

$^{77}$Se NMR Spectroscopy\textsuperscript{57}

Selenium has six naturally occurring isotopes. $^{77}$Se, with natural abundance 7.6%, has spin $I = \frac{1}{2}$ and a relative receptivity to hydrogen of $5.26 \times 10^{-4}$ making it suitable for study by NMR spectroscopy. $^{77}$Se chemical shift are referenced to the $^{77}$Se resonance of neat $\text{Me}_2\text{Se}$ which is assigned $\delta = 0$\textsuperscript{58}. As for $^{31}$P NMR chemical shifts, a high frequency shift is observed with electron rich substituents. When an M-Se $\sigma$ bond is formed on coordination the Se centre is deshielded and the resulting shift is usually to high frequency.
The coordination shift, ΔR, reviewed by Garrou\textsuperscript{55} can also be applied to selenoether systems and corresponding shifts have been observed in transition metal complexes.\textsuperscript{59}

\textbf{125}\textsuperscript{Te NMR Spectroscopy}\textsuperscript{57}  
Tellurium has seven naturally occurring isotopes of which it is \textsuperscript{125}Te, with spin I = \frac{1}{2}, natural abundance 7.0 % and a relative receptivity to hydrogen of 2.21 x 10\textsuperscript{-3}, which is used in NMR spectroscopic studies. Detracting from this is the negative magnetogyric ratio (γ = -8.453 x 10\textsuperscript{7} rad T\textsuperscript{-1} s\textsuperscript{-1}) which may lead to signal diminution via the Nuclear Overhauser Effect (NOE) (discussed in the \textsuperscript{119}Sn NMR spectroscopy).\textsuperscript{57} Resonances for \textsuperscript{125}Te are referenced to the resonance of neat Me\textsubscript{2}Te. The same high frequency shifts discussed for other nuclei are observed with electron-rich substituents. With coordination, a low frequency shift is observed as the tellurium nucleus is deshielded.

\textbf{73}\textsuperscript{Ge NMR Spectroscopy}\textsuperscript{57}  
\textsuperscript{73}Ge NMR spectroscopy is hampered by the combination of a very low NMR frequency, 3.488 MHz, and a quadrupole moment arising from the spin of \frac{9}{2}. This means that the difference in energy between the ground and excited states is small and the signals obtained are consequently weak. The quadrupole moment then has the effect of broadening the lines. Combined with these problems \textsuperscript{73}Ge also possesses a negative magnetogyric ratio which also decreases the signal strength. The net effect of this is that only molecules with high symmetry (e.g. GeX\textsubscript{4}, GeX\textsubscript{6}) have linewidths narrow enough to be discernible from background. In this study GeCl\textsubscript{4} is observed at +30.9 ppm and this is unchanged in the presence of a chelating ligand (MeS(CH\textsubscript{2})\textsubscript{2}SMe) suggesting that no adduct formation occurs that would lower the symmetry and increase the linewidth.

\textbf{\textsuperscript{119}Sn NMR spectroscopy}\textsuperscript{57}  
Tin has three nuclei suitable for study by NMR spectroscopy, \textsuperscript{115}Sn, \textsuperscript{117}Sn and \textsuperscript{119}Sn. All three nuclei have spin I = \frac{1}{2}. Of these, \textsuperscript{115}Sn is rarely used due to its low natural abundance, 0.35 %. \textsuperscript{117}Sn and \textsuperscript{119}Sn both have similar relative receptivities to hydrogen, \textsuperscript{117}Sn = 3.5 x 10\textsuperscript{-3}, \textsuperscript{119}Sn = 4.5 x 10\textsuperscript{-3}, and similar natural abundances, \textsuperscript{117}Sn 7.6 %, \textsuperscript{119}Sn 8.6 %, but it is \textsuperscript{119}Sn which is commonly studied as it is slightly superior in both aspects. \textsuperscript{119}Sn resonances are referenced relative to that of neat Me\textsubscript{4}Sn (8 0 ppm).
Very distinct regions are observed in the tin(IV) halides dictated by the halide donor. Thus with the chloride, SnCl₄ is observed at δ ≈ 150 ppm and the complexes formed in this study are typically in the range δ ≈ 500 to 600 ppm. In contrast, SnBr₄ is observed at δ ≈ 638 ppm with complexes formed observed in the range δ ≈ 1100 to 1300.

¹¹⁹Sn also possesses a large negative magnetogyric ratio, γ = -9.9707 x 10⁻⁷ rad T⁻¹ s⁻¹, which means that the resonances observed are heavily affected by signal diminuation from the NOE. For most nuclei this ratio is positive and has the effect of enhancing the signal by an amount defined by:

\[
NOE_{\text{max}} = 1 + \frac{X_s}{2X_i}
\]

\[X_s = \text{magnetogyric ratio of observed species}\]
\[X_i = \text{magnetogyric ratio of irradiated species}\]

When the negative magnetogyric ratio is placed in this equation a negative effect is observed, i.e. signal diminuation. For spectra of this nucleus, a paramagnetic centre, such as Cr(acac)₃, is added to the solution to reduce very long spin-lattice relaxation times and remove the NOE. This is achieved by providing a second relaxation mechanism which over-rides the nuclear dipole-dipole relaxation process.

1.3.3. Infra-red Spectroscopy

Previous studies of tin(IV) halides had shown that the ν(Sn-X) bands lie within the regions 290 – 340 cm⁻¹ for X = Cl and 190 – 240 cm⁻¹ for X = Br. Therefore in order to access this region nujol mulls of the samples are supported on caesium iodide windows, which are transparent across the range 4000 – 200 cm⁻¹, and used either a Perkin-Elmer 983G grating spectrophotometer or a Perkin-Elmer FTIR 1710 spectrophotometer which employs caesium iodide beam splitter and covers the same range. The bismuth(III) chloride complexes were found to show several features assigned as ν(Bi-Cl) in the range 230 – 280 cm⁻¹. The heavier bromine atom meant that the analogous ν(Bi-Br) bands fall below the cut-off point of the caesium iodide windows.
For the tin(IV) halide systems studied two different symmetries are anticipated. For the monodentate systems, *trans*-\([\text{SnX}_4L_2]\) is the expected form and would exhibit \(D_{4h}\) symmetry, while for the bidentate systems the chelate, *cis*-\([\text{SnX}_4(L-L)]\), with \(C_{2v}\) symmetry is expected. By applying the reduction formula (Figure 1.10) to the reducible representation of symmetry operations within the molecules it is possible to find the IR active bands to be expected.

**Figure 1.10. Infrared Reduction Formula**

\[
n_i = \frac{1}{h} \sum g_i \times \chi_i \times \chi_r\]

\(h = \text{number of operations in the group}\)
\(g_i = \text{number of symmetry operations in the class}\)
\(\chi_i = \text{character of the irreducible representation}\)
\(\chi_r = \text{character of the reducible representation}\)

Thus for molecules of the type *cis*-\([\text{SnX}_4(L-L)]\) with \(C_{2v}\) symmetry the reducible representation is:

<table>
<thead>
<tr>
<th>(C_{2v})</th>
<th>(E)</th>
<th>(C_2)</th>
<th>(\sigma_v)</th>
<th>(\sigma'_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_{\text{Sn-X}})</td>
<td>4</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Which, when the reduction formula is applied predicts four active bands \((2A_1 + B_1 + B_2)\) in the infrared.

For the BiCl\(_3\) complexes the bands are observed in the region 230 – 280 cm\(^{-1}\), however, as is seen from the literature the number of different structural motifs observed in this coordination chemistry,\(^{26}\) even within one reaction mixture, makes prediction of bands for these systems hazardous.
1.4. **Aims of this study**

The aims of this research study were to synthesise and characterise a variety of main group metal complexes with mono- and bi-dentate ligands of groups 15 and 16. These complexes have been characterised using spectroscopic techniques and, in a number of cases, structurally using single crystal X-ray diffraction.

By using multinuclear NMR spectroscopic techniques incorporating variable temperature studies, it has been possible to study the dynamic processes of ligand dissociation and pyramidal inversion that occurs in solution for the tin(IV) halide complexes with group 16 donor ligands. The data obtained for a wide variety of complexes from their X-ray structural analysis has permitted correlations to be drawn between the solution and solid states. By studying the analogous thio-, seleno- and telluro-ether complexes of the tin(IV) halides it has been possible to draw conclusions about their relative stabilities. The effects of altering the halide species, ligand substituent and chelate-ring size have also been studied and conclusions have been drawn from the results about the relative stabilities of the complexes formed.

The same spectroscopic techniques have been used to study the tin(IV) halide complexes with group 15 donor ligands, and allowed conclusions to be made on the relative stabilities of the complexes formed. X-ray structural analysis has also been used to study characteristics in the solid state. The tin(IV) halide complexes of the oxidised ligand o-C₆H₄(P(O)Ph₂)₂ were synthesised to allow comparison with the phosphine complexes in solution.

The same group 15 and 16 bidentate ligands have been studied with the bismuth(III) halides. The main emphasis of this study has been on structural analysis which has revealed a large variety of structural motifs including seven-coordinate monomers, halide-bridged dimers, and extended polymeric arrays incorporating dimers and pseudo-cuboids.
References


Chapter I

Introduction

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57 NMR and the Periodic Table, R. K. Harris and B. E. Mann (Editors), Academic Press, London, 1978, p. 402 ($^{77}$Se); p. 412 ($^{125}$Te); p. 10 (NOE); p. 340 ($^{73}$Ge); p. 342 ($^{119}$Sn).


Chapter 2

Group 14 Halide Complexes With Mono- and Bidentate Thioethers
2.1 Introduction

Studies of complexes of the tin(IV) halides with neutral thioether donors are rare, although not unknown. The bulk of work carried out previously has looked at monodentate dialkyl sulfides. A review of group 14 complexes, including thioethers, was compiled by Dumas & Gomel (1974). Of particular interest in these SnX₄L₂ 1:2 adducts is the cis/trans isomerisation mechanisms which occur in solution. Beattie and Rule (1964) first studied this process as part of a general study of cis/trans isomerisation in octahedral 1:2 adducts using infrared spectroscopy. In this study the patterns in the caesium bromide region in both solution and in the solid state (nujol mull) were investigated. In the cases of diethyl and dibutyl sulfides the compounds are assigned as the trans adduct in the solid state. This line of investigation was continued by Ruzicka and Merbach (1976) who carried out a vibrational study of the cis/trans isomerism in solution. As well as diethyl sulfide, they also studied the dimethyl sulfide complexes. Using solid state IR and Raman spectroscopy they confirm the previous assignments of the trans isomer for these systems. Using solution Raman spectroscopy however, they were able to observe more absorption bands signifying a cis/trans equilibrium as a result of both cis-trans isomerisation and ligand exchange. Merbach et al. continued these studies using NMR spectroscopy. Firstly, from studies using variable temperature ¹H NMR spectroscopy on solutions containing an excess of ligand, they were able to establish that the cis isomer was the more labile of the two, with the dissociative mechanisms involving the free ligand starting at lower temperatures than the trans isomer. However these experiments revealed little about the cis-trans isomerisation mechanisms in solution. By carrying out a combination of variable pressure proton NMR and magnetisation transfer ¹¹⁹Sn NMR spectroscopy experiments they were able to study this intermolecular cis-trans isomerisation process. When an adduct undergoes an intra-molecular ligand exchange process with free ligand there should be a corresponding change in the pressure of the system. The intramolecule ligand exchange of the cis isomer was seen to commence at ca. 223 K and when Merbach et al. varied the pressure of the system at this temperature a cessation of the process was observed to the point where ¹¹⁷/¹¹⁹Sn satellites are partially resolved. The same would be true for the trans isomer if intramolecular ligand exchanges were the dominant process. However, since this is not seen, intermolecular exchange was assigned as the dominant process. Further confirmation of this came
from the $^{119}$Sn magnetisation transfer NMR spectroscopy experiments. By selectively saturating one signal in the $^{119}$Sn NMR spectra by using a selective 180° pulse and then observing the spectra over time, Merbach et al. were able to observe the return of the magnetisation to equilibrium (Figure 2.1). A decrease in the trans isomer intensity was observed as the equilibrium was restored, with increasing cis intensity proving the presence of the cis-trans isomerisation process. From these studies they were able to isolate trends within the system. They observe an increased lability for the cis isomer over the trans isomer which is assigned to the increased trans effect of the halide anion over that of another neutral donor atom. The increased lability of the bromide over the chloride systems is also observed and assigned to the reduced effective charge on the tin.

**Figure 2.1.** $^{119}$Sn-$^1$H NMR spectra of [SnCl$_4$(Me$_2$S)$_2$] in CD$_2$Cl$_2$ solution at 285 K as a function of the time interval $t$ between the inversion pulse train and the observation pulse. (taken from ref. 7)
The other process occurring within these systems is the pyramidal inversion of the donor ligand. This was studied for these monodentate systems by Abel et al., again using variable temperature NMR spectroscopy. This was done via proton NMR spectra for systems with a prochiral methylene group and observing the resonances resulting from the two protons H_A and H_B. If rapid interchange of the two sulfur lone pairs (i.e. pyramidal inversion) is occurring, these two protons will appear equivalent, but if this inversion can be slowed, these protons become non-equivalent on an NMR timescale and give rise to an AB quartet. To further clarify this behaviour Abel et al. used systems where further proton coupling did not occur (e.g. (C_6H_5CH_2)_2S, ((CH_3)_3SiCH_2)_2S and ((CH_3)_3SiCH_2)_2Se), providing a clean AB quartet. At ca. 173 K two distinct AB quartets were observed for the cis and trans isomers with the cessation of pyramidal inversion along with a single sharp signal corresponding to free ligand. As Merbach et al. had observed, the cis isomer was the more labile with pyramidal inversion beginning at ca. 191 K leading to a broad singlet as the protons became equivalent. At ca. 237 K the AB quartet arising from the trans isomer had also collapsed to a singlet, but remained separate from the free ligand/cis isomer signal. The crystal structure of [SnBr_4(Me_2S_2)] has also been reported.

Complexes involving bidentate thioether ligands are much less well studied. The first example dates back to 1922 when Morgan and Ledbury reported the synthesis of [SnCl_4{MeS(CH_2)_2SMe}], albeit with very little spectroscopic evidence. Further work was conducted by Abel et al., who have studied pyramidal inversion processes in this and similar compounds. The 2,5-dithiahexane complex of SnCl_4 was found to be either too insoluble or too unstable in solution to make these studies possible, hence two other related complexes, [SnCl_3Ph{MeS(CH_2)_2SMe}] and [SnCl_4{(CH_3S)_2C_6H_5(CH_3)}] were studied instead. Below ca. 178 K they were able to distinguish the various meso and dl isomers for these complexes. Above this temperature coalescence takes place in the ^1H NMR spectrum. Adapting the findings of Merbach et al. they assign this observation to the onset of both pyramidal inversion at sulfur and ligand exchange processes with the conclusion that k_l (ligand exchange) \approx k_i (atomic inversion).

The only other multidentate thioether ligands to be studied with tin tetrahalides are macrocyclic ligands. Willey et al. have studied the complexes formed between tin(IV) chloride and 1,4,7-trithiacyclononane ([9]aneS_3) and 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS_6). Reaction of [9]aneS_3 with SnCl_4 yields
[SnCl₃([9]aneS₃)]₂[SnCl₆] (cation shown in Figure 2.2). The cation features tridentate binding to SnCl₅⁺. The [18]aneS₆ complex involves cis bidentate exocyclic binding of [18]aneS₆ to two molecules of SnCl₄. The trans complex of tin(IV) chloride with 1,5-dithiacyclooctane has also been studied, and this also features a distorted octahedral tin(IV) centre.¹²

**Figure 2.2.** View of the structure of [SnCl₃([9]aneS₃)]⁺ (taken from ref. 11)

The following work provides a detailed investigation into the behaviour of the tin(IV) halides with monodentate ligands (R₂S where R = Me or Ph) and bidentate ligands of the type RS(CH₂)ₙSR (where R = Me or Ph for n = 2 or 3; R = Me for n = 1) and α-C₆H₄(SMe)₂ forming part of a study of the coordination of group 16 ligands to Sn(IV) halides both in solution and in the solid state. The effects of changing halide and ligand interdonor linkage and substituents are studied. Variable temperature¹¹H and¹¹⁹Sn NMR spectra have been recorded to investigate the pyramidal inversion and ligand exchange processes in these systems. Infrared spectroscopy,¹¹⁹Sn MASNMR spectroscopy and single crystal X-ray diffraction have been used to study the behaviour of these complexes in the solid state. The analogous selenoether complexes will be discussed in chapter 3, with the telluroether complexes and overall trends and comparisons brought together in chapter 4.
2.2 Results & Discussion

2.2.1 Synthesis and Properties of Monodentate Thioether Complexes

A range of complexes of type [SnX₄L₂] (where X = Cl, Br or I; L = Me₂S or Ph₂S) has been prepared by reaction of SnX₄ with two molar equivalents of thioether ligand L in strictly anhydrous, degassed CH₂Cl₂. For the chloro derivatives, IR spectra of the solid complexes formed all showed one broad peak around 300 cm⁻¹ for ν(SnCl) probably corresponding to the trans isomer (D₄h symmetry) and indicating that this is the principal isomer present in the solid state. There was no evidence of ligand oxidation (ν(S=O) 900 – 1300 cm⁻¹). Similarly, no bands were present in the region 400 - 470 cm⁻¹ characteristic of ν(SnO) stretching frequencies. IR spectroscopic and analytical data are presented in Table 2.1. The compounds formed were hydrolytically unstable and were stored and manipulated in a dry, dinitrogen purged glove box.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>%C¹</th>
<th>%H</th>
<th>ν(Sn-X)⁰ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄(Me₂S)₂]</td>
<td>Pale cream</td>
<td>12.5(12.4)</td>
<td>3.1(3.2)</td>
<td>306</td>
</tr>
<tr>
<td>[SnCl₄(Ph₂S)₂]</td>
<td>Pale cream</td>
<td>45.7(45.5)</td>
<td>3.1(3.1)</td>
<td>306</td>
</tr>
<tr>
<td>[SnBr₄(Me₂S)₂]</td>
<td>Pale yellow</td>
<td>8.6(8.5)</td>
<td>2.1(2.1)</td>
<td>230</td>
</tr>
<tr>
<td>[SnBr₄(Ph₂S)₂]</td>
<td>Yellow</td>
<td>35.4(35.6)</td>
<td>2.5(2.5)</td>
<td>232</td>
</tr>
</tbody>
</table>

¹ Calculated values in parentheses
² Nujol mulls.

2.2.2 Variable Temperature ¹¹⁹Sn{¹H} NMR Spectroscopy

¹¹⁹Sn-{¹H} NMR spectroscopic data are presented in Table 2.2. The [SnCl₄(Me₂S)₂] + Me₂S system recorded in CH₂Cl₂ solution at room temperature, exhibits two resonances at δ ~572 and δ ~578 ppm, attributable to the cis and trans isomers respectively (Figure 2.3). On cooling the system there is little change except for a sharpening of the signals and slight shifts due to the temperature change. This system has already been studied in the presence of excess Me₂S by Knight and
Merbach, who assigned the processes (in order of decreasing rate) as Me₂S exchange with the cis isomer, cis-trans isomerisation, and Me₂S exchange with the trans isomer.

The analogous SnBr₄ system was also examined as part of this study. In the \(^{119}\text{Sn-}{\text{¹H}}\) NMR spectra of the 1:2 complex at room temperature, no signals are observed. On lowering the temperature to 280 K, a single broad resonance appears which broadens on further cooling and splits into two below ca. 240 K. At 180 K two sharp resonances of approximately equal intensity are present at δ -1174 and δ -1222 ppm, assignable to cis and trans forms. The same solution with an excess of Me₂S shows the same two sharp resonances of δ -1179 and δ -1228 ppm at 180 K. On warming to ca. 230 K the higher frequency resonance arising from the cis isomer broadens and then sharpens on further heating. At ca. 250 K the same behaviour is observed in the trans isomer. However in the presence of excess ligand the two resonances arising from the two geometric isomers are still observable at room temperature.

Figure 2.3. \(^{119}\text{Sn-}{\text{¹H}}\) NMR spectrum of [SnCl₄(Me₂S)₂] in CD₂Cl₂ solution
Continuing this trend of increased lability with weakening Lewis acid no resonances for the SnI₄-thioether 1:2 complex were seen at any accessible temperature (173 – 300 K), either as a 1:2 mixture or with an excess of ligand.

The effects of altering the substituent was also studied by looking at the complexes of the tin(IV) halides with Ph₂S. A CH₂Cl₂ solution of SnCl₄ with an excess of Ph₂S displays a broad $^{119}\text{Sn}\{^1\text{H}\}$ resonance at $\delta$ -599 ppm at 190 K that broadens rapidly and disappears above ca. 200 K. As would be predicted from the observations of the methyl substituted systems no resonances were observed for the corresponding SnBr₄-Ph₂S-CH₂Cl₂ systems even at 190 K.

SnF₄ does not dissolve in CH₂Cl₂ even in the presence of a large excess of Me₂S and in situ $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra again show no resonances at any temperatures.

Table 2.2. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectroscopic data for [SnX₄(Me₂S)₂] complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{119}\text{Sn}{^1\text{H}}$ ($\delta$)°</th>
<th>300 K</th>
<th>180 K</th>
<th>cis:trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄(Me₂S)₂]</td>
<td>-572, -578</td>
<td>-561, -572</td>
<td>2:1</td>
<td></td>
</tr>
<tr>
<td>[SnBr₄(Me₂S)₂]</td>
<td>n.o. b</td>
<td>-1174, -1222</td>
<td>1:1</td>
<td></td>
</tr>
<tr>
<td>[SnI₄(Me₂S)₂]</td>
<td>n.o. b</td>
<td>n.o.</td>
<td>n.o.</td>
<td>—</td>
</tr>
</tbody>
</table>

a. Relative to external SnMe₄ in CH₂Cl₂-CD₂Cl₂ solution.

n.o. = No resonance observed.
2.2.3. $^{119}$Sn Magic Angle Spinning NMR Spectroscopy

The $^{119}$Sn Magic Angle Spinning NMR (MASNMR) spectrum of [SnCl$_4$(Me$_2$S)$_2$] was also studied (Figure 2.4). A single broad resonance was observed at $\delta$ = -626.7 ppm. This resonance is typical of a six-co-ordinate tin(IV) chloro species$^{19}$ and the chemical shift difference of $\sim$65 ppm between solid state and solution NMR studies are probably attributable to solvent effects.$^{20}$ The chemical shift range of solution $^{119}$Sn NMR spectroscopy is some 4000 ppm,$^{21}$ which suggest that significant differences might be expected in $\delta(^{119}$Sn) on going from solution to the solid state. For example, studies on [Sn(C$_6$H$_{11}$)$_3$(OH)]$^{20}$ have shown $\delta(^{119}$Sn) 11.6 ppm in CDC$_3$ solution and $\delta$ -217 ppm in the solid state. Although the most dramatic differences are expected when a change in co-ordination occurs on going into solution, even slight geometrical changes can cause a shift of 50 – 100 ppm.$^{20}$

Figure 2.4. $^{119}$Sn MASNMR spectrum of [SnCl$_4$(Me$_2$S)$_2$]
2.2.4. Synthesis and Properties of Bidentate Thioether Complexes

A range of complexes of type \([SnX_4\{L-L\}]\) (where \(X = \text{Cl}, \text{Br} \text{ or I}; \ L-L = \text{MeSCH}_2\text{SMe}, \ \text{O-C}_6\text{H}_4(\text{SMe})_2 \text{ or RS(CH}_2)_n\text{SR}; \text{where R = Ph or Me, n = 2 or 3}) have been prepared by reaction of \(\text{SnX}_4\) with a molar equivalent of thioether ligand \(L-L\) in degassed \(\text{CHCl}_3\). In most cases this gave precipitates of powdered white solids (Me substituted ligands), or crystalline solids (Ph substituted ligands), in good yield. In the case of \([SnBr_4\{\text{PhS(CH}_2)_3\text{SPh}\}]\) a viscous yellow solution was formed from which it was not possible to isolate a solid, and no solids were isolable for reactions involving \(\text{SnI}_4\). Due to the extreme moisture sensitivity of the tin(IV) halides all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. While these complexes were found to be stable over a period of several months in the solid state they were susceptible to hydrolysis in solution, necessitating the use of dry solvents when studied in solution. If dry solvents are not used hydrolysis occurs readily resulting in the formation of hydrates of varying stoichiometries or oxidation of the ligand as discussed later within this chapter. \(\text{SnF}_4\) was also studied with the methyl substituted ligands \(\text{MeS(CH}_2)_n\text{SMe} \text{ (n = 2 or 3}).\) Previous complexes of \(\text{SnF}_4\) with harder oxygen- and nitrogen-donor ligands such as pyridine, triethylamine, acetonitrile and tetrahydrofuran (thf) suggested that \(\text{SnF}_4\) only achieved reasonable solubility in warm thf solution. This method was employed with the dithioether systems but failed to yield any solid product which displayed either \(v(\text{Sn-F})\) bands in the IR spectrum or any \(^{119}\text{Sn}\) NMR resonances at any accessible temperature (173 - 300 K).

IR spectra of the solid complexes formed all showed the expected four \(v(\text{Sn-Cl})\) bands (theory: \(2A_1 + B_1 + B_2\)) in the range 300 - 340 cm\(^{-1}\) consistent with \(C_{2v}\) symmetry. The presence of strong bands from the nujol the complexes were studied in made assignment of associated ligand bands difficult. When the spectrum of \([\text{SnCl}_4\{\text{MeS(CH}_2)_3\text{SMe}\}]\) was recorded as a CsI disc, the disc turned a dark brown very rapidly, suggesting a reaction had occurred between the complex and the CsI. There were no strong bands present in the range 900 - 1300 cm\(^{-1}\) as have been reported for complexes incorporating sulfoxide (S=O) functions.\(^{13-17}\) Similarly, there were no bands in the region 400 - 470 cm\(^{-1}\) characteristic of the associated \(v(\text{SnO})\) stretching frequencies.\(^{18}\) IR spectroscopic and analytical data are presented in Table 2.3

As tin has the greatest number of naturally occurring isotopes of any element, mass spectrometry would seem to be an extremely effective means of identifying the
tin species present. Unfortunately despite trying a variety of matrices, no peaks with the required isotope patterns were observed either by fast atom bombardment, or by positive electrospray. This is most likely to be due to the sensitivity of the compounds which decompose in the solvent or matrix media.

Table 2.3. Analytical and spectroscopic data for \([SnX_4(dithioether)]\) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>%C(^a)</th>
<th>%H</th>
<th>(v(Sn-X))^b (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([SnCl_4{MeS(CH_2)_2SMe}]</td>
<td>White</td>
<td>12.5(12.6)</td>
<td>2.4(2.6)</td>
<td>326, 316, 307, 301</td>
</tr>
<tr>
<td>([SnCl_4{MeS(CH_2)_3SMe}]</td>
<td>Yellow</td>
<td>15.3(15.1)</td>
<td>2.9(3.1)</td>
<td>331, 321, 315, 308</td>
</tr>
<tr>
<td>([SnCl_4{PhS(CH_2)_2PhMe}]</td>
<td>Yellow</td>
<td>33.0(33.2)</td>
<td>3.0(2.8)</td>
<td>334, 327, 315, 302</td>
</tr>
<tr>
<td>([SnCl_4{PhS(CH_2)_3PhMe}]</td>
<td>Orange</td>
<td>34.8(34.6)</td>
<td>3.4(3.1)</td>
<td>339, 323, 316, 309</td>
</tr>
<tr>
<td>([SnCl_4{o-C_6H_4(SMe)_2}]</td>
<td>White</td>
<td>21.8(22.3)</td>
<td>2.2(2.3)</td>
<td>332, 320, 311, 304</td>
</tr>
<tr>
<td>([SnBr_4{MeS(CH_2)_2SMe}]</td>
<td>Yellow</td>
<td>8.8(8.5)</td>
<td>2.0(1.8)</td>
<td>238, 220, 216, 209</td>
</tr>
<tr>
<td>([SnBr_4{MeS(CH_2)_3SMe}]</td>
<td>Yellow</td>
<td>10.3(10.4)</td>
<td>1.9(2.1)</td>
<td>241, 220, 206, 200</td>
</tr>
<tr>
<td>([SnBr_4{o-C_6H_4(SMe)_2}]</td>
<td>Yellow</td>
<td>15.5(15.8)</td>
<td>1.3(1.6)</td>
<td>236, 224, 221, 212</td>
</tr>
</tbody>
</table>

\(^a\) Calculated values in parentheses
\(^b\) Nujol mulls
2.2.5. **Single Crystal X-ray Diffraction Studies**

Prior to this work, structurally characterised examples of thioether complexes with tin(IV) had been restricted to the monodentate ligand Me₂S, and the multidentate cyclic thioethers [9]aneS₃, [18]aneS₆, and 1,5-dithiacyclooctane. In order to attempt to identify trends in their geometric parameters, and to correlate these with their observed behaviour within solution (by variable temperature $^{119}$Sn{$^1$H} and $^1$H NMR spectroscopy) single crystal X-ray structure analyses on several of the products were undertaken.

Figure 2.5. View of the structure of [SnCl₄{MeS(CH₂)₂SMe}] with the numbering scheme adopted. Ellipsoids are shown at 40 % probability and atoms marked with an asterisk are related by a crystallographic two-fold axis at ($\frac{1}{2}$, 0, z)
Table 2.4. Selected bond lengths (Å) with e.s.d’s for the [SnX₄{dithioether}] complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn-X(1)a</th>
<th>Sn-X(2)b</th>
<th>Sn-X(3)b</th>
<th>Sn-X(4)b</th>
<th>Sn-S(1)</th>
<th>Sn-S(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄{MeSCH₂SMe}]</td>
<td>2.402(2)</td>
<td>2.390(2)</td>
<td>2.343(2)</td>
<td>2.362(2)</td>
<td>2.647(2)</td>
<td>2.710(2)</td>
</tr>
<tr>
<td>[SnCl₄{MeS(CH₂)₂SMe}]</td>
<td>2.413(3)</td>
<td>(--)c</td>
<td>2.372(4)</td>
<td>(--)c</td>
<td>2.619(4)</td>
<td>(--)c</td>
</tr>
<tr>
<td>[SnCl₄{MeS(CH₂)₃SMe}]</td>
<td>2.409(2)</td>
<td>(--)d</td>
<td>2.378(2)</td>
<td>(--)d</td>
<td>2.667(2)</td>
<td>(--)d</td>
</tr>
<tr>
<td>[SnBr₄{MeS(CH₂)₃SMe}]</td>
<td>2.562(3)</td>
<td>(--)d</td>
<td>2.533(3)</td>
<td>(--)d</td>
<td>2.700(7)</td>
<td>(--)d</td>
</tr>
<tr>
<td>[SnCl₄{η-C₆H₄(SMe)₂}]</td>
<td>2.401(2)</td>
<td>2.383(2)</td>
<td>2.357(2)</td>
<td>2.357(2)</td>
<td>2.659(2)</td>
<td>2.677(2)</td>
</tr>
<tr>
<td>[SnCl₄{PhS(CH₂)₃SPh}]</td>
<td>2.385(5)</td>
<td>2.379(6)</td>
<td>2.376(4)</td>
<td>2.380(5)</td>
<td>2.724(5)</td>
<td>2.725(5)</td>
</tr>
</tbody>
</table>

a. X atoms trans X atoms
b. X atoms trans S atoms
c. Atoms related by crystallographic two-fold axis at (½, 0, z)
d. Atoms related by crystallographic two-fold axis at (1, 0, z)
Table 2.5 Selected bond angles (°) for the [SnX₄{dithioether}] complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>[SnCl₄{MeS(CH₂)₂SMe}]</th>
<th>[SnCl₄{MeS(CH₂)₂SMe}]</th>
<th>[SnCl₄{MeS(CH₂)₂SMe}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X(1)-Sn-X(2)</td>
<td>167.15(5)</td>
<td>169.9(2)</td>
<td>172.04(8)</td>
</tr>
<tr>
<td>X(1)-Sn-X(3)</td>
<td>93.94(6)</td>
<td>93.2(1)</td>
<td>94.94(6)</td>
</tr>
<tr>
<td>X(1)-Sn-X(4)</td>
<td>94.69(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X(1)-Sn-S(1)</td>
<td>88.08(5)</td>
<td>91.3(1)</td>
<td>89.27(6)</td>
</tr>
<tr>
<td>X(1)-Sn-S(2)</td>
<td>78.70(5)</td>
<td>81.2(1)</td>
<td>84.80(6)</td>
</tr>
<tr>
<td>X(2)-Sn-X(3)</td>
<td>95.45(6)</td>
<td>93.4(1)</td>
<td>90.37(6)</td>
</tr>
<tr>
<td>X(2)-Sn-X(4)</td>
<td>92.39(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X(2)-Sn-S(1)</td>
<td>82.09(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X(2)-Sn-S(2)</td>
<td>89.90(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X(3)-Sn-X(4)</td>
<td>99.51(6)</td>
<td>98.2(2)</td>
<td>96.32(8)</td>
</tr>
<tr>
<td>X(3)-Sn-S(1)</td>
<td>97.05(5)</td>
<td>89.04(10)</td>
<td>89.27(6)</td>
</tr>
<tr>
<td>X(3)-Sn-S(2)</td>
<td>163.15(6)</td>
<td>171.1(1)</td>
<td>172.24(6)</td>
</tr>
<tr>
<td>X(4)-Sn-S(1)</td>
<td>162.97(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X(4)-Sn-S(2)</td>
<td>96.20(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S(1)-Sn-S(2)</td>
<td>67.82(5)</td>
<td>84.2(2)</td>
<td>83.73(7)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>[SnBr₄{MeS(CH₂)₂SMe}³]</th>
<th>[SnBr₄{MeS(CH₂)₂SMe}³]</th>
<th>[SnBr₄{MeS(CH₂)₂SMe}³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X(1)-Sn-X(2)</td>
<td>172.3(1)</td>
<td>169.00(7)</td>
<td>167.69(5)</td>
</tr>
<tr>
<td>X(1)-Sn-X(3)</td>
<td>94.71(9)</td>
<td>93.14(7)</td>
<td>94.6(2)</td>
</tr>
<tr>
<td>X(1)-Sn-X(4)</td>
<td>-</td>
<td>91.79(7)</td>
<td>94.1(2)</td>
</tr>
<tr>
<td>X(1)-Sn-S(1)</td>
<td>89.9(2)</td>
<td>83.28(6)</td>
<td>84.0(2)</td>
</tr>
<tr>
<td>X(1)-Sn-S(2)</td>
<td>84.3(2)</td>
<td>83.17(6)</td>
<td>86.7(2)</td>
</tr>
<tr>
<td>X(2)-Sn-X(3)</td>
<td>90.46(9)</td>
<td>95.57(8)</td>
<td>94.4(2)</td>
</tr>
<tr>
<td>X(2)-Sn-X(4)</td>
<td>-</td>
<td>92.83(7)</td>
<td>93.2(2)</td>
</tr>
<tr>
<td>X(2)-Sn-S(1)</td>
<td>-</td>
<td>89.87(6)</td>
<td>87.5(2)</td>
</tr>
<tr>
<td>X(2)-Sn-S(2)</td>
<td>-</td>
<td>86.70(7)</td>
<td>83.3(2)</td>
</tr>
<tr>
<td>X(3)-Sn-X(4)</td>
<td>95.9(1)</td>
<td>102.73(7)</td>
<td>96.55(5)</td>
</tr>
<tr>
<td>X(3)-Sn-S(1)</td>
<td>91.0(2)</td>
<td>90.95(6)</td>
<td>90.6(2)</td>
</tr>
<tr>
<td>X(3)-Sn-S(2)</td>
<td>171.7(2)</td>
<td>165.01(6)</td>
<td>172.0(2)</td>
</tr>
<tr>
<td>X(4)-Sn-S(1)</td>
<td>-</td>
<td>165.72(7)</td>
<td>172.7(2)</td>
</tr>
<tr>
<td>X(4)-Sn-S(2)</td>
<td>-</td>
<td>91.93(6)</td>
<td>91.2(2)</td>
</tr>
<tr>
<td>S(1)-Sn-S(2)</td>
<td>82.5(3)</td>
<td>74.21(6)</td>
<td>81.67(4)</td>
</tr>
</tbody>
</table>

a. X(2) and X(4) refer to Cl(1*) and Cl(3*) in the numbering scheme adopted, related by a crystallographic two-fold axis at (½, 0, z)

b. X(2) and X(4) refer to X(1*) and X(3*) in the numbering scheme adopted, related by a crystallographic two-fold axis at (1, 0, z)
Figure 2.6. View of the structure of \([\text{SnCl}_4\{\text{MeS(CH}_2)_3\text{SMe}\}]\) with the numbering scheme adopted. Ellipsoids are shown at 40% probability and atoms marked by an asterisk are related by a crystallographic two-fold axis at (1, 0, z).

The structure for \([\text{SnCl}_4\{\text{MeS(CH}_2)_2\text{SMe}\}]\) (Figure 2.5) shows a distorted octahedral arrangement with the tin centre occupying a crystallographic 2-fold axis (0.5, 0, z). Similarly the structure for \([\text{SnCl}_4\{\text{MeS(CH}_2)_3\text{SMe}\}]\) (Figure 2.6) also shows a distorted octahedral arrangement with the tin centre, and carbon (3), occupying a crystallographic 2-fold axis (1, 0, z), and the tin(IV) bromide system, \([\text{SnBr}_4\{\text{MeS(CH}_2)_3\text{SMe}\}]\), is isostructural with this (Figure 2.7). The other structures for \([\text{SnCl}_4(\text{MeSCH}_2\text{SMe})]\) (Figure 2.8), \([\text{SnCl}_4(\omega-\text{C}_6\text{H}_4(\text{SMe})_2)]\) (Figure 2.9) and \([\text{SnCl}_4(\text{PhS(CH}_2)_3\text{SPh})]\) (Figure 2.10) also show distorted octahedral arrangements but in these structures the tin centres occupy crystallographic general positions.

Selected bond lengths (Å) and angles (°) are presented for these structures in Tables 2.4 and 2.5 respectively. The Sn-S and Sn-X distances determined from these studies (Sn-S 2.619(4) – 2.725(5), Sn-Cl 2.372(4) – 2.409(2), Sn-Br 2.533(3) & 2.562(3) Å) are in good agreement with the few structurally characterised examples in the literature, e.g. \([\text{SnCl}_3([\text{9}]	ext{aneS}_3)]^+\) [Sn-S 2.618(3), 2.636(3) and 2.657(4), Sn-Cl 2.366(4), 2.369(3) and 2.371(4) Å],\(^{11}\) 2SnCl₄.[18]aneS₆ [Sn-S 2.535(10), 2.56(2), 2.687(13) and 2.689(13), Sn-Cl 2.30(2), 2.31(2), 2.38(2), 2.391(2), 2.421(2) and
Figure 2.7. View of the structure of $[\text{SnBr}_4\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}]$ with numbering scheme adopted. Details as in Figure 2.5

2.42(2)$^{11}$ cis-$[\text{SnBr}_4(\text{Me}_2\text{S})_2]$ [Sn-S 2.692(8) and 2.692(9), Sn-Br 2.554(4), 2.532(4), 2.557(4) and 2.539(4) Å$^9$ and trans-$[\text{SnCl}_4(\eta^6\text{C}_6\text{H}_{12}\text{S}_2-1,5)_2]$ (C$_6$H$_{12}$S$_2$-1,5 = 1,5-dithiacyclooctane) [Sn-S 2.602(1), Sn-Cl 2.414(1), 2.428(1) Å].$^{12}$ However, the number of structures determined in this work allow comparisons to be drawn and, from these, a number of observations can be made on the stability of the complexes. In all cases there are variations in the Sn-X bond distances with d(Sn-Cl) for Cl trans to Cl being longer than those trans to S (e.g. 2.372(4) and 2.413(3) Å respectively in $[\text{SnCl}_4\{\text{MeS}(\text{CH}_2)_2\text{SMe}\}]$) presumably reflecting the greater trans influence of Cl over S(thioether) in these hard Sn(IV) species that was suggested by Ruzicka and Merbach.$^{3,4,5}$ This is a trend that is also observed in the complexes $[[\text{SnCl}_4][\text{18} \text{aneS}_6]]^{11}$ (cf. Sn-Cl(trans Cl) 2.421(2) and 2.391(2) Å vs. Sn-Cl(trans S) 2.30(2) and 2.31(2) Å) and cis-$[\text{SnBr}_4(\text{Me}_2\text{S})_2]$$^9$ (cf. Sn-Br(trans Br) 2.557(4) and 2.554(4) Å vs. Sn-Br(trans S) 2.532(4) and 2.539(4) Å). It is also noted that there is a distortion in the octahedral geometry with the mutually trans halides tilted towards the coordinated dithioether ligand (e.g. 169.9° in $[\text{SnCl}_4\{\text{MeS}(\text{CH}_2)_2\text{SMe}\}]$). Also of interest are the Sn-S bond distances which shed some light on the relative stabilities of the various systems studied.
There are significant variations in these Sn-S bond distances across the series of complexes. Comparing the three different chelate ring-sizes studied with tin(IV) chloride (four, five and six membered chelates), we see that the shortest distance occurs for the five membered chelate ring, $[\text{SnCl}_4\{\text{MeS(CH}_2\text{)}_2\text{SMe}\}]$ 2.619(4) Å. The next shortest is seen for six membered chelate, $[\text{SnCl}_4\{\text{MeS(CH}_2\text{)}_3\text{SMe}\}]$ 2.667(2) Å, with the longest Sn-S bond distances seen in the four membered chelate system, $[\text{SnCl}_4(\text{MeSCH}_2\text{SMe})]$ 2.647(2) and 2.710(2) Å suggesting that the five-membered chelate-ring is preferred to the six-member chelate ring, with the four-membered chelate-ring least favourable, as would be expected due to the ring strain in this system.

The presence of the more rigid $\alpha$-C$_6$H$_4$ backbone within $[\text{SnCl}_4\{\alpha$-C$_6$H$_4(\text{SMe})_2\}]$ also has the effect of reducing the stability of the five-membered chelate-ring so the Sn-S bond distances here (2.659(2) and 2.677(2) Å) are significantly longer than those of $[\text{SnCl}_4\{\text{MeS(CH}_2\text{)}_2\text{SMe}\}]$, with the more flexible backbone (2.619(4) Å).

The Sn-S bond distances observed for the Ph substituted species, $[\text{SnCl}_4\{\text{PhS(CH}_2\text{)}_3\text{SPh}\}]$ [Sn-S 2.724(5) and 2.725(5) Å], are significantly longer than those of the methyl substituted analogue, $[\text{SnCl}_4\{\text{MeS(CH}_2\text{)}_3\text{SMe}\}]$ [Sn-S 2.667(2) Å].
This increase in \( d(\text{Sn-S}) \) parallels the observed decrease in stability observed in solution in the NMR studies that follow.

**Figure 2.9.** View of the structure of \([\text{SnCl}_4\\{\text{o-C}_6\text{H}_4(\text{SMe})_2\}]\) with the numbering scheme adopted. Ellipsoids are shown at 40 % probability

The highly strained nature of the complex of MeSCH\(_2\)SMc with tin(IV) chloride leading to the high lability of this complex in solution is well illustrated by the X-ray diffraction study. The S-Sn-S angle of 67.82(5)\(^\circ\) is significantly more acute than the ideal octahedral angle of 90\(^\circ\), and is markedly more strained than the other two Me-substituted dithioether systems studied. This is the first example of a chelating methylene linked dithio-, diseleno or ditelluro-ether. Previously characterised examples with this methylene linked dithioether ligand have featured \( \eta^1 \)-coordination within systems of the type \([\text{ML}_2\text{Cl}_2]\)\(^{24}\) (where \( M = \text{Pd} \) or \( \text{Pt} \); \( L = \text{PhSCH}_2\text{SPh}, \text{MeSCH}_2\text{SMc} \)) or bridging ligands interlinking the SnCl\(_4\) units oligomers seen previously for Cu\(^1\) and Ag\(^1\) systems.\(^{25}\) \([\text{SnCl}_4\{\text{MeS(CH}_2)_2\text{SMc}\}]\) with an S-Sn-S angle of 84.2(2)\(^\circ\) is closer to this ideal than \([\text{SnCl}_4\{\text{MeS(CH}_2)_3\text{SMc}\}]\) with an angle of 83.73(7)\(^\circ\) showing that the five membered chelate ring is preferred in terms of strain over the six membered ring with the four membered chelate ring worst of all.
Comparison between the SnCl$_4$ and SnBr$_4$ adducts with MeS(CH$_2$)$_3$SMe shows a variation in the Sn-S bond distances, those of the chloride [Sn-S 2.667(2) Å] being significantly shorter than those of the bromide [2.700(7) Å]. Whether for steric or electronic reasons this shows that the bond between tin and sulfur is weaker in the bromide complex so it is of no surprise that the phenyl substituted ligands, that have been seen to be poorer donors, form no isolable solid adducts.

Figure 2.10. View of the structure of [SnCl$_4$(PhS(CH$_2$)$_3$SPh)] with numbering scheme adopted. Ellipsoids are shown at 40 % probability.
2.2.6. Variable Temperature Solution $^1$H NMR Studies

At room temperature these bidentate dithioether complexes are expected to undergo exchange via a dissociative process and also sulfur inversion, both of which are rapid on an NMR timescale. As a result, in the NMR spectra recorded at room temperature protons, which in the absence of these processes are magnetically non-equivalent, appear equivalent and the resulting spectra appear very simple. On lowering the temperature to ca. 200 K the ligand exchange is slowed to a rate observable by NMR and, in some cases, the sulfur inversion process is also slowed sufficiently that the resultant isomers are distinguishable. The sulfurs undergo inversion independently to give the $dl$ and $meso$ configurations.

Table 2.6. $^1$H NMR spectroscopic data for methyl substituted [SnX₄{dithioether}] complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H (δ) a</th>
<th>300 K</th>
<th>175 K</th>
<th>$dl$:meso</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄{MeS(CH₂)₂SMe}]</td>
<td>2.50</td>
<td>2.48, 2.61</td>
<td>2:1</td>
<td></td>
</tr>
<tr>
<td>[SnCl₄{MeS(CH₂)₃SMe}]</td>
<td>2.37</td>
<td>2.48, 2.64</td>
<td>1:2</td>
<td></td>
</tr>
<tr>
<td>[SnCl₄{o-C₆H₄(SMe)₂}]</td>
<td>2.75</td>
<td>2.80, 3.05</td>
<td>1:10</td>
<td></td>
</tr>
<tr>
<td>[SnBr₄{MeS(CH₂)₂SMe}]</td>
<td>2.24</td>
<td>2.26, 2.41</td>
<td>1:1</td>
<td></td>
</tr>
<tr>
<td>[SnBr₄{MeS(CH₂)₃SMe}]</td>
<td>2.18</td>
<td>2.05, 2.41</td>
<td>3:1</td>
<td></td>
</tr>
<tr>
<td>[SnBr₄{o-C₆H₄(SMe)₂}]</td>
<td>2.50</td>
<td>2.86</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

a. In CD₂Cl₂, Me resonances only.

For the methyl substituted complexes of SnCl₄ ([SnCl₄{MeS(CH₂)ₙSMe}], n = 2 or 3; [SnCl₄{o-C₆H₄(SMe)₂}]) the δ(CH₂) resonances for each complex can clearly be seen to broaden on cooling, before splitting into two separate doublet resonances (< ca. 200 K) representing the AB coupling of the two separate diastereoisomers. Also at low
Figure 2.11. $^1$H NMR spectra of [SnCl$_4$(MeS(CH$_2$)$_2$SMe)$_2$] in CD$_2$Cl$_2$ solution at a) 300 K and b) 175 K.
temperature it is possible to observe coupling to the tin isotopes with \( I = \frac{1}{2} (3^J(117/119\text{Sn} - 1^1\text{H}) \sim 40 \text{ Hz, Figure 2.11}) \). At ca. 220 K these tin satellites are lost, indicating that at this temperature ligand dissociation mechanisms also become important in the exchange processes. For complexes of SnBr4 the same patterns are seen for the complexes of with alkyl backbones (MeS(CH2)nSMe), with invertomers observable at the lowest temperature studied (180 K). However, even at this temperature, the \( \delta(\text{Me}) \) resonance for the \( \alpha \)-phenylene ligand (\( \alpha-C_6H_4(S\text{Me})_2 \)) merely broadens signifying that for this system the low temperature limiting spectrum has not been reached. In the case of complexes of SnI4, where no solid is isolable, it was not possible to identify any signals at all in an \textit{in situ} experiment over the entire temperature range (175 – 300 K).

The approximate ratios of \textit{meso} : \textit{dl} isomers can also be determined from the \textit{1H} NMR (CD2Cl2, 180 K) spectra of the methyl substituted complexes. For the complexes [SnCl4{MeS(CH2)nSMe}] the ratio \textit{meso} : \textit{dl} are 1 : 2 (n = 2) and 2 : 1 (n = 3). However for the complex [SnCl4{\( \alpha \)-C6H4(SMe)2}] the ratio is approximately 10 : 1.

In the cases of the phenyl substituted complexes ([SnCl4{PhS(CH2)nSPh}]; n = 2 or 3) the resonances from the phenyl rings are not very informative. The information can be gained instead by examining the \( \delta(\text{CH}_2) \) resonances. For [SnCl4{PhS(CH2)2SPh}], the \( \delta(\text{CH}_2) \) resonance can clearly be seen to broaden on lowering the temperature, before splitting and sharpening on lowering the temperature down to 180 K. For the species [SnCl4{PhS(CH2)3SPh}] it was only possible to produce a broad, single peak even at the lowest temperature achieved (175 K). This indicates that the low temperature limiting spectrum has not been reached and the inversion barrier is lowered by having a phenyl group rather than a methyl group bound to the inverting atom. This may be due to the increased steric bulk or the electronic effects of the phenyl ring. This is in accordance with the observations reported by Abel \textit{et al.} who also assign the ligands in this order of decreasing inversion barrier and also the results of our single crystal X-ray diffraction studies where the Sn-S bond distances were seen to increase with the poorer phenyl substituted donors. As was observed for the bromide systems of the methyl substituted ligands, the phenyl substituted complexes of tin(IV) bromide proved too labile in solution to reach the low temperature limiting spectrum, and this is in accordance with the observation that no solid was isolable for the SnBr4 – PhS(CH2)3SPh system, and consistent with the X-ray diffraction study where the Sn-S bond distance for the SnBr4 system is longer than those of the SnCl4 systems. Continuing the pattern there was no obvious reaction.
between these phenyl substituted ligands and tin(IV) iodide either in the reaction mix or in terms of resonance shifts in the $^1$H NMR spectra which would correspond to co-ordination.

2.2.7. Variable Temperature Solution $^{119}$Sn NMR Studies

As has been observed$^{5,9}$ for related species the solubility of these complexes in chlorocarbon solvents is extremely poor. A range of other solvents was also examined, including MeNO$_2$, Me$_2$CO, thf and propane-1,2-diol carbonate, but these proved unsatisfactory and there was some evidence that the observed resonances were due to adducts with O-donors$^{25}$ and displacement of the dithioether ligand. CD$_2$Cl$_2$ was therefore used even although the compounds were not very soluble in this solvent.

The $^{119}$Sn{$^1$H} NMR spectra (134.2 MHz, CD$_2$Cl$_2$) were recorded over a range of temperatures (300 - 180 K) in order to observe the effects of ligand exchange by dissociation and sulfur inversion. Resonances for the various tin(IV) species were observed in characteristic regions. Resonances for the tin(IV) chloride-dithioether complexes were observed within the range $\delta$ -500 to $\delta$ -600 ppm, similar to the chemical shifts observed for the cis and trans isomers of [SnCl$_4$(Me$_2$S)$_2$] by Merbach et al. ($\delta$ -569 and $\delta$ -574 respectively)$^{6,7}$ and also similar to $\delta$($^{119}$Sn) for the six coordinate tin system, [SnCl$_4$(PBu$_3$)$_2$], ($\delta$ -573 ppm).$^{27}$ The complexes of tin(IV) bromide were characteristically observed over the range $\delta$ -1100 to $\delta$ -1300 ppm. Complexes of tin(IV) iodide fall in the region $\delta$ -2600 to $\delta$ -2800 ppm where the closest characterised analogue is the resonance at $\delta$ -1701 ppm for tin(IV) iodide in CS$_2$ solution.$^{27}$

Over the entire temperature range studied (300 K - 180 K) the resonances for these complexes were weak, due to the poor solubility of the compounds in CH$_2$Cl$_2$. Variable temperature $^{119}$Sn{$^1$H} NMR data are presented in Table 2.7.

The complexes of MeSCH$_2$SMe, were rather more soluble in CD$_2$Cl$_2$, possibly due to ring opening in this strained molecule. No signal is observed in the $^{119}$Sn{$^1$H} NMR spectrum above 230 K. Below this a single broad resonance becomes observable, which then sharpens on cooling and eventually splits at 180 K to show two distinct resonances for dl and meso invertomers at $\delta$ -585.3 and -585.7 ppm. This is within the same region of the spectra as the other [SnCl$_4$(L-L)] species studied confirming a chelate is formed in solution as well as the solid state. Given the highly strained nature of the four-membered chelate-ring formed this is a surprise.
Above 230 K the ligand is probably dissociating rapidly to give a mix of chelate and $\eta^1$ co-ordination.

Table 2.7. Variable temperature $^{119}\text{Sn-}^{1\text{H}}$ NMR spectroscopic data for [SnX$_4${dithioether}] complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{119}\text{Sn-}^{1\text{H}}$ $^\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 K</td>
</tr>
<tr>
<td>[SnCl$_4${MeS(CH$_2$)$_2$SMe}]</td>
<td>n.o.$^b$</td>
</tr>
<tr>
<td>[SnCl$_4${MeS(CH$_2$)$_3$SMe}]</td>
<td>-572, -578</td>
</tr>
<tr>
<td>[SnCl$_4${MeS(CH$_2$)$_2$SMe}]</td>
<td>-560 (br)</td>
</tr>
<tr>
<td>[SnCl$_4${PhS(CH$_2$)$_2$SPh}]</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnCl$_4${PhS(CH$_2$)$_3$SPh}]</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnBr$_4${MeS(CH$_2$)$_2$SMe}]</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnBr$_4${MeS(CH$_2$)$_3$SMe}]</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnBr$_4${PhS(CH$_2$)$_2$SPh}]</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnBr$_4${PhS(CH$_2$)$_3$SPh}]</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnI$_4${MeS(CH$_2$)$_2$SMe}]</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnI$_4${MeS(CH$_2$)$_3$SMe}]</td>
<td>n.o.</td>
</tr>
</tbody>
</table>

$^a$ Relative to neat external SnMe$_4$ in CH$_2$Cl$_2$-CD$_2$Cl$_2$ solution.

$b$ n.o. = No resonance observed.

For the compound [SnCl$_4${MeS(CH$_2$)$_2$SMe}] at 300 K a single resonance was observed at $\delta$ -560 ppm. Lowering the temperature to 250 K results in a small shift in the resonance, probably due to temperature drift. This continues until at the lowest observed temperature (180 K) there are two discernible resonances at $\delta$ -549.0 ppm and $\delta$ -548.6 ppm. On warming the solution again, the two signals merge once more.
The same behaviour was observed for the complex \([\text{SnCl}_4\{\text{MeS(CH}_2)_3\text{SMe}\}\}]\) with a single resonance at \(\delta -567\) ppm at 300 K (Figure 2.12a). Cooling the sample to 250 K produces a slight shift to \(\delta -564\) ppm and this continued until at ca. 220 K the resonance was seen to split into two closely spaced resonances attributable to the meso and dl invertomers at \(\delta -563\) ppm and \(\delta -558\) ppm (Figure 2.12b). The two signals once again merge into one upon warming. The complex of \(\text{SnCl}_4\) with \(\alpha\text{-C}_6\text{H}_4(\text{SMe})_2\), showed no resonance at 300 K. Ligand exchange in solution at this temperature is rapid resulting in no resonance being observed until the temperature is lowered to ca. 240 K. At this point the exchange processes occurring are slowed sufficiently to allow this resonance to be observed on the NMR timescale. At this temperature a signal was observed at \(\delta -507\) ppm which, on further cooling to 180 K, split into two separate resonances at \(\delta -504.2\) ppm and \(\delta -504.9\) ppm for the meso and dl invertomers.

The analogous phenyl substituted systems, \(\text{PhS(CH}_2)_n\text{SPh}\) (\(n = 2\) or 3), of \(\text{SnCl}_4\) prove still more labile, consistent with the observed increase in Sn-S bond distances observed in the solid state X-ray diffraction studies. For the complex \([\text{SnCl}_4\{\text{PhS(CH}_2)_2\text{SPh}\}\}]\) no signals are evident at 300 K. At 220 K a very broad resonance was observed at ca. \(\delta -518\) ppm. At 200 K this resonance sharpened and was clearly discernible at \(\delta -517.8\) ppm. Further cooling to 180 K eventually slowed inversion sufficiently so that two resonances were now seen at \(\delta -516.2\) ppm and \(\delta -515.0\) ppm. \(\text{PhS(CH}_2)_3\text{SPh}\) proved to be the weakest donor of all. For this ligand no signals were observed until the very lowest temperature reached, 180 K, when a resonance was seen at \(\delta -570\) ppm. The fact that the signals for the phenyl substituted ligand systems were not observed until lower temperatures shows that these ligands are more labile than their methyl substituted analogues, resulting in dissociative ligand exchange processes beginning at lower temperatures.
Figure 2.12. $^{119}\text{Sn-}^{1}\text{H}$ NMR spectra of $[\text{SnCl}_4\{\text{MeS(CH}_2)_3\text{SMe}\}]$ in CH$_2$Cl$_2$-CD$_2$Cl$_2$ solution at a) 300 K and b) 180 K. Poor solubility and short accumulation periods restrict resolution.
For the systems of SnBr₄ the same general trends are observed, but with the dynamic processes in solution commencing at lower temperatures. This overall trend is in accordance with the X-ray diffraction results that show significantly longer bond distances for the bromide systems compared to the analogous chloride systems. [SnBr₄(MeSCH₂SMe)] is again extremely soluble in CH₂Cl₂ as the ligand is labile so even at the lowest recorded temperatures, no signals are observed within the ¹¹⁹Sn{¹H} spectra. For [SnBr₄{MeS(CH₂)₂SMe}] a resonance only became evident at ca. 230 K. At this temperature a weak resonance was observed at δ -1121 ppm and at 180 K, this split giving two distinct resonances at δ -1124.0 ppm and δ -1123.2 ppm for the two invertomers. The same pattern was observed for [SnBr₄{MeS(CH₂)₃SMe}] with the first signal observed at δ -1188 ppm at ca. 230 K and again at 180 K two resonances assigned to the two invertomers were observed at δ -1180.0 ppm and δ -1178.8 ppm. The difference between the chloride and bromide complexes was most clearly seen in the cases of the o-C₆H₄(SMe)₂ and PhS(CH₂)nSPh complexes. The only resonance to be observed was for [SnBr₄{PhS(CH₂)₂SPh}] in the presence of excess ligand at 175 K, with a broad resonance at δ -1127 ppm. Further evidence for the increased lability of these phenyl substituted ligands comes from the fact that it was not possible to isolate a solid product from the reaction of SnBr₄ with PhS(CH₂)₃SPh.

As expected, these trends are continued in the complexes of SnI₄. No solid complexes were isolable for any of these products, so all NMR studies were performed in situ. SnI₄ dissolves in CH₂Cl₂ solution readily in the presence of an excess of MeS(CH₂)nSMe (n = 2 or 3). At 180 K broad resonances were observed at δ - 2725 ppm (n = 2) and δ -2645 ppm (n = 3) which are assigned to the formation of an SnI₄S₂ adduct (cf. SnI₄ in CS₂ has δ -1701 ppm). Both resonances were lost above 190 K.

Although problems arising from the onset of ligand dissociation and pyramidal inversion at similar temperatures (as observed previously by Abel et al.⁸) precludes more detailed and quantitative analyses, there are a number of qualitative observations that can be made and trends that have become apparent within these systems. The inversion barrier for meso/dl isomerisation is affected by altering both the ligand and the tin(IV) halide species. Of the two terminal substituents on the sulfur (Me and Ph) it is clear that the methyl substituted ligand is less labile, leading to these dynamic processes occurring at higher temperatures relative to the phenyl substituted ligand complexes. Altering the ligand backbone has the same effect, with the inversion barrier lowered for the less favoured six and four-membered chelates. Adding unsaturation to
the backbone in the form of an o-phenylene ring also lowers the inversion barriers relative to the dimethylene backbone, with pyramidal inversion and ligand dissociation starting at lower temperatures. These inversion barriers also lower with weakening Lewis acidity, thus tin(IV) chloride forms the most stable complexes, followed by tin(IV) bromide, with tin(IV) iodide adducts only observable in situ at lower temperatures. All of these observations are consistent with the conclusions drawn from the single crystal X-ray diffraction studies of these systems, indicating the complimentarity of the two analytical techniques.

2.2.8. $^{119}$Sn Magic Angle Spinning NMR Spectroscopy

The SnCl$_4$-dithioether species were also investigated in the solid state using $^{119}$Sn magic angle spinning NMR spectroscopy. Resonances were observed in the range $-600$ to $-660$ ppm for the systems studied. The $^{119}$Sn MASNMR spectroscopic data is presented in Table 2.8.

Table 2.8. $^{119}$Sn Magic Angle Spinning NMR spectroscopic data for [SnCl$_4${dithioether}] complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{119}$Sn ($\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl$_4${MeS(CH$_2$)$_2$SMe}]</td>
<td>-630</td>
</tr>
<tr>
<td>[SnCl$_4${MeS(CH$_2$)$_3$SMe}]</td>
<td>-654</td>
</tr>
<tr>
<td>[SnCl$_4${Q-C$_6$H$_4$(SMe)$_2$}]</td>
<td>-617</td>
</tr>
<tr>
<td>[SnCl$_4${PhS(CH$_2$)$_2$SPh}]</td>
<td>-618</td>
</tr>
<tr>
<td>[SnCl$_4${PhS(CH$_2$)$_3$SPh}]</td>
<td>-653</td>
</tr>
</tbody>
</table>

Of note is the small chemical shift range observed for the various SnCl$_4$-dithioether species (40 ppm) in the solid state, and these are shifted by up to 100 ppm from the observed solution resonances. The observed resonances at $\delta$ ca. $-600$ ppm are typical of a six-co-ordinate tin(IV) chloro species. In the solid state the small chemical shift range observed between all the SnCl$_4$-dithioether complexes suggests that the tin centres are in very similar environments.
In all cases a singlet was observed for the SnCl₄-dithioether systems studied. The resonance broadens with the lowering symmetry in the molecular crystal structure, e.g. [SnCl₄{MeS(CH₂)₃SMe}] (Figure 2.13, tetragonal space group, C₂ local symmetry at tin, δ -654 ppm, full width half height (f.w.h.m.) 335.7 Hz) and [SnCl₄{α-C₆H₄(SMe)₂}] (triclinic space group, C₁ local symmetry at tin, δ -617 ppm, f.w.h.m. 4476.4 Hz). In addition to the resonances broadening on reduction of the symmetry, additional spinning side bands appeared which did not collapse even at the highest possible spinning rate (6.5 kHz). The appearance of spinning side bands in the solid-state spectra is also indicative of a more anisotropic environment.

The observation of a single broad line in the solid-state spectra contrasts markedly with the low temperature solution spectra which exhibit two sharp lines (separated by 1 – 2 ppm, attributed to the dl and meso isomers), and precludes identification of stereoisomers in the solid state.

No resonance was observed in the solid state for any of the SnBr₄-dithioether series despite long acquisition times and a variety of pulse/delay routines.

**Figure 2.13.** MAS $^{119}$Sn NMR spectrum of [SnCl₄{MeS(CH₂)₃SMe}] recorded at 4.5 KHz
2.2.9. Attempted Synthesis of Bidentate Thioether Complexes With Germanium(IV) and Silicon(IV) Halides

In addition to the bidentate thioether complexes of the tin(IV) halides reported here, similar reactions were attempted with silicon(IV) and germanium(IV) halides. The same general method of synthesis was employed as for the tin(IV) halide complexes, i.e. direct reaction of MCl₄ (M = Si or Ge) with one mole equivalent of ligand in dry, degassed CH₂Cl₂. No evidence was observed for the formation of any adducts by variable temperature ¹H NMR spectroscopy, contrasting with the immediate reactions seen for the SnCl₄ and SnBr₄ chemistry. The ¹H NMR spectra showed only free ligand with no change in chemical shift occurring as the temperature was varied between 180 – 300 K. Similar results were observed by ⁷²Ge-¹H and ²⁹Si-¹H NMR spectroscopy which only showed the presence of the free MCl₄ species.
2.2.10. Crystal Structure of \( \text{cis} \cdot [\text{SnI}_4\{\eta^1\cdot\text{O-MeS(O)(CH}_2\}_3\text{SMe}\}] \)

The formation of \([\text{SnI}_4\{\text{MeS(CH}_2\}_3\text{SMe}\}]\) was achieved \textit{in situ} and confirmed by solution \( ^{119}\text{Sn-}^1\text{H} \) NMR spectroscopy with a single resonance at \( \delta -2645 \) ppm. In an effort to obtain a crystal suitable for an X-ray structure analysis, a CHCl\(_3\) solution containing a 1:1 molar ratio of SnI\(_4\) and MeS(CH\(_2\)_3SMe was allowed to evaporate slowly. This resulted in a viscous orange oil with a few red-orange crystals forming on further evaporation. While there were too few of these crystals to permit detailed spectroscopic characterisation, they were of suitable quality for an X-ray crystallographic analysis.

The structure obtained from this analysis (Figure 2.14) showed that during crystallisation oxidation of the ligand had occurred forming MeS(O)(CH\(_2\)_3SMe. The structure shows that the material isolated was in fact \( \text{cis} \cdot [\text{SnI}_4\{\eta^1\cdot\text{O-MeS(O)(CH}_2\}_3\text{SMe}\}]_2 \), involving a distorted octahedral arrangement at Sn(IV) via four iodide ligands and two mutually cis MeS(O)(CH\(_2\)_3SMe ligands both of which are coordinated \textit{via} the O-donor of the sulfoxide function.

**Figure 2.14.** View of the structure of \( \text{cis} \cdot [\text{SnI}_4\{\eta^1\cdot\text{O-MeS(O)(CH}_2\}_3\text{SMe}\}]_2 \) with the numbering scheme adopted. Ellipsoids are shown at 40 % probability.
Selected bond angles (°) are presented in Table 2.10. The Sn-I bond distances (Table 2.9) and Sn-O bond distances (Table 2.9) are in good agreement with other literature examples of tin(IV) sulfoxide adducts.\textsuperscript{28-30} However, \textit{cis}-[SnI\textsubscript{4}\{η\textsuperscript{1}-O-MeS(O)(CH\textsubscript{2})\textsubscript{3}SMe\}\textsubscript{2}] is unusual in that the monosulfoxide formed by oxidation of the dithioether in the presence of SnI\textsubscript{4}. This presumably occurred as a result of trace amounts of water and iodine in the reaction mixture. Attempts to reproduce this reaction using wet solvents failed, with unreacted tin(IV) iodide recovered at the end.

<table>
<thead>
<tr>
<th>Table 2.9. Bond lengths (Å) with e.s.d.s for \textit{cis}-[SnI\textsubscript{4}{η\textsuperscript{1}-O-MeS(O)(CH\textsubscript{2})\textsubscript{3}SMe}\textsubscript{2}]</th>
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<tr>
<td>I(1) Sn 2.789(4) S(2) C(5) 1.75(5)</td>
</tr>
<tr>
<td>I(2) Sn 2.762(4) S(3) O(2) 1.52(2)</td>
</tr>
<tr>
<td>I(3) Sn 2.780(4) S(3) C(6) 1.80(3)</td>
</tr>
<tr>
<td>I(4) Sn 2.802(4) S(3) C(7) 1.79(3)</td>
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<tr>
<td>Sn O(1) 2.21(3) S(4) C(9) 1.80(4)</td>
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<tr>
<td>Sn O(2) 2.18(2) S(4) C(10) 1.76(5)</td>
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<tr>
<td>S(1) O(1) 1.47(2) C(2) C(3) 1.47(5)</td>
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<td>S(1) C(1) 1.78(4) C(3) C(4) 1.53(6)</td>
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<td>S(1) C(2) 1.78(5) C(7) C(8) 1.49(4)</td>
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<td>S(2) C(4) 1.79(4) C(8) C(9) 1.55(5)</td>
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Table 2.10. Selected bond angles (°) with e.s.d.s for cis-[SnI₄\{η⁴-O-MeS(O)(CH₂)₃SMe\}]₂

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<th>e.s.d. (°)</th>
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<td>I(2) Sn I(4)</td>
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<td>I(3) Sn O(1)</td>
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<tr>
<td>I(4) Sn O(1)</td>
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<tr>
<td>O(1) Sn O(2)</td>
<td>77.9(5)</td>
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</tr>
<tr>
<td>O(1) Sn C(2)</td>
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</tr>
<tr>
<td>O(2) S(3) C(7)</td>
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<td></td>
</tr>
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</table>
2.3. Conclusions

The products \([\text{SnX}_4(\text{R}_2\text{S})]\) (where \(\text{X} = \text{Cl}, \text{Br} \text{ or I}; \text{R} = \text{Me} \text{ or Ph}\)) and \([\text{SnX}_4\{\text{MeS}(\text{CH}_2)_n\text{SMe}\}\}] (where \(n = 1, 2 \text{ or 3}\), \([\text{SnX}_4\{\text{PhS}(\text{CH}_2)_n\text{SPh}\}\}] (where \(n = 2 \text{ or 3}\)) and \([\text{SnX}_4\{\text{C}_6\text{H}_4(\text{SMe})_2\}\}] have been prepared in high yield. A detailed examination of the variable temperature \(^1\text{H}\) and \(^{119}\text{Sn}-\{^1\text{H}\} \text{NMR spectroscopy over the temperature range 300 – 180 K has been presented. Particular emphasis for the bidentate systems has been on the study of the dynamic processes occurring in solution. The onset of pyramidal inversion and ligand dissociation have been detected, both of which begin at similar temperatures. It was possible to distinguish the \(dl\) and \(meso\) isomers within the NMR spectra at low temperature (180 K) for the majority of the systems, and a number of qualitative trends have been identified. Examples involving phenyl substituents are typically less stable than those with methyl substituents, and the stability of the complexes formed decreases with the \(\text{SnX}_4\) acceptor: \(\text{X} = \text{Cl} > \text{Br} > \text{I}\). The results also confirmed that five-membered chelate-ring systems are more stable than six membered chelates with the highly strained four membered chelate least favoured. Both single crystal X-ray diffraction studies on \([\text{SnCl}_4\{\text{MeS}(\text{CH}_2)_2\text{SMe}\}\}], \([\text{SnX}_4\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}\}] (where \(\text{X} = \text{Cl} \text{ or Br}\), \([\text{SnCl}_4\{\text{C}_6\text{H}_4(\text{SMe})_2\}\}], \([\text{SnCl}_4\{\text{PhS}(\text{CH}_2)_3\text{SPh}\}\}] and the highly strained four-membered chelate-ring species, and \(^{119}\text{Sn MASNMR spectroscopy were also used with both proving highly complementary to the solution studies and providing further support for the trends seen.}

The crystal structure of \(\text{cis-}[\text{SnI}_4\{\text{I}_1-\text{O-MeS(O)(CH}_2)_3\text{SMe}\}]_2\) is also reported which features the selective oxidation of one S-donor of the dithioether ligand giving a sulfoxide which binds \(via\) the O-donor to the hard Sn(IV) centre.
2.4. Experimental

The tin(IV) chloride, bromide and iodide and the ligands Me₂S, Ph₂S and MeSCH₂SMe were purchased from Aldrich Chemicals. The ligands MeS(CH₂)nSMe, PhS(CH₂)nSPh (where n = 2 or 3) and o-C₆H₄(SMe)₂ were prepared by following literature methods. Tin(IV) fluoride was prepared by Dr. Andrew Hector by reaction of tin powder with fluorine at 300 °C/3 atm. in a Monel autoclave.

Single Crystal X-ray Diffraction

Single crystals of [SnCl₄{MeS(CH₂)₂SMe}], [SnCl₄{MeS(CH₂)₃SMe}], [SnCl₄{PhS(CH₂)₂SPh}] and [SnBr₄{MeS(CH₂)₂SMe}] were obtained by slow evaporation from a solution of the appropriate complex in Me₂CO, [SnCl₄{o-C₆H₄(SMe)₂}] by slow cooling of the reaction mixture in CH₂Cl₂ and [SnCl₄(MeSCH₂SMe)] by slow evaporation of a CH₂Cl₂ solution. For each compound the selected crystal was coated with mineral oil and mounted on a glass fibre. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low temperature attachment operating at 150 K, using graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å), T = 150 K, ω-2θ scans. The intensities of three standard reflections were monitored every 150 reflections. No significant crystal decay or movement was observed. As there were no identifiable faces the raw data were corrected for absorption using psi-scans. The weighting scheme \( w^{-1} = a^2(F) \) gave satisfactory agreement analyses in each case. Crystallographic data is presented in Table 2.11.

The structures of [SnCl₄{MeS(CH₂)₂SMe}], [SnCl₄{MeS(CH₂)₃SMe}], [SnCl₄{o-C₆H₄(SMe)₂}] were solved by direct methods, while the structures of [SnCl₄{PhS(CH₂)₂SPh}] and [SnBr₄{MeS(CH₂)₂SMe}] were solved by heavy atom methods. All of the structures were then developed by iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms in the asymmetric unit. In each case all non-H atoms in the structures were refined anisotropically and H-atoms were placed in fixed, calculated positions. For [SnCl₄{MeS(CH₂)₃SMe}] and [SnBr₄{MeS(CH₂)₂SMe}], both of which crystallise in the polar space group I42d, the absolute configuration was confirmed by inverting and translating the co-ordinates and re-refining to convergence. In both cases, the enantiomorph chosen gave lower R-factors and e.s.d.s associated with the atomic
### Table 2.11. Crystallographic data

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<th>[SnCl₄(MeS(CH₂)₂SMe)]</th>
<th>[SnCl₄(MeS(CH₂)₂SMe)]</th>
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<th>[SnBr₄(MeS(CH₂)₂SMe)]</th>
<th>[SnBr₄(MeS(CH₂)₂SMe)]</th>
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\[
R = \frac{\sum |F_{\text{obs}}| - |F_{\text{calc}}|}{\sum |F_{\text{obs}}|}
\]

\[
R_w = \sqrt{\frac{\sum w(F_{\text{obs}} - F_{\text{calc}})^2}{\sum w(F_{\text{obs}})^2}}
\]

\[
\text{GOF} = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{(n - m)}
\]

(R = \text{Goodness of fit}, R_w = \text{Weighted R factor}, \text{GOF} = \text{Goodness of fit})
positions. The Hamilton R-factor ratio statistical check was also used to determine a significance value for each of the chosen configurations. The structure chosen for \([\text{SnCl}_4\{\text{MeS(CH}_2)_3\text{SMe}\}]\) was determined to be significant to 99.5 % and that for \([\text{SnBr}_4\{\text{MeS(CH}_2)_3\text{SMe}\}]\) 95 %, confirming the assignments made.

**Complex Synthesis**

**[SnCl\(_4\)(Me\(_2\)S)\(_2\)]**

Dimethyl sulfide (0.024 g, 2 mmol) was dissolved in degassed CHCl\(_3\) (5 cm\(^3\)) in a 3-neck RB flask under an atmosphere of dry N\(_2\) and the solution further degassed. Addition of SnCl\(_4\) (0.26 g, 1 mmol) to the solution gave a very exothermic reaction with the immediate formation of a pale cream precipitate. This was filtered and dried in vacuo. 0.134 g, 93 %.

**[SnCl\(_4\)(Ph\(_2\)S)\(_2\)]**

Diphenyl sulfide (0.037 g, 2 mmol) was dissolved in degassed CHCl\(_3\) (5 cm\(^3\)), addition of SnCl\(_4\) (0.26 g, 1 mmol) producing a pale cream precipitate. 0.249 g, 84 %.

**[SnBr\(_4\)(Me\(_2\)S)\(_2\)]**

Similar reaction between dimethyl sulfide (0.024 g, 2 mmol) and SnBr\(_4\) (0.44 g, 1 mmol) in degassed CHCl\(_3\) (5 cm\(^3\)) gave a pale cream precipitate. 0.403 g, 87 %.

**[SnBr\(_4\)(Ph\(_2\)S)\(_2\)]**

Diphenyl sulfide (0.037 g, 2 mmol) with SnBr\(_4\) (0.44 g, 1 mmol) in degassed CHCl\(_3\) (5 cm\(^3\)) formed a pale cream precipitate. 0.362 g, 76 %.

**[SnCl\(_4\){MeS(CH\(_2\)\(_2\)SMe)}]**

2,5-Dithiahexane (0.12 g, 1 mmol) was added to degassed CHCl\(_3\) (5 cm\(^3\)) in a 3-neck RB flask under an atmosphere of dry N\(_2\) and the solution was further degassed. SnCl\(_4\) (0.26 g, 1 mmol) was added to the flask with stirring. A violently exothermic reaction occurred as the SnCl\(_4\) was added and a white precipitate was seen to form from solution immediately. This was filtered through a Schlenk filter and dried in vacuo. 0.277 g, 73 %. \(^1\)H NMR spectrum (360 MHz, CD\(_2\)Cl\(_2\), 300 K): 3.25 (s, CH\(_2\), 4H), 2.50 (s, SMe, 6H) ppm.
[SnCl₄{MeS(CH₂)₃SMe}]

Addition of SnCl₄ (0.26 g, 1 mmol) to a solution of 1,3-bis(methylthio)propane (0.13 g, 1 mmol) formed a yellow precipitate immediately. This was filtered through a Schlenk filter and dried in vacuo. 0.33 g, 83 %. ¹H NMR spectrum (360 MHz, CD₂Cl₂, 300 K): 2.95 (SCH₂, 4H), 2.37(SMe, 6H), 2.12(CH₂, 2H) ppm.

[SnCl₄{PhS(CH₂)₂SPh}]

Addition of SnCl₄ (0.26 g, 1 mmol) to a solution of 1,2-bis(phenylthio)ethane (0.242 g, 1 mmol) in CHCl₃ (5 cm³) formed a yellow precipitate immediately from solution. This was filtered through a Schlenk filter, washed with CHCl₃ to remove unreacted solid ligand, and dried in vacuo. 0.39 g, 77 %. ¹H NMR spectrum (360 MHz, CD₂Cl₂, 300 K): 7.3(m, 5H, SPh), 3.43 (s, 2H, CH₂).

[SnCl₄{PhS(CH₂)₃SPh}]

Addition of SnCl₄ (0.26 g, 1 mmol) to a solution of 1,3-bis(phenylthio)propane (0.244 g, 1 mmol) in CHCl₃ (10 cm³) formed a crop of orange crystals from solution. These were filtered through a Schlenk filter and dried in vacuo. 0.38 g, 73 %. ¹H NMR spectrum (360 MHz, CD₂Cl₂, 300 K): 7.3(m, 10H, SPh), 3.12(m, 4H, SCH₂), 1.93(m, 2H, CH₂) ppm.

[SnCl₄(o-C₆H₄(SMe)₂}]

Addition of SnCl₄ (0.26 g, 1 mmol) to a solution of o-C₆H₄(SMe)₂ (0.17 g, 1 mmol) in CHCl₃ (10 cm³) formed a white crystalline from solution. This was filtered through a Schlenk filter and dried in vacuo. 0.34 g, 79 %. ¹H NMR spectrum (360 MHz, CD₂Cl₂, 300 K): 7.5(m, 4H C₆H₄), 2.75(s, 6H, SMe).

[SnBr₄{MeS(CH₂)₂SMe}]

SnBr₄ (0.88 g, 2 mmol) was dissolved in degassed CHCl₃ (10 cm³) in a 3-neck RB flask under an atmosphere of dry N₂. 2,5-Dithiahexane (0.24 g, 2 mmol) was dissolved in degassed CHCl₃ (10 cm³). This solution was added dropwise with stirring to the SnBr₄ solution. A yellow precipitate was seen to form from solution immediately. This precipitate was filtered through a Schlenk filter and dried in vacuo. 0.67 g, 60 %. Found: C, 8.8; H, 2.0. ¹H NMR spectrum (360 MHz, CD₂Cl₂, 300 K): 2.80 (s, CH₂, 4H), 2.24(s, SMe, 6H) ppm.
[SnBr₄{MeS(CH₂)₃SMe}]

Addition of a solution of 1,3-bis(methylthio)propane (0.26 g, 2 mmol) in CHCl₃ (10 cm³) to a solution of SnBr₄ (0.88 g, 2 mmol) formed a yellow precipitate immediately from solution. This precipitate was filtered through a Schlenk filter and dried in vacuo. 0.69 g, 61 %. ¹H NMR spectrum (360 MHz, CD₂Cl₂, 300 K): 2.72(t, SCH₂, 4H), 2.18(s, SMe, 6H), 1.91(d, CH₂, 2H) ppm.

[SnBr₄{C₆H₄(SMe)₂}]

Addition of o-C₆H₄(SMe)₂ (0.34 g, 2 mmol) in CHCl₃ (10 cm³) to a solution of SnBr₄ (0.88 g, 2 mmol) gave a yellow precipitate which formed immediately from solution. This precipitate was filtered through a Schlenk filter and dried in vacuo. 0.70 g, 58 %. ¹H NMR spectrum (360 MHz, CD₂Cl₂, 300 K): ~7.3(C₆H₄, 4H), 2.5(s, SMe, 6H) ppm.
Chapter 2  Group 14 Halide Complexes With Mono- and Bidentate Thioethers

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Chapter 3

Group 14 Halide Complexes With Mono- and Bidentate Selenoethers
3.1. Introduction

Compared to the thioether complexes studied in chapter 2 very little prior work has been done on selenoether complexes of the tin(IV) halides. The only prior reports of selenoether complexes are studies of $[\text{SnX}_4(\text{R}_2\text{Se})_2]$ (where $X = \text{Cl}$ or $\text{Br}$, $R = \text{Me}^{1,3}$ or $\text{Me}_3\text{SiCH}_2$). In the first series of studies on these systems Ruzicka and Merbach used infrared and Raman spectroscopy to investigate the vibrational spectra in the solid and solution states and compared this system with these containing a range of other ligand types. In the solid state the trans isomer was identified as predominant, while solution Raman spectroscopy identified the presence of a cis/trans equilibrium, again with the trans isomer preferred. They continued to study the same system using $^{19}\text{Sn}$-$^1\text{H}$ NMR spectroscopy and arrived at a number of conclusions for these systems. As discussed in chapter 2, they observed an increased lability for the cis isomer, attributed to the larger trans effect of the halide anion over a neutral donor in the trans isomer, and increased lability for bromide systems, assigned to the reduced effective charge on the tin(IV) centre.

Abel et al. repeated and confirmed these results using $^{19}\text{Sn}$-$^1\text{H}$ NMR spectroscopy but also observed the cessation of pyramidal inversion at the selenium at temperatures below ca. 200 K.

The following work provides a detailed investigation into the behaviour of the tin(IV) halides with monodentate ligands of type $\text{R}_2\text{Se}$ (where $R = \text{Me}$ or $\text{Ph}$) and bidentate ligands of the type $\text{RSe(CH}_2\text{nSeR}$ (where $R = \text{Me}$ for $n = 1$, 2 or 3; $R = \text{Ph}$ for $n = 2$ or 3) and $\text{o-C}_6\text{H}_4(\text{SeMe})_2$ continuing a study of group 16 ligand complexes, both in solution and in the solid state. The effects of changing halide and ligand interdonor linkage and substituents are studied. Variable temperature $^1\text{H}$, $^{19}\text{Sn}$-$^1\text{H}$ and $^{77}\text{Se}$-$^1\text{H}$ NMR spectra have been recorded investigating the pyramidal inversion and ligand exchange processes in solution for these systems, with infrared spectroscopy and single crystal X-ray diffraction used to study the behaviour of these complexes in the solid state. The analogous thioether complexes were discussed in chapter 2 and the telluroether complexes and overall trends and comparisons will be brought together in chapter 4.
3.2. Results & Discussion

3.2.1. Synthesis and Properties of Monodentate Selenoether Complexes

Complexes of the type \([\text{SnX}_4(\text{R}_2\text{Se})_2]\) (where \(X = \text{Cl}, \text{Br}, \text{R} = \text{Me or Ph}; X = I, \text{R} = \text{Me}\)) have been prepared by reaction of \(\text{SnX}_4\) with two molar equivalents of \(\text{R}_2\text{Se}\) in degassed \(\text{CH}_2\text{Cl}_2\). Only complexes of the \(\text{Me}_2\text{Se}\) ligand with \(\text{SnCl}_4\) and \(\text{SnBr}_4\) were isolable as solids. For these solid complexes IR spectra showed one broad peak at 300 \((\nu(\text{SnCl}))\) or 220 \(\text{cm}^{-1}\) \((\nu(\text{SnBr}))\) probably corresponding to the \textit{trans} isomer (\(D_{4h}\) symmetry) being the principal isomer present in the solid state. There was no evidence of ligand oxidation, no bands were present in the region 400 - 470 \(\text{cm}^{-1}\) characteristic of \(\nu(\text{SnO})\) stretching frequencies. Satisfactory microanalyses were collected for all species isolated.

3.2.2. Single Crystal X-ray Diffraction Studies

Prior to this study there were no structurally characterised examples of tin(IV) halide-selenoether complexes, so an analysis was carried out on crystals of \([\text{SnCl}_4(\text{Me}_2\text{Se})_2]\) (Figure 3.1) and \([\text{SnBr}_4(\text{Me}_2\text{Se})_2]\) (Figure 3.2) to allow comparison between the solid state and solution. The analogous thioether complex, \([\text{SnBr}_4(\text{Me}_2\text{S})_2]\), synthesised by reaction of tin metal with \(\text{Me}_2\text{SBr}_2\), has been structurally characterised by Bricklebank et al. and features both the \textit{cis} and \textit{trans} forms within the unit cell.

Table 3.1. Bond lengths (Å) with e.s.d.s for \textit{trans-[SnX}_4(\text{Me}_2\text{Se})_2]\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>\textit{trans-[SnCl}_4(\text{Me}_2\text{Se})_2])</th>
<th>\textit{trans-[SnBr}_4(\text{Me}_2\text{Se})_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-X(1)</td>
<td>2.7001(9)</td>
<td>2.576(2)</td>
</tr>
<tr>
<td>Sn-X(2)</td>
<td>2.413(2)</td>
<td>2.587(2)</td>
</tr>
<tr>
<td>Sn-Se(1)</td>
<td>2.427(2)</td>
<td>2.731(2)</td>
</tr>
<tr>
<td>Se(1)-C(1)</td>
<td>1.957(10)</td>
<td>1.96(2)</td>
</tr>
<tr>
<td>Se(1)-C(2)</td>
<td>1.952(9)</td>
<td>1.94(2)</td>
</tr>
</tbody>
</table>
Table 3.2. Bond angles (°) with e.s.d.s for \( \text{trans}-[\text{SnX}_4(\text{Me}_2\text{Se})_2] \)

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \text{trans}-[\text{SnCl}_4(\text{Me}_2\text{Se})_2] )</th>
<th>( \text{trans}-[\text{SnBr}_4(\text{Me}_2\text{Se})_2] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X(1)-Sn-X(2)</td>
<td>89.54(8)</td>
<td>90.47(5)</td>
</tr>
<tr>
<td>X(1)-Sn-Se(1)</td>
<td>89.40(6)</td>
<td>90.63(5)</td>
</tr>
<tr>
<td>X(2)-Sn-Se(1)</td>
<td>91.25(6)</td>
<td>88.46(5)</td>
</tr>
<tr>
<td>Sn-Se(1)-C(1)</td>
<td>100.7(3)</td>
<td>100.9(4)</td>
</tr>
<tr>
<td>Sn-Se(1)-C(2)</td>
<td>100.2(3)</td>
<td>102.2(5)</td>
</tr>
<tr>
<td>C(1)-Se(1)-C(2)</td>
<td>97.3(4)</td>
<td>96.9(7)</td>
</tr>
</tbody>
</table>

Both Me\(_2\)Se complexes are isostructural, with the same space group and with unit cells of similar sizes, with the bromide slightly larger, consistent with the increased radii of the bromine atoms over the chlorine. In both structures the central Sn(IV) occupies a crystallographic inversion centre, co-ordinated via four precisely planar X atoms, with two mutually \textit{trans} Me\(_2\)Se ligands completing the slightly distorted octahedral geometry. In both cases the angles around the central tin atom are very close to the 90 and 180\(^\circ\) angles expected for a regular octahedron.

Bond lengths (\(\text{Å}\)) and angles (\(\text{°}\)) for \( \text{trans}-[\text{SnX}_4(\text{Me}_2\text{Se})_2] \) (X = Cl and Br) are presented in Table 3.1 and 3.2 respectively. The Sn-X distances for these two structures are in good agreement with the few structurally characterised examples of thioether complexes of tin(IV) halides discussed in chapter 2, \textit{e.g.} \([\text{SnCl}_3([\text{9}][\text{aneS}_3])]^+ \) [Sn-Cl 2.366(4), 2.369(3) and 2.371(4) \(\text{Å} \)], \(2\text{SnCl}_4.\text{[18]aneS}_6 \) [Sn-Cl 2.30(2), 2.31(2), 2.38(2), 2.391(2), 2.421(2) and 2.42(2)] \(6\text{cis-[SnBr}_4(\text{Me}_2\text{S})_2] \) [Sn-Br 2.554(4), 2.532(4), 2.557(4) and 2.539(4) \(\text{Å} \)] \(5\text{ and trans-[SnCl}_4(\eta^{1}-\text{C}_6\text{H}_{12}\text{S}_2-1,5)_2] \) [Sn-Cl 2.414(1), 2.428(1) \(\text{Å} \)] \(7\).

As was observed for \( \text{trans}-[\text{SnBr}_4(\text{Me}_2\text{S})_2] \), the bond distance Sn-E (E = S or Se) is longer for the bromide complex, most likely a consequence of SnBr\(_4\) being a poorer acceptor than SnCl\(_4\). Comparison of the Sn-Br bond lengths in \( \text{trans}-[\text{SnBr}_4(\text{Me}_2\text{Se})_2] \) with those in \( \text{trans}-[\text{SnBr}_4(\text{Me}_2\text{S})_2] \) \(5\) shows that they are very similar and the Sn-Se distances are \( \text{ca.} 0.1 \text{ Å} \) longer than the Sn-S distances, consistent with the larger radius of Se over S.
Figure 3.1. View of the structure of trans-[SnCl₄(Me₂Se)₂] with numbering scheme adopted. Ellipsoids are shown at 40% probability and atoms marked with an asterisk are related by a crystallographic inversion centre.

Figure 3.2. View of the structure of trans-[SnBr₄(Me₂Se)₂] with numbering scheme adopted. Details as for Fig. 3.1.
3.2.3. Variable Temperature $^1\text{H}$ NMR Spectroscopy

The SnX₄/Me₂Se (X = Cl or Br) systems have previously been examined via $^1\text{H}$ NMR spectroscopy.¹³ A solution of [SnCl₄(Me₂Se)₂] with excess Me₂Se in CD₂Cl₂ at 300 K exhibits a single δ(Me) at 2.51 ppm. At this temperature there is no evidence of $^3J(^1\text{H} - ^{117/119}\text{Sn})$ satellites. However, on cooling the solution to ca. 250 K the resonance is seen to split, giving two resonances due to the trans and cis isomers, and ill defined satellites are also seen to appear. At the lowest temperature studied, 180 K, the two resonances are present in the ratio ca. 1.5 : 1 due to trans and cis isomers at δ 2.44 and 2.54 ppm respectively, with $^3J(^1\text{H} - ^{117/119}\text{Sn})$ couplings of ca. 50-60 Hz now clearly defined.

The $^1\text{H}$ NMR spectrum of [SnBr₄(Me₂Se)₂] in CD₂Cl₂ with an excess of Me₂Se at 300 K consists of a single broad resonance at δ 2.36 ppm. On lowering the temperature to 250 K the signal splits to give two resonances for the cis and trans isomers. At 180 K these two resonances have sharpened at δ 2.26 and 2.40 ppm respectively and the $^3J(^1\text{H} - ^{117/119}\text{Sn})$ satellites are seen with couplings of ca. 50-60 Hz. For this complex the trans and cis isomers are observed in the ratio ca. 3 : 1. This is to be expected for the larger SnBr₄ compared to SnCl₄, with the trans isomer preferred sterically.

Studies of SnF₄ and SnI₄ with an excess of Me₂Se in CD₂Cl₂ solution exhibit no evidence for adduct formation even at the lowest temperatures studied (173 K).

Reaction of tin(IV) halides with the monodentate ligand Ph₂Se yielded no isolable solid products, although colour changes were evident for tin(IV) chloride and bromide. In the $^1\text{H}$ NMR spectra no resonances consistent with adduct formation were observed for any of the species even at the lowest studied temperature (173 K).
3.2.4. Variable Temperature $^{119}\text{Sn}$-$^1\text{H}$ NMR Spectroscopy

As has been observed\textsuperscript{2,5} the solubility of these complexes in CH$_2$Cl$_2$ is extremely poor. A range of other solvents was also examined including MeNO$_2$, Me$_2$CO, thf and propane-1,2-diol carbonate, but these proved unsatisfactory and there was a possibility that the observed resonances were due to adducts with O-donors.\textsuperscript{8} CD$_2$Cl$_2$ was therefore again used even though the compounds were not very soluble in this solvent, necessitating long data collection times.

At 300 K the system [SnCl$_4$(Me$_2$Se)$_2$] in CD$_2$Cl$_2$ exhibits a single broad resonance at $\delta$ ~693 ppm, shifted to low frequency by 100 – 150 ppm from the region of the spectrum observed for the SnCl$_4$-thioether complexes studied in chapter 2. On cooling the system the resonance is seen to split at ca. 260 K where resonances attributable to the cis and trans isomers are observed. On cooling further the resonances sharpen to give two signals at $\delta$ ~691 and 695 ppm for the cis and trans isomers respectively. At this temperature $^1J(^{119}\text{Sn}-^{77}\text{Se})$ couplings of ca. 460 – 490 Hz are also clearly seen (Figure 3.3). In contrast no resonance is observed for the species [SnBr$_4$(Me$_2$Se)$_2$] in CH$_2$Cl$_2$ at 300 K due to rapid exchange in solution. A single resonance becomes apparent on cooling to ca. 280 K at $\delta$ -1360 ppm which then splits on further cooling and resolves clearly at 180 K to show the two resonances expected for cis and trans isomers at $\delta$ -1296 and -1319 ppm respectively. Also present is similar $^1J(^{119}\text{Sn}-^{77}\text{Se})$ coupling to that observed in the [SnCl$_4$(Me$_2$Se)$_2$] system, with values of ca. 500 – 550 Hz.

These two [SnX$_4$(Me$_2$Se)$_2$] (X = Cl or Br) systems were also studied with an excess of Me$_2$Se in CH$_2$Cl$_2$ solution over the temperature range 180 – 300 K. At 180 K in the $^{119}\text{Sn}$-$^1\text{H}$ NMR spectrum of the chloride species both cis and trans resonances are observed at $\delta$ ~690.5 and ~694.0 ppm with the $^1J(^{119}\text{Sn}-^{77}\text{Se})$ coupling again present. Warming the solution results in the signal for the cis isomer broadening as exchange with free ligand starts at ca. 230 K before disappearing at ca. 270 K. The trans isomer remains largely unchanged until ambient temperatures are reached consistent with a higher barrier to exchange in the trans isomer. The corresponding SnBr$_4$ species displayed largely similar behaviour, at 180 K the two resonances for cis and trans isomers are observed at $\delta$ ~1293 and ~1315 ppm in the $^{119}\text{Sn}$-$^1\text{H}$ NMR spectrum with the $^1J(^{119}\text{Sn}-^{77}\text{Se})$ coupling present. For this system the onset of ligand exchange with free ligand in the cis isomer begins at ca. 210 K when the cis resonance

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weakens and broadens before disappearing at ca. 245 K. The trans resonance starts to weaken and broaden with ligand exchange at ca. 250 K and at ambient temperatures has become unresolvable. These results are qualitatively again consistent with the results of the analogous [SnX4(Me2S)2]-Me2S systems studied by Knight and Merbach,\(^9\) discussed in chapter 2. The onset of ligand exchange at lower temperatures in the [SnBr4(Me2Se)2]-Me2Se system relative to the chloride system is consistent with the observations made in chapter 2 that SnBr4 is a poorer acceptor than the chloride.

While no isolable solids were produced from the reactions of SnL4 or SnF4 with Me2Se \textit{in situ} \(^{119}\text{Sn}-\{^1\text{H}\} \) NMR studies were tried. SnF4 proved to insoluble in non-coordinating solvent, precluding studies of these systems. For SnI4 no resonances resulting from adduct formation were observed even at 175 K, again consistent with the results of chapter 2 where these tin species were assigned as poorer acceptors than SnCl4 and SnBr4.

Figure 3.3. \(^{119}\text{Sn}-\{^1\text{H}\} \) NMR spectrum of [SnCl4(Me2Se)2] in CD2Cl2 solution at 180 K
3.2.5. Variable Temperature $^{77}\text{Se-}^1\text{H} \text{ NMR Spectroscopy}

The presence of selenium within the ligand provides another nucleus ($^{77}\text{Se}$) with spin $I = \frac{1}{2}$ (abundance = 7.6 %) and these complexes can therefore be studied using $^{77}\text{Se-}^1\text{H} \text{ NMR spectroscopy and corresponding } ^1J(^{119}\text{Sn-}^{77}\text{Se}) \text{ couplings in the } ^{119}\text{Sn-}\text{ }^1\text{H} \text{ NMR spectra have already been observed.}

In the $^{77}\text{Se-}^1\text{H} \text{ NMR spectra of both the chloride and bromide systems large high-frequency co-ordination shifts } \Delta ( = \delta_{\text{complex}} - \delta_{\text{ligand}}) \text{ of approximately } +200 \text{ are observed, with the resonance of the cis isomer slightly to high frequency of the trans isomer. In general, the behaviour in the } ^{77}\text{Se-}^1\text{H} \text{ NMR spectra mirrored those of the } ^{119}\text{Sn-}^1\text{H} \text{ NMR spectra. At 300 K the spectrum of } [\text{SnCl}_4(\text{Me}_2\text{Se})_2] \text{ in CD}_2\text{Cl}_2 \text{ exhibits a single resonance at } \delta +176 \text{ ppm, indicating that ligand exchange is too rapid to resolve the two isomers. Upon lowering the temperature to } \text{ca.} 240 \text{ K the signal broadens and splits to give the two resonances for cis and trans isomers at } \delta +199 \text{ and } +180 \text{ ppm, and these become sharper as the temperature is lowered further. Eventually, at 180 K, the resonances are at } \delta +204 \text{ and } 185 \text{ ppm with satellites due to } ^1J(^{77}\text{Se-}^{117/119}\text{Sn}) \text{ coupling clearly resolved (Figure 3.4). These couplings are consistent with those observed in the } ^{119}\text{Sn-}^1\text{H} \text{ NMR spectra with values of ca. } 460 - 490 \text{ Hz. Since tin has two nuclei with spin } I = \frac{1}{2} \text{ and similar abundances (}^{117}\text{Sn and }^{119}\text{Sn), we were unable to resolve two sets of satellites. Since the } \gamma(^{119}\text{Sn}) : \gamma(^{117}\text{Sn}) \text{ ratio is 0.956 : 1, these couplings are nearly coincident and often cannot be resolved.}

The behaviour observed for [SnBr$_4$(Me$_2$Se)$_2$] in the $^{77}\text{Se-}^1\text{H} \text{ NMR spectra again mirrors that in the } ^{119}\text{Sn-}^1\text{H} \text{ NMR spectra. At 300 K no resonance is seen due to rapid ligand exchange at this temperature. A resonance first appears at } \text{ca.} 280 \text{ K at } \delta 195 \text{ ppm. At } \text{ca.} 220 \text{ K a second broad signal at } \delta \sim 216 \text{ ppm begins to appear, as the cis and trans isomers become resolved. At 200 K both resonances are observed clearly and at 180 K both resonances at } \delta 204.0 \text{ and } 218.8 \text{ ppm display } ^1J(^{77}\text{Se-}^{117/119}\text{Sn}) \text{ couplings with values consistent with those observed in the } ^{119}\text{Sn NMR spectra, 500 and 550 Hz respectively.}

The behaviour of the systems in the presence of an excess of Me$_2$Se again mirror that observed in the $^{119}\text{Sn-}^1\text{H} \text{ NMR spectra. However, in the } ^{77}\text{Se-}^1\text{H} \text{ NMR spectra the free ligand (Me}_2\text{Se } \delta 0 \text{ ppm) is also observed. At 300 K only one resonance at } \delta 174 \text{ ppm is seen in the spectrum of } [\text{SnCl}_4(\text{Me}_2\text{Se})_2]\text{-Me}_2\text{Se as exchange between the adduct and free ligand is rapid. At } \text{ca.} 240 \text{ K two separate resonances are evident at}
Figure 3.4. Variable temperature $^{77}$Se-$^{1}$H NMR spectrum of $[\text{SnCl}_4(\text{Me}_2\text{Se})_2]$ in $\text{CH}_2\text{Cl}_2$-$\text{CD}_2\text{Cl}_2$ solution
δ 177 and -8.9 ppm for the complex and free ligand respectively, the shift from δ 0 to
-8.9 ppm arising from temperature effects. At ca. 220 K all three species are observed,
and at 180 K resonances are clearly resolved at δ 204, 189 and -8.5 ppm for cis and
trans isomers and free ligand. The $^1J(^{77}\text{Se}-^{119/119}\text{Sn})$ coupling is also clearly resolved
with values, ca. 500 – 550 Hz, consistent with the previous observed couplings. The
bromide system, [SnBr₄(Me₂Se)₂]-Me₂Se, again mirrors the results from the $^{119}\text{Sn}-\{^1\text{H}\}$
NMR spectra and follows the same behaviour as the chloride system. At 300 K the
only resonance observed is an averaged signal at δ 9 ppm. At ca. 260 K this signal has
broadened and diminished with a second sharp resonance forming at δ 196 ppm, for the
trans isomer. At ca. 240 K the free ligand resonance has sharpened again as ligand
exchange with the trans isomer is slowed. At ca. 200 K the resonance of the cis isomer
is seen, and at 180 K all three species are clearly resolved at δ 219, 204 and -7 ppm for
the cis, trans isomers and free ligand, with $^1J(^{77}\text{Se}-^{119/119}\text{Sn})$ couplings clearly observed
for the cis and trans isomers, values of ca. 500 – 560 Hz again consistent with the
observation in the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectra. On returning to ambient temperatures the
same behaviour is seen in reverse, with the onset of ligand exchange in the cis isomer
occurring first, followed by exchange in the trans isomer, before these mechanisms
become too fast to be observed on the NMR timescale. The onset of exchange at lower
temperatures in the bromide systems is again consistent with SnBr₄ being a poorer
acceptor than SnCl₄. All of these results are consistent with those for the analogous
thioether system studied by Knight and Merbach.⁹

Although the $^{119}\text{Sn}$ NMR spectra of SnI₄ and SnF₄ with Me₂Se showed no
resonances over the temperature range 173 – 300 K, the $^{77}\text{Se}-\{^1\text{H}\}$ NMR spectra of
SnI₄ in the presence of a large excess of Me₂Se shows a single resonance at δ 152 ppm
at 180 K. It is likely that this resonance is representative of adduct formation, probably
trans-[SnI₄(Me₂Se)₂], in solution at these low temperatures. This is consistent with the
weaker Lewis acid, SnI₄, being a poorer acceptor than SnBr₄ and SnCl₄ as seen in
chapter 2.

Attempts were made to record the $^{77}\text{Se}-\{^1\text{H}\}$ NMR spectra of the corresponding
Ph₂Se systems, [SnX₄(Ph₂Se)₂] (where X = Cl or Br), over the temperature range 173 –
300 K. No resonances were observed for either of the systems at any temperature with
only free ligand observed at δ 413 ppm. This result supports the conclusion of chapter
2 where phenyl substituted ligands were assigned as poorer donors than the methyl
substituted analogues, though whether this is due to steric or electronic effects has not been established.
3.2.6. Synthesis and Properties of Bidentate Selenoether Complexes

A range of complexes of type \([\text{SnX}_4\{L-L\}]\) (where X = Cl or Br; L-L = MeSeCH$_2$SeMe, o-C$_6$H$_4$(SeMe)$_2$ or RSe(CH$_2$)$_n$SeR; where R = Ph or Me, n = 2 or 3) have been prepared by reaction of SnX$_4$ with a molar equivalent of thioether ligand L-L in degassed CH$_2$Cl$_2$. In most cases this gave precipitates of powdered white or yellow solids (Me substituted ligands), or orange crystalline solids (Ph substituted ligands), in good yield. In the case of the \([\text{SnBr}_4\{\text{PhSe(CH$_2$)$_n$SePh}\}]\) species, viscous yellow solutions were formed from which it was not possible to isolate a solid, and no solids were isolable for reactions involving SnI$_4$. Due to the extreme moisture sensitivity of the tin(IV) halides, all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. Whereas the thioether complexes of the tin(IV) halides were found to be stable over a period of months in the solid state, the corresponding selenoether complexes prove to be far more sensitive to hydrolysis and decompose to dark oils over a period of days. As a result, all complexes were stored in a dry-box under an atmosphere of dry nitrogen. If dry solvents are not used hydrolysis occurs resulting in the formation of hydrates of varying stoichiometries or oxidation of the ligand as discussed later within this chapter.

IR spectra of the solid complexes formed all showed the expected four $\nu$(Sn-Cl) bands (theory: $2A_1 + B_1 + B_2$) in the range 300 - 340 cm$^{-1}$ consistent with $C_{2v}$ symmetry. Satisfactory microanalyses were recorded for all solid \([\text{SnX}_4\{L-L\}]\) produced.

3.2.7. Single Crystal X-ray Diffraction Studies

Prior to this study there were no structurally characterised examples of selenoether complexes of any tin(IV) halides, and the two structures of trans-[SnCl$_4$(Me$_2$Se)$_2$] (Section 3.2.2, Figure 3.1) and trans-[SnBr$_4$(Me$_2$Se)$_2$] (Section 3.2.2, Figure 3.2) are the only examples of selenoether complexes available for comparison.\textsuperscript{10} In order to attempt to identify trends in their geometric parameters, and to correlate these with their behaviour observed in solution (by variable temperature \textsuperscript{119}Sn-$\{^1$H\}, \textsuperscript{77}Se-$\{^1$H\} and \textsuperscript{1}H NMR spectroscopy), single crystal X-ray structure analyses were undertaken on several of the products.
Single crystal X-ray diffraction studies were carried out on the two complexes of the orthophenylene selenoethers, \([\text{Sn}X_4\{\text{o-C}_6\text{H}_4(\text{SeMe})_2\}]\) [where \(X = \text{Cl}\) (Figure 3.5) or \(\text{Br}\) (Figure 3.6)], and the single methylene backboned species \([\text{SnCl}_4\{\text{MeSeCH}_2\text{SeMe}\}]\) (Figure 3.7), which features a highly strained four-membered chelate-ring system that has not been seen before for this ligand. All structures feature distorted octahedral arrangements. In the cases of \([\text{SnBr}_4\{\text{o-C}_6\text{H}_4(\text{SeMe})_2\}]\) (Figure 3.6) and \([\text{SnCl}_4\{\text{MeSeCH}_2\text{SeMe}\}]\) (Figure 3.7) only half the molecule is found in the asymmetric cell with the second half generated by a mirror plane \((x, 0.5 - y, z)\) upon which the tin atom and two axial halide atoms lie. Single crystals of \([\text{SnCl}_4\{\text{MeSe(CH}_3)_2\text{SeMe}\}]\) (Figure 3.8) and \([\text{SnCl}_4\{\text{PhSe(CH}_2)_2\text{SePh}\}]\) (Figure 3.9) were also studied but they were of rather poor quality and weakly diffracting and consequently the overall data quality was low. However, the analyses were sufficient to confirm unambiguously that these two complexes feature chelating ligands both of which adopt the \(dl\) configuration.

Figure 3.5. View of the structure of \([\text{SnCl}_4\{\text{o-C}_6\text{H}_4(\text{SeMe})_2\}]\) with numbering scheme adopted. Ellipsoids are shown at 40 % probability
Selected bond lengths (Å) and angles are presented in Tables 3.3 and 3.4 respectively. The Sn-X distances for these structures are again in good agreement with the thioether analogues, e.g. [SnCl₃(9]aneS₃)]⁺ [Sn-Cl 2.366(4), 2.369(3) and 2.371(4) Å], ⁵ 2SnCl₄[18]aneS₆ [Sn-Cl 2.30(2), 2.31(2), 2.38(2), 2.391(2), 2.421(2) and 2.42(2)],⁶ cis-[SnBr₄(Me₂S)₂] [Sn-Br 2.554(4), 2.532(4), 2.557(4) and 2.539(4) Å]⁵ and trans-[SnCl₄(η₁-C₆H₁₂S₂-1,5)] [Sn-Cl 2.414(1), 2.428(1) Å].⁷

Table 3.3. Bond lengths (Å) with e.s.d.s for [SnX₄{diselenoether}] complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>[SnCl₄(MeSeCH₂SeMe)]</th>
<th>[SnCl₄(o-C₆H₄(SeMe)₂)]</th>
<th>[SnBr₄(o-C₆H₄(SeMe)₂)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-X(1)</td>
<td>2.406(4)</td>
<td>2.426(3)</td>
<td>2.600(2)</td>
</tr>
<tr>
<td>Sn-X(2)</td>
<td>2.407(4)</td>
<td>2.389(3)</td>
<td>2.547(2)</td>
</tr>
<tr>
<td>Sn-X(3)</td>
<td>2.376(3)</td>
<td>2.360(3)</td>
<td>2.512(1)</td>
</tr>
<tr>
<td>Sn-X(4)</td>
<td>2.364(3)</td>
<td>2.364(3)</td>
<td>2.364(3)</td>
</tr>
<tr>
<td>Sn-Se(1)</td>
<td>2.782(1)</td>
<td>2.749(1)</td>
<td>2.841(2)</td>
</tr>
<tr>
<td>Sn-Se(2)</td>
<td>2.787(2)</td>
<td>2.787(2)</td>
<td>2.787(2)</td>
</tr>
</tbody>
</table>

a. atom related to X(3), in the numbering scheme adopted, by crystallographic mirror plane
b. atom related to Se(1), in the numbering scheme adopted, by crystallographic mirror plane

Figure 3.6. View of the structure of [SnBr₄{o-C₆H₄(SeMe)₂}] with numbering scheme adopted. Ellipsoids are shown at 40% probability and atoms marked with an asterisk are related by a crystallographic mirror plane.
Table 3.4. Selected bond angles (°) with e.s.d.s for $[\text{SnX}_4\{\text{diselenoether}\}]$ complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$[\text{SnCl}_4{\text{MeSeCH}_2\text{SeMe}}]$</th>
<th>$[\text{SnCl}_4{\text{Q}-\text{C}_6\text{H}_4(\text{SeMe})_2}]$</th>
<th>$[\text{SnBr}_4{\text{Q}-\text{C}_6\text{H}_4(\text{SeMe})_2}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X(1)-Sn-X(2)</td>
<td>175.5(1)</td>
<td>169.7(1)</td>
<td>169.12(7)</td>
</tr>
<tr>
<td>X(1)-Sn-X(3)</td>
<td>91.77(9)</td>
<td>91.4(1)</td>
<td>92.44(5)</td>
</tr>
<tr>
<td>X(1)-Sn-X(4)</td>
<td>95.4(1)</td>
<td>95.4(1)</td>
<td>95.4(1)</td>
</tr>
<tr>
<td>X(1)-Sn-Se(1)</td>
<td>87.53(8)</td>
<td>82.41(8)</td>
<td>87.81(5)</td>
</tr>
<tr>
<td>X(1)-Sn-Se(2)</td>
<td>83.16(8)</td>
<td>83.16(8)</td>
<td>83.16(8)</td>
</tr>
<tr>
<td>X(2)-Sn-X(3)</td>
<td>91.05(9)</td>
<td>93.0(1)</td>
<td>94.40(5)</td>
</tr>
<tr>
<td>X(2)-Sn-X(4)</td>
<td>87.40(9)</td>
<td>87.40(9)</td>
<td>87.40(9)</td>
</tr>
<tr>
<td>X(2)-Sn-Se(1)</td>
<td>88.75(8)</td>
<td>91.27(9)</td>
<td>83.38(5)</td>
</tr>
<tr>
<td>X(2)-Sn-Se(2)</td>
<td>102.6(1)</td>
<td>101.7(1)</td>
<td>102.08(7)</td>
</tr>
<tr>
<td>X(3)-Sn-X(4)</td>
<td>163.26(7)</td>
<td>166.60(9)</td>
<td>164.74(5)</td>
</tr>
<tr>
<td>X(3)-Sn-Se(1)</td>
<td>94.15(7)</td>
<td>91.41(9)</td>
<td>93.15(4)</td>
</tr>
<tr>
<td>X(3)-Sn-Se(2)</td>
<td>90.50(9)</td>
<td>90.50(9)</td>
<td>90.50(9)</td>
</tr>
<tr>
<td>X(4)-Sn-Se(1)</td>
<td>166.37(9)</td>
<td>166.37(9)</td>
<td>166.37(9)</td>
</tr>
<tr>
<td>X(4)-Sn-Se(2)</td>
<td>69.11(5)</td>
<td>76.08(4)</td>
<td>71.60(6)</td>
</tr>
</tbody>
</table>

a. X(4) refers to X(3*), and is related to X(3) by a crystallographic mirror plane.

As was observed in the analogous thioether complexes in chapter 2 there are variations in the Sn-X bond distances. $d$(Sn-X) for halides that are $trans$ to another halide atom are consistently longer than those $trans$ to an Se donor atom. This is reflected when compared to the Sn-X distances of the monodentate selenoether complexes characterised earlier. In those cases all halide atoms are $trans$ to another halide atom and closely match those $trans$ to another halide in these chelate systems e.g. $trans$-$[\text{SnCl}_4\{\text{Me}_2\text{Se}\}_2]$ [Figure 3.1, Sn-Cl 2.413(2) and 2.427(2) Å] and $trans$-$[\text{SnBr}_4\{\text{Me}_2\text{Se}\}_2]$ [Figure 3.2, Sn-Br 2.576(2) and 2.587(2) Å]. Again this presumably reflects the greater $trans$ influence of a halide over selenoether.² Further evidence for this is seen in the Sn-Se distances when compared between monodentate and bidentate systems. In the bidentate systems the Se donor atoms are $trans$ to a halide and are consequently markedly longer than those $trans$ to another Se donor atom as observed for the monodentate systems, the influence of the $trans$ atoms being less (cf. $d$(Sn-Se) $trans$ Se, 2.7001(9) and 2.731(2) Å vs. $d$(Sn-Se) $trans$ X 2.749(1), 2.782(1), 2.787(2) and 2.841(2) Å). Again the distortion of the octahedron has the axial halide atoms...
leaning towards the Se₂ donor system resembling the tetrahedral geometry of the starting tin(IV) halide, where the trans-[SnX₄(Me₂Se)₂] complexes had featured almost ideal octahedra. However, as was seen in the thioether systems it is the Sn-Se distances and Se-Sn-Se angles that provide the best indicators of the relative stabilities of the complexes.

Figure 3.7. View of the structure of [SnCl₄(MeSeCH₂SeMe)] with numbering scheme adopted. Details as for Fig. 3.6

The strain in the four-membered chelate-ring system in [SnCl₄(MeSeCH₂SeMe)] (Figure 3.7) which has not been observed before for an acyclic selenoether ligand, is clear to see when compared to the other chloride characterised, [SnCl₄{ο-C₆H₄(SeMe)₂}] (Figure 3.5), which features a five-membered chelate-ring. The d(Sn-Se) is markedly longer for the four-membered chelate-ring system (2.782(1) Å) than that seen for the five-membered chelate-ring (2.749(1) Å). The bond angle Se-Sn-Se is also markedly more strained for the four-membered chelate-ring at 69.11(5)° relative to the angle of 76.08(4)° for the five-membered chelate-ring which is still well short of the 90° ideal. It is also worth noting that for the thioether study this unsaturated phenylene system was seen to be more strained than the
Figure 3.8. View of the structure of \([\text{SnCl}_4\{\text{MeSe(CH}_2)\text{3SeMe}\}]\) with numbering scheme adopted. Ellipsoids are shown at 40% probability and atoms marked with an asterisk are related by a crystallographic two-fold axis at \((-x, \frac{1}{2} -y, z)\)

saturated five and six-membered chelate-ring systems. The structures of \([\text{SnCl}_4\{\text{MeSe(CH}_2)\text{3SeMe}\}]\) (Figure 3.8) and \([\text{SnCl}_4\{\text{PhSe(CH}_2)\text{2SePh}\}]\) (Figure 3.9) have Se-Sn-Se angles of 85.9° and 86.1°, and while the overall data quality was not good it is probable that these are representative.

Comparing Sn-Se bond distances within the two comparable structures, \([\text{SnCl}_4\{\text{C}_6\text{H}_4(\text{SeMe})\text{2}\}]\) and \([\text{SnBr}_4\{\text{C}_6\text{H}_4(\text{SeMe})\text{2}\}]\), further evidence is found for SnBr\(_4\) being a poorer acceptor than SnCl\(_4\). The \(d(\text{Sn-Se})\) for \([\text{SnBr}_4\{\text{C}_6\text{H}_4(\text{SeMe})\text{2}\}]\), 2.841(1) Å, is markedly longer than those seen in either \([\text{SnCl}_4\{\text{C}_6\text{H}_4(\text{SeMe})\text{2}\}]\) or \([\text{SnCl}_4(\text{MeSeCH}_2\text{SeMe})]\), 2.749(1) and 2.782(1) Å respectively. The Se-Sn-Se bond angle is also considerably more strained (71.60(6)°) than that in the corresponding chloride (76.08(4)°).
Figure 3.9. View of the structure of [SnCl₄(PhSe(CH₂)₂SePh)] with numbering scheme adopted. Ellipsoids are shown at 40% probability.
3.2.8. Variable Temperature $^1$H NMR Studies

As was found for the corresponding thioether complexes, the selenoether complexes prove to be extremely poorly soluble in CD$_2$Cl$_2$. A variety of other solvents including thf and acetone were tried and offered better solubility. However, the spectra obtained were significantly different to those observed in CD$_2$Cl$_2$, so it seems likely that these harder oxygen donor solvents provide alternative ligands for the tin,$^{11}$ so these studies were not pursued.

Table 3.5. Variable temperature $^1$H NMR spectroscopic data for [Sn$X_4${diselenoether}] complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H (δ)$^a$</th>
<th>300 K</th>
<th>180 K</th>
<th>approximate ratio (meso:dl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl$_4${MeSe(CH$_2$)$_2$SeMe}]</td>
<td>2.48 (3 H), 3.30 (2 H)</td>
<td>2.40, 2.46, 3.10, 3.40</td>
<td>1:1</td>
<td></td>
</tr>
<tr>
<td>[SnCl$_4${MeSe(CH$_3$)$_3$SeMe}]</td>
<td>2.30 (1 H), 2.46 (3 H), 3.2 (2 H)</td>
<td>2.40, 2.45, 2.51, 3.11, 3.42</td>
<td>1:5</td>
<td></td>
</tr>
<tr>
<td>[SnCl$_4${O-C$_6$H$_4$(SeMe)$_2$}]</td>
<td>2.83 (3 H), 7.5, 7.65 (2 H)</td>
<td>2.99, 2.79, 7.55</td>
<td>1:3</td>
<td></td>
</tr>
<tr>
<td>[SnCl$_4${PhSe(CH$_2$)$_2$SePh}]</td>
<td>3.39 (2 H), 7.2-7.7 (5 H)</td>
<td>3.5, 3.8, 7.0-7.8</td>
<td>1:1</td>
<td></td>
</tr>
<tr>
<td>[SnCl$_4${PhSe(CH$_2$)$_3$SePh}]</td>
<td>2.10 (1 H), 3.25 (2 H), 7.2-7.7 (5 H)</td>
<td>Ill defined (see text)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[SnBr$_4${MeSe(CH$_2$)$_2$SeMe}]</td>
<td>2.25 (3 H), 3.15 (2 H)</td>
<td>2.21, 2.30, 3.10, 3.30</td>
<td>2:1</td>
<td></td>
</tr>
<tr>
<td>[SnBr$_4${MeSe(CH$_3$)$_3$SeMe}]</td>
<td>2.41 (1 H + 3 H), 3.1 (2 H)</td>
<td>2.38, 2.44, 3.05, 3.25</td>
<td>1:5</td>
<td></td>
</tr>
<tr>
<td>[SnBr$_4${O-C$_6$H$_4$(SeMe)$_2$}]</td>
<td>2.45 (3 H), 7.25, 7.38 (2 H)</td>
<td>2.76 [2.55 (sh)], 7.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. In CD$_2$Cl$_2$ solution
As for a thioether, the presence of two lone pairs of electrons on the selenium donor atoms in these selenoethers results in the occurrence of diastereoisomers (dl and meso configurations). At 300 K the exchange and inversion processes are too fast on an NMR timescale to distinguish between them. If the temperature is reduced however, the exchange mechanisms and then the inversion processes are slowed sufficiently that the resultant isomers, that appeared equivalent, become resolvable. Variable temperature $^1$H NMR spectroscopic data are presented in Table 3.5.

The $^1$H NMR spectrum of $[SnCl_4(MeSeCH_2SeMe)]$ shows no splitting at any temperature studied (173 - 300 K). The four-membered chelate-ring that is seen to be highly strained in the X-ray diffraction analysis, is still undergoing rapid ring opening and ligand exchange in solution, even at 173 K. At 300 K the $^1$H NMR spectrum of $[SnCl_4\{MeSe(CH_2)_2SeMe\}]$ exhibits two resonances for $\delta$(Me) and $\delta$(CH$_2$). On reducing the temperature to ca. 250 K the resonances are seen to split as the ligand exchange and inversion processes are slowed to show the AB $-$CH$_2$ coupling of the two separate diastereoisomers. At 180 K the peaks are clearly resolved for the dl and meso isomers. However, they are not clear enough to distinguish the $^3J(^{117/119}$Sn - $^1$H) coupling that was seen for the thioether systems. For $[SnCl_4\{MeSe(CH_2)_3SeMe\}]$ three resonances are observed at 300 K for the three different proton environments. These resonances do not split until ca. 220 K where the dynamic processes in solution are slowed sufficiently, and $^3J(^{117/119}$Sn - $^1$H) coupling is again unobserved even at 180 K. For the phenyl substituted system, $[SnCl_4\{PhSe(CH_2)_2SePh\}]$, no splitting is seen in the proton NMR spectra until 180 K, where splitting becomes obvious in the $\delta$(CH$_2$) resonance, while for the trimethylene backboned species $[SnCl_4\{PhSe(CH_2)_3SePh\}]$ the resonances remain broad even at the lowest temperature studied (173 K). $[SnCl_4\{\omega$-$C_6H_4(SeMe)_2\}]$ was found to be more soluble in CD$_2$Cl$_2$, so the resulting spectra were clearer. The $\delta$(Me) resonance observed for this species splits at ca. 230 K and at 175 K $^3J(^{117/119}$Sn - $^1$H) coupling of ca. 40 Hz can be distinguished.

In general, the behaviour seen in the bromide systems mirrors that of the chloride, but with the onset of pyramidal inversion and ligand exchange beginning at lower temperatures such that no splitting can be seen for the phenyl substituted adducts even at 173 K and for $[SnBr_4\{\omega$-$C_6H_4(SeMe)_2\}]$ the splitting is only present as a weak shoulder that is not fully resolved.

A number of trends become apparent from these results. The fact that no splitting can be distinguished for $[SnCl_4(MeSeCH_2SeMe)]$ shows the extreme
lability of this ligand, and is consistent with the highly strained nature of the four-membered chelate-ring that was observed in the X-ray crystallography. The observation that the bromide systems undergo exchange mechanisms at lower temperatures is consistent with the observation that has already been made for the monodentate systems, and the \([\text{SnX}_4\{\text{O-Cl}\_2\text{H}_4(\text{SeMe})_2\}]\) (where \(X = \text{Cl} \) or \(\text{Br}\)) systems from the X-ray crystallographic study, that \(\text{SnBr}_4\) is a poorer acceptor than \(\text{SnCl}_4\). This is also consistent with the overall trends found for the thioether systems in chapter 2.

### 3.2.9. Variable Temperature \(^{119}\text{Sn}\{^1\text{H}\} \) NMR Spectroscopy

The \(^{119}\text{Sn}\{^1\text{H}\} \) NMR spectra (133.4 MHz, \(\text{CD}_2\text{Cl}_2\)) were recorded over a range of temperatures (300 - 180 K) in order to observe the effects of ligand exchange by dissociation and selenium inversion. Resonances for the various tin(IV) species were observed in characteristic regions. Tin(IV) chloride complexes were observed over the range \(\delta -600 \) to \(\delta -700 \) ppm which is consistent with the range observed for the \(\text{cis}\) and \(\text{trans}\) isomers of \([\text{SnCl}_4(\text{Me}_2\text{Se})_2]\) (\(\delta -691 \) and \(-695 \) ppm) discussed earlier and the chemical shift is approximately 110 - 150 ppm to lower frequency to those observed for the thioether systems (\(\delta -500 \) to \(\delta -600 \) ppm). The complexes of tin(IV) bromide were characteristically observed over the range \(\delta -1200 \) to \(\delta -1350 \) ppm, consistent with the shift of \([\text{SnBr}_4(\text{Me}_2\text{Se})_2]\) (\(\delta -1296 \) and \(-1319 \) ppm) and again shifted by approximately 100 ppm to lower frequency than the thioether analogues. \(^{119}\text{Sn}\{^1\text{H}\} \) NMR spectroscopic data at 180 K for these \([\text{SnX}_4\{\text{diselenoether}\}]\) complexes are presented in Table 3.6.

These complexes again proved extremely poorly soluble in chlorocarbon solvents. This resulted in spectra with relatively poor signal-to-noise ratios even after long accumulations, and prevented identification of satellites from \(^{1}\text{J}(^{119}\text{Sn} - ^{77}\text{Se})\) coupling. Coordinating solvents were again avoided to prevent risk of displacing the selenoether.

As for the thioether analogue, the exception to this insolubility was the \(\text{MeSeCH}_2\text{SeMe}\) complex of \(\text{SnCl}_4\). The extremely strained nature of the four-membered chelate-ring, characterised by X-ray crystallography, leads to this complex being very labile in solution. The result is that no resonance is observed over the entire temperature range, supporting the observation that the selenoether ligands are poorer donors than the thioether analogues.
None of the other SnCl₄ complexes exhibit a resonance at 300 K, most likely due to reversible ring opening occurring rapidly in solution. In all cases resolved resonances are not seen in the ¹¹⁹Sn-¹¹H spectra until very low temperatures (< 200 K) are reached. The dl and meso isomers can be resolved for the SnCl₄ species [SnCl₄{MeSe(CH₂)ₙSeMe}] (where n = 2 or 3) and at 180 K the resonance for [SnCl₄{ω-C₆H₄(SeMe)₂}] is evident in the appearance of splitting, with a resonance at δ -632 ppm with a second resonance becoming discernible at δ -635 ppm. Consistent with the observed trend that phenyl substituted ligands are poorer donors, no splitting was seen in the resonances of the [SnCl₄{PhSe(CH₂)ₙSePh}] species even at 173 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹¹⁹Sn-¹¹H (δ)</th>
<th>⁷⁷Se-¹¹H (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄{MeSeCH₂SeMe}]</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>[SnCl₄{MeSe(CH₂)₂SeMe}]</td>
<td>-680, -682</td>
<td>482, 487 (1:1)</td>
</tr>
<tr>
<td>[SnCl₄{MeSe(CH₂)₃SeMe}]</td>
<td>-685, -686.5</td>
<td>231, 232 (5:1)</td>
</tr>
<tr>
<td>[SnCl₄{ω-C₆H₄(SeMe)₂}]</td>
<td>-632, -635</td>
<td>323, 338 (1:5)</td>
</tr>
<tr>
<td>[SnCl₄{PhSe(CH₂)₂SePh}]</td>
<td>n.o.</td>
<td>436</td>
</tr>
<tr>
<td>[SnBr₄{MeSe(CH₂)₂SeMe}]</td>
<td>-1238, -1288</td>
<td>493, 496 (2:1)</td>
</tr>
<tr>
<td>[SnBr₄{MeSe(CH₂)₃SeMe}]</td>
<td>-1305, -1308</td>
<td>261, 263 (1:2)</td>
</tr>
<tr>
<td>[SnBr₄{ω-C₆H₄(SeMe)₂}]</td>
<td>-1258 (br)</td>
<td>355</td>
</tr>
</tbody>
</table>

Free selenoether: δ(⁷⁷Se) MeSe(CH₂)₂SeMe, 121; MeSe(CH₂)₃SeMe, 74; PhSe(CH₂)₂SePh, 340; ω-C₆H₄(SeMe)₂, 202.¹⁴

a. In anhydrous CH₂Cl₂-CD₂Cl₂ solution containing [Cr(acac)₃].
b. Relative to neat external SnMe₄.
c. Relative to neat external Me₂Se, approximate dl:meso ratios in parentheses.
d. n.o. = not observed
The $^{119}\text{Sn}$-$^{1}{\text{H}}$ NMR spectra of the complexes of SnBr$_4$ exhibit largely similar behaviour to the SnCl$_4$ systems. Once again exchange mechanisms begin at lower temperatures for these systems meaning splitting is now not seen for the phenylene example, [SnBr$_4$(o-C$_6$H$_4$(SeMe)$_2$)]. Even at 173 K the resonance for this system is still extremely broad. For [SnBr$_4$(PhSe(CH$_2$)$_3$SePh)] a resonance is observed at 180 K but it is not possible to resolve splitting for the two diastereoisomers. While a visible colour change in solution may indicate adduct formation, no solid was isolated from the attempted synthesis of [SnBr$_4$(PhSe(CH$_2$)$_2$SePh)], and no resonances were observed in the in situ $^{119}\text{Sn}$-$^{1}{\text{H}}$ NMR spectra over the entire temperature range studied, again consistent with phenyl substituted ligands being poorer donors.

The synthesis of [SnI$_4$(MeSe(CH$_2$)$_2$SeMe)] was also attempted. Despite a vivid colour change from orange to red when the ligand was added to the solution of SnI$_4$ in CH$_2$Cl$_2$ no solid was isolated. In situ $^{119}\text{Sn}$-$^{1}{\text{H}}$ NMR spectra over the temperature range 180 – 300 K exhibited no resonance indicative of adduct formation, presumably as exchange mechanisms at this temperature are too rapid on an NMR timescale. The analogous thioether complex was only observed at 180 K, so this again supports the observed trend that these selenoethers are poorer ligands than their corresponding thioether analogues.

3.2.10. Variable Temperature $^{77}\text{Se}$-$^{1}{\text{H}}$ NMR Spectroscopy

The $^{77}\text{Se}$-$^{1}{\text{H}}$ NMR spectra of the complexes formed were studied over the temperature range 173 – 300 K. As in the $^{119}\text{Sn}$-$^{1}{\text{H}}$ NMR spectroscopy the aim is to slow ligand exchange and pyramidal inversion sufficiently to observe separate resonances for the $dl$ and $meso$ diastereoisomers. $^{77}\text{Se}$-$^{1}{\text{H}}$ NMR spectroscopic data at 180 K for these [SnX$_4${diselenoether}] complexes are presented in Table 3.6.

For the complex [SnCl$_4$(MeSe(CH$_2$)$_2$SeMe)] no resonance was observed in the $^{77}\text{Se}$-$^{1}{\text{H}}$ NMR spectra over the entire temperature range. This result is consistent with this ligand being highly labile and has already been seen to form a highly strained four-membered chelate-ring from the X-ray crystallographic study. At 300 K a single resonance at $\delta$ 486 ppm is observed in the spectrum of [SnCl$_4$(MeSe(CH$_2$)$_2$SeMe)], which splits below ca. 200 K giving peaks at $\delta$ 482 and 487 ppm assigned to the two diastereoisomers. Nothing is observed at 300 K for [SnCl$_4$(MeSe(CH$_2$)$_3$SeMe)], a resonance only becoming obvious at ca. 255 K, and it is not until ca. 180 K that the resonance is seen to split as exchange and inversion is reduced sufficiently and the
diastereoisomers are observed. Neither of the phenyl substituted systems [SnCl₄{PhSe(CH₂)ₙSePh}] (n = 2 or 3) exhibit splitting even at 173 K. For [SnCl₄{PhSe(CH₂)₂SePh}] a single resonance is observed at δ 436 ppm, while no resonance for [SnCl₄{PhSe(CH₂)₃SePh}] is observed at any temperature, supporting the assignment of these phenyl substituted ligands as poorer than the methyl substituted equivalents, and also with the five-membered chelate-ring being preferred over the six-membered chelate-ring. The ⁷⁷Se-{¹H} NMR spectrum of [SnCl₄{ω-C₆H₄(SeMe)₂}] was run in the presence of excess ligand. At 180 K three resonances are observed at δ 323, 338 and 193 ppm consistent with the two diastereoisomers and free ligand. Raising the temperature to ca. 220 K the signals were clearly broadening, and by 235 K had disappeared showing fast ligand exchange at this temperature.

The bromide systems again display the onset of exchange and inversion at lower temperatures. For the methyl substituted system, [SnBr₄{MeSe(CH₂)₂SeMe}], a resonance is not observed until ca. 225 K at δ 496 ppm, with splitting not observed until below ca. 200 K. For [SnBr₄{MeSe(CH₂)₃SeMe}] the recorded temperatures are lower still, a resonance at δ 261 ppm only apparent at ca. 200 K and splitting not until 180 K. Even at 180 K the ⁷⁷Se-{¹H} NMR spectrum of [SnBr₄{ω-C₆H₄(SeMe)₂}] displays a single resonance at δ 355 ppm with no evidence for splitting. No solid was isolated from the attempted synthesis of [SnBr₄{PhSe(CH₂)₂SePh}] but a resonance was observed at δ 440 ppm indicative of adduct formation at lowest temperatures. Exchange was still too rapid to allow a resonance to be observed for [SnBr₄{PhSe(CH₂)₃SePh}] at any temperature.

As for the ¹¹⁹Sn-{¹H} NMR spectrum, no evidence of adduct formation was seen at any temperature in a solution containing SnI₄ and MeSe(CH₂)₂SeMe.

One trend arising from the ⁷⁷Se-{¹H} NMR data is the large changes in coordination shift with chelate-ring size. These large changes have previously been studied for transition metal complexes of selenoethers¹² and since data has been obtained on monodentate systems as well as bidentate systems incorporating chelate-rings of varying sizes, it is possible to identify similar trends here. Following the approach first employed by Garrou¹³ for diphosphine complexes, the coordination shift Δ for each of the complexes is calculated as Δ = δcomplex - δligand. The chelate-ring-parameter AR is then defined as Δ(chelate complex) - Δ(equivalent monodentate complex). For the purposes of this study the species cis-[SnX₄(Me₂Se)₂] are considered
to be the "equivalent monodentate complex" for the complexes \([\text{SnX}_4\{\text{MeSe(CH}_2)_n\text{SeMe}\}]\) \((n = 2 \text{ or } 3)\).

Free MeSe(CH\(_2\)_2SeMe has \(\delta 121 \text{ ppm},^4\) leading to co-ordination shifts \((\Delta)\) of 365 for the SnCl\(_4\) complex and 374 for the corresponding bromide complex. From these the values of \(\Delta R\) for these five-membered chelate-ring systems are 161 and 155 for the chloride and bromide complexes respectively. When applied to the six-membered chelate-ring system \([\text{SnX}_4\{\text{MeSe(CH}_2)_3\text{SeMe}\}]\), free ligand has \(\delta 74 \text{ ppm,}\) leading to \(\Delta 158\) and \(\Delta 188\) for the chloride and bromide complexes and chelate-ring-parameters of \(\Delta R -46\) and \(\Delta R -31\) respectively. These negative shifts for six-membered chelate-rings and positive shifts for the corresponding five-membered chelate-rings provide clear evidence for the presence of a chelate-ring-parameter effect in the selenium chemical shift values. This is the first time this has been established in complexes of a main-group metal, though the trends are similar to those observed in d-block metal complexes.\(^{12}\) The origins of the chelate-ring effect is unclear even in the much studied diphosphine systems,\(^{15}\) but the observation of such an effect in the tin complexes here, where the metal is behaving as a simple \(\sigma\) acceptor, supports the suggestion that it involves the strain in different ring sizes.\(^{14}\) The degree of straining in these systems relative to the octahedral ideal has been seen in the X-ray crystallography discussed earlier and, by analogy, in the diffraction studies on thioethers in chapter 2.

Since the complexes of PhMeSe, which would be considered the "equivalent monodentate complex" for the complexes of PhSe(CH\(_2\)_2SePh and \(\text{C}_6\text{H}_4\text{(SeMe)}_2\), were not studied similar, calculations of \(\Delta R\) cannot be carried out for these bidentate compounds. However, for \([\text{SnX}_4\{\text{C}_6\text{H}_4\text{(SeMe)}_2\}]\) the substantial high frequency co-ordination shifts in themselves strongly suggest that the chelate structures identified by X-ray crystallography are also retained in solution.
3.3. Conclusions

The products \([\text{SnX}_4(R_2\text{Se})_2]\) (where \(X = \text{Cl} \) or \(\text{Br} \); \(R = \text{Me} \) or \(\text{Ph} \)) arising from the reactions of \(\text{SnX}_4\) with monodentate selenoethers and those with bidentate selenoethers, \([\text{SnX}_4\{\text{MeSe(CH}_2)_n\text{SeMe}\}]\) (where \(n = 1, 2 \) or \(3 \)), \([\text{SnX}_4\{\text{PhSe(CH}_2)_n\text{SePh}\}]\) (where \(n = 2 \) or \(3 \)) and \([\text{SnX}_4\{\text{o-C}_6\text{H}_4(\text{SeMe})_2\}]\) have been prepared in high yield, including a highly strained four-membered chelate-ring species involving the \(\text{MeSeCH}_2\text{SeMe}\) ligand. A detailed examination of the variable temperature \(^1\text{H}, ^{119}\text{Sn-}^1\text{H}\) and \(^{77}\text{Se-}^1\text{H}\) NMR spectroscopy over the temperature range \(300 - 180 \) K has been presented. As with the thioether systems of chapter 2, particular emphasis for the bidentate systems has been on the study of the dynamic processes occurring in solution. The variable temperature NMR studies again identified the onset of pyramidal inversion and ligand dissociation in a number of the complexes, both beginning at similar temperatures preventing quantitative analysis. It was possible to distinguish the \(dl\) and \(meso\) isomers within the NMR spectra at low temperature (180 K) for a large number of the systems and the onset of these observations allowed a number of qualitative trends to be identified. The trends observed were consistent with those of the thioether analogues in chapter 2, examples involving phenyl substituents are typically less stable than those with methyl substituents, that the stability of the complexes formed decreases with the \(\text{SnX}_4\) acceptor: \(X = \text{Cl} \gg \text{Br} \gg 1 \). The results again confirmed that five-membered chelate-ring systems are more stable than six-membered chelate-rings with the highly strained four-membered chelate-ring least favoured. Single crystal X-ray diffraction studies again proved highly complementary to the solution studies and providing further support for the trends seen.
3.4. Experimental

The tin(IV) chloride, bromide and iodide were purchased from Aldrich Chemicals. The ligands Me₂Se, Ph₂Se, MeSe(CH₂)nSeMe (where n = 1, 2 or 3), PhSe(CH₂)nSePh (where n = 2 or 3) and α-C₆H₄(SeMe)₂ were prepared by following literature methods. Tin(IV) fluoride was prepared by Dr. Andrew Hector by reaction of tin powder with fluorine at 300 °C/3 atm. in a Monel autoclave.

Tin(IV) halides are moisture sensitive, therefore all of the reactions were carried out under an atmosphere of dry nitrogen, using standard Schlenk, vacuum-line and dry box techniques.

Single Crystal X-ray Diffraction

Single crystals of [SnCl₄(Me₂Se)₂], [SnBr₄(Me₂Se)₂], [SnCl₄(α-C₆H₄(SeMe)₂)], [SnBr₄(α-C₆H₄(SeMe)₂)] were obtained from a solution of the appropriate complex in CHCl₃. The compounds were extremely sensitive to hydrolysis on exposure to moist air. Therefore, in each case the selected crystal was coated in mineral oil, mounted on a glass fibre using silicone grease as adhesive, and immediately placed in a stream of cold nitrogen gas and cooled to 150 K. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low temperature attachment operating at 150 K, using graphite-monochromated Mo-Kα X-radiation (\(\lambda = 0.71073 \text{ Å}\)), T = 150 K, \(\omega-2\theta\) scans. The intensities of three standard reflections were monitored every 150 reflections. No significant crystal decay or movement was observed. As there were no identifiable faces the raw data were corrected for absorption using psi-scans. The weighting scheme \(w^{-1} = \sigma^2 (F)\) gave satisfactory agreement analyses in each case.

All four structures were solved by direct methods, and then developed by iterative cycles of full-matrix least-squares refinement (based on \(F\)) and difference Fourier syntheses which located all non-H atoms in the asymmetric unit. For [SnBr₄(Me₂Se)₂] and [SnBr₄(α-C₆H₄(SeMe)₂)] an empirical absorption correction using DIFABS was applied to the raw data at isotropic convergence. All non-H atoms in the structures were refined anisotropically (with the exception of [SnBr₄(α-C₆H₄(SeMe)₂)] for which the C atoms were refined isotropically), and H atoms were placed in fixed, calculated positions with \(d(C-H) = 0.96 \text{ Å}\).
Data collection was also undertaken on poorly diffracting crystals of 
$[\text{SnCl}_4\{\text{MeSe(CH}_2)_2\text{SeMe}\}]$ and $[\text{SnCl}_4\{\text{PhSe(CH}_2)_2\text{SePh}\}]$ both obtained by the same method as the other complexes using solutions of the appropriate complex in CHCl$_3$. The overall data quality was poor and the residuals rather high, preventing satisfactory refinement, but the analysis was sufficient to confirm unambiguously that the compounds do contain a chelating ligand in the $dl$ arrangement for both complexes.

Crystallographic data for these structures are presented in Table 3.7.
### Table 3.7. Crystallographic data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Formula Weight</th>
<th>Colour, morphology</th>
<th>Crystal dimensions/mm</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>α°</th>
<th>β°</th>
<th>γ°</th>
<th>U/Å³</th>
<th>Scan Type</th>
<th>F(000)</th>
<th>D_c/g cm⁻³</th>
<th>μ(Mo-Kα)/cm⁻¹</th>
<th>Transmission factors (max. and min.)</th>
<th>No. of Unique obs. reflections</th>
<th>R_int (based on F²)</th>
<th>Unique obs. reflections with</th>
<th>No. of parameters</th>
<th>Goodness of fit</th>
<th>R(F⁰)</th>
<th>R_w(F²)</th>
<th>Max. residual peak/eÅ⁻³</th>
<th>Max. residual trough/eÅ⁻³</th>
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<tr>
<td>trans-[SnCl₂(Me₂Se)₂]</td>
<td>C₂H₅Cl₃Se₂Sn</td>
<td>347.56</td>
<td>Colourless, block</td>
<td>0.25 x 0.10 x 0.10</td>
<td>Monoclinic</td>
<td>P2₁/n</td>
<td>6.539(2)</td>
<td>12.16(3)</td>
<td>8.111(2)</td>
<td>107.67(2)</td>
<td>637.2(2)</td>
<td>2</td>
<td>444</td>
<td>2.494</td>
<td>85.04</td>
<td>184.63</td>
<td>1.000, 0.694</td>
<td>1189</td>
<td>0.031</td>
<td>925</td>
<td>2</td>
<td>2.29</td>
<td>0.036</td>
<td>0.043</td>
<td>1.19</td>
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<td>478.56</td>
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<td>P2₁/n</td>
<td>6.768(3)</td>
<td>13.000(3)</td>
<td>8.373(3)</td>
<td>108.47(3)</td>
<td>698.7(4)</td>
<td>2</td>
<td>588</td>
<td>3.119</td>
<td>184.63</td>
<td>184.63</td>
<td>1.000, 0.645</td>
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<td>0.132</td>
<td>1039</td>
<td>52</td>
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<td>0.057</td>
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<td>2.15</td>
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<td>11.323(3)</td>
<td>8.251(1)</td>
<td>90.32(2)</td>
<td>731.8(3)</td>
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<td>488</td>
<td>2.380</td>
<td>73.85</td>
<td>184.63</td>
<td>1.000, 0.717</td>
<td>2563</td>
<td>0.028</td>
<td>1763</td>
<td>136</td>
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<td>0.052</td>
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<td>[SnCl₄{(C₆H₅)(SeMe)}]</td>
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<td>702.39</td>
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<td>Monoclinic</td>
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<td>9.936(2)</td>
<td>109.67(2)</td>
<td>754.7(3)</td>
<td>2</td>
<td>632</td>
<td>3.119</td>
<td>184.63</td>
<td>184.63</td>
<td>1.000, 0.645</td>
<td>1402</td>
<td>0.043</td>
<td>1143</td>
<td>50</td>
<td>3.49</td>
<td>0.049</td>
<td>0.062</td>
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<tr>
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<td>Colourless, block</td>
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<td>P2₁/n</td>
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<td>25.702(10)</td>
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<tr>
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<td>600.69</td>
<td>Colourless, plate</td>
<td>0.30 x 0.15 x 0.07</td>
<td>Monoclinic</td>
<td>P2₁/n</td>
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<td>7.006(3)</td>
<td>20.28(3)</td>
<td></td>
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</tbody>
</table>

\[ R = \frac{\sum |F_{\text{obs}}| - |F_{\text{calc}}|}{\sum |F_{\text{obs}}|} \]
\[ R_w = \sqrt{\frac{\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum w|F_{\text{obs}}|^2}} \]
\[ \text{GOF} = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sigma^2}(n - m) = 1 \]
Complex Synthesis

\[ \text{[SnCl}_4\text{(Me}_2\text{Se)}_2 \text{]} \]

Tin(IV) chloride (0.26 g, 1 mmol) was added to a solution of \( \text{Me}_2\text{Se} \) (0.22 g, 2 mmol) in chloroform (10 cm\(^3\)). The complex formed immediately as a white precipitate which was filtered off and dried \textit{in vacuo}. The product was stored in a nitrogen dry-box. Yield 0.44 g, 92 %. Found: C, 9.75; H 2.7. Calculated for \( \text{C}_4\text{H}_1\text{Cl}_4\text{Se}_2\text{Sn} \): C, 10.05; H, 2.5 %. IR spectrum (nujol mull) \( \nu/\text{cm}^{-1} \) (Sn-Cl) 312.

\[ \text{[SnBr}_4\text{(Me}_2\text{Se)}_2 \text{]} \]

A saturated solution of tin(IV) bromide (0.44 g, 1 mmol) in chloroform (5 cm\(^3\)) was added dropwise to a solution of \( \text{Me}_2\text{Se} \) (0.22 g, 2 mmol) in chloroform (5 cm\(^3\)). On reducing the volume \textit{in vacuo} the complex slowly formed as yellow crystals that were filtered off and dried \textit{in vacuo}. Yield 0.54 g, 82 %. Found: C, 7.4; H, 1.9. Calculated for \( \text{C}_4\text{H}_1\text{Br}_4\text{Se}_2\text{Sn} \): C, 7.3; H, 1.85 %. IR spectrum (nujol mull) \( \nu/\text{cm}^{-1} \) (Sn-Br) 220.

\[ \text{[SnCl}_4\text{(MeSeCH}_2\text{SeMe)}_2 \text{]} \]

Tin(IV) chloride (0.52 g, 2 mmol) was added to a solution of \( \text{MeSeCH}_2\text{SeMe} \) (0.40 g, 2 mmol) in anhydrous \( \text{CH}_2\text{Cl}_2 \) (10 cm\(^3\)). Stirring at room temperature followed by concentration of the solution \textit{in vacuo}, afforded a yellow precipitate which was collected by filtration and dried \textit{in vacuo}. Yield 0.5 g, 54 %. Found: C, 7.9; H, 2.0. Calculated for \( \text{C}_3\text{H}_8\text{Cl}_4\text{Se}_2\text{Sn} \): C, 7.8; H, 1.7 %. IR spectrum (nujol mull) \( \nu/\text{cm}^{-1} \) (Sn-Cl) 326(br).

\[ \text{[SnCl}_4\text{(MeSe(CH}_2)_2\text{SeMe)}_2 \text{]} \]

Tin(IV) chloride (0.26 g, 1 mmol) was added to a solution of \( \text{MeSe(CH}_2)_2\text{SeMe} \) (0.22 g, 1 mmol) in chloroform (10 cm\(^3\)). The complex formed as a white powder which was filtered off and dried \textit{in vacuo}. Yield 0.45 g, 72 %. Found: C, 10.3; H, 2.5. Calculated for \( \text{C}_4\text{H}_{10}\text{Cl}_4\text{Se}_2\text{Sn} \): C, 10.1; H, 2.1 %. IR spectrum (nujol mull) \( \nu/\text{cm}^{-1} \) (Sn-Cl) 339, 331, 320 and 312.
[SnCl$_4$\{MeSe(CH$_2$)$_3$SeMe\}]

Addition of SnCl$_4$ (0.26 g, 1 mmol) to a solution of MeSe(CH$_2$)$_3$SeMe (0.23 g, 1 mmol) formed a white precipitate immediately. This was filtered off and dried in vacuo. Yield 0.72 g, 93%. Found: C, 12.5; H, 2.6. Calculated for C$_5$H$_{12}$Cl$_4$Se$_2$Sn: C, 12.25; H, 2.45 %. IR spectrum (nujol mull) ν/cm$^{-1}$ (Sn-Cl) 336, 331, 325 and 313.

[SnCl$_4$\{PhSe(CH$_2$)$_2$SePh\}]

Addition of SnCl$_4$ (0.26 g, 1 mmol) to a solution of PhSe(CH$_2$)$_2$SePh (0.34 g, 1 mmol) formed a yellow crystalline product immediately. This was filtered off and dried in vacuo. Yield 0.59 g, 81 %. Found: C, 27.2; H, 2.5. Calculated for C$_{14}$H$_{14}$Cl$_4$Se$_2$Sn: C, 28.0; H, 2.35 %. IR spectrum (nujol mull) ν/cm$^{-1}$ (Sn-Cl) 330, 324, 319 and 313.

[SnCl$_4$\{PhSe(CH$_2$)$_3$SePh\}]

Addition of SnCl$_4$ (0.26 g, 1 mmol) to a solution of PhSe(CH$_2$)$_3$SePh (0.35 g, 1 mmol) formed an orange crystalline product immediately. This was filtered off and dried in vacuo. Yield 0.53 g, 86 %. Found: C, 29.5; H, 2.7. Calculated for C$_{15}$H$_{16}$Cl$_4$Se$_2$Sn: C, 29.8; H, 2.65 %. IR spectrum (nujol mull) ν/cm$^{-1}$ (Sn-Cl) 330, 324, 315 and 304.

[SnCl$_4$\{α-C$_6$H$_4$(SeMe)$_2$\}]

Addition of SnCl$_4$ (0.26 g, 1 mmol) to a solution of α-C$_6$H$_4$(SeMe)$_2$ (0.26 g, 1 mmol) formed a white crystalline product immediately. This was filtered off and dried in vacuo. Yield 0.49 g, 94%. Found: C, 18.35; H, 2.0. Calculated for C$_8$H$_{10}$Cl$_4$Se$_2$Sn: C, 18.3; H, 1.9 %. IR spectrum (nujol mull) ν/cm$^{-1}$ (Sn-Cl) 338, 328, 323 and 317.

[SnBr$_4$\{MeSe(CH$_2$)$_3$SeMe\}]

A saturated solution of tin(IV) bromide (0.44 g, 1 mmol) in chloroform (5 cm$^3$) was added dropwise to a solution of MeSe(CH$_2$)$_3$SeMe (0.22 g, 1 mmol) in chloroform (5 cm$^3$). A pale yellow precipitate formed immediately which was filtered off and dried in vacuo. Yield 0.50 g, 69%. Found: C, 7.5; H, 1.8. Calculated for C$_4$H$_{10}$Br$_4$Se$_2$Sn: C, 7.35; H, 1.55 %. IR spectrum (nujol mull) ν/cm$^{-1}$ (Sn-Br) 220, 218, 216 and 214.
[SnBr₄{MeSe(CH₂)₃SeMe}]

Addition of SnBr₄ (0.44 g, 1 mmol) to a solution of MeSe(CH₂)₃SeMe (0.23 g, 1 mmol) formed a yellow precipitate immediately. This was filtered off and dried in vacuo. Yield 0.48 g, 81 %. Found: C, 9.3; H, 1.9. Calculated for C₅H₁₂Br₄Se₂Sn: C, 9.0; H, 1.8 %. IR spectrum (nujol mull) ν/cm⁻¹ (Sn-Br) 219, 214, 206 and 201.

[SnBr₄{o-C₆H₄(SeMe)₂}]

Addition of SnBr₄ (0.44 g, 1 mmol) to a solution of o-C₆H₄(SeMe)₂ (0.26 g, 1 mmol) formed an orange crystalline product slowly from solution. This was filtered off and dried in vacuo. Yield 0.67 g, 86 %. Found: C, 13.9; H, 1.7. Calculated for C₉H₁₀Br₄Se₂Sn: C, 13.65; H, 1.4 %. IR spectrum (nujol mull) ν/cm⁻¹ (Sn-Br) 230, 228, 224 and 222.
References

Chapter 4

Group 14 Halide Complexes

With Mono- and Bidentate Telluroethers
4.1. Introduction

In chapters 2 and 3 the group 14 halide complexes of thioethers and selenoethers were characterised and trends identified. No tin telluroethers appear in the literature, although RTe-Sn bonds are established.\textsuperscript{1}

The following work provides a detailed investigation into the behaviour of the tin(IV) halides (Cl, Br or I) with the monodentate ligand Me\textsubscript{2}Te, and bidentate ligands of the type RTe(CH\textsubscript{2})\textsubscript{3}TeR (where R = Me or Ph) and \textsc{c}-C\textsubscript{6}H\textsubscript{4}(TeMe)\textsubscript{2}. The effects of changing halide and ligand interdonor linkage and substituents are studied. Variable temperature \textsuperscript{1}H, \textsuperscript{119}Sn and \textsuperscript{125}Te NMR spectra have been recorded in attempts to investigate the pyramidal inversion and ligand exchange processes in these systems. IR spectroscopy and single crystal X-ray diffraction have been used to study the behaviour of these complexes in the solid state. Overall trends observed for these tin(IV) halide complexes of group 16 ligands will be discussed here.
4.2. Results & Discussion

4.2.1. Synthesis and Properties of Monodentate Telluroether Complexes

The complexes $[\text{SnCl}_4(\text{Me}_2\text{Te})_2]$ and $[\text{SnBr}_4(\text{Me}_2\text{Te})_2]$ have been prepared by reaction of the appropriate $\text{SnX}_4$ with two molar equivalents of $\text{Me}_2\text{Te}$ in thoroughly degassed, anhydrous $\text{CH}_2\text{Cl}_2$. The solids formed are hydrolysed easily, even the briefest exposure to the laboratory atmosphere causing them to turn orange-red with liberation of $\text{Me}_2\text{Te}$, and then cream with oxidation of the ligand. All complexes were therefore stored and handled in a dinitrogen filled dry-box. Even here the compounds decompose to give dark brown solids. The far-IR spectrum of the chloride complex shows one broad peak at 312 cm$^{-1}$ for $v(\text{SnCl})$ probably corresponding to the trans isomer ($D_{4h}$) being the principal isomer present in the solid state (compare trans-$[\text{SnCl}_4(\text{Me}_2\text{Se})_2]$ 312 cm$^{-1}$ in chapter 3). The same observation is made for the bromide species with a broad band observed at 220 cm$^{-1}$ (compare trans-$[\text{SnBr}_4(\text{Me}_2\text{Se})_2]$ 220 cm$^{-1}$, chapter 3). Satisfactory elemental analyses were obtained for both species.

Reaction of $\text{SnI}_4$ with $\text{Me}_2\text{Te}$ in $\text{CH}_2\text{Cl}_2$ solution was also tried and produced a brown precipitate immediately. The product was tentatively assigned as the adduct, $[\text{SnI}_4(\text{Me}_2\text{Te})_2]$, but while it was isolable due to its low solubility in $\text{CH}_2\text{Cl}_2$, the complex proved extremely susceptible to hydrolysis decomposing immediately in the laboratory atmosphere, and overnight in the dinitrogen filled dry-box. In situ NMR experiments displayed no peaks other than those corresponding to hydrolysed product, presumably due to trace amounts of water in the solvents.

4.2.2. Variable Temperature $^1\text{H}$ NMR Spectroscopy

$^1\text{H}$ NMR spectroscopic data are presented in Table 4.1. The $^1\text{H}$ NMR spectrum of a solution of $[\text{SnCl}_4(\text{Me}_2\text{Te})_2]$ in $\text{CD}_2\text{Cl}_2$ at 300 K (Figure 4.1a) consists of a single resonance at $\delta$ 3.0 ppm. This is little changed on cooling the solution to 200 K, but on further cooling the resonance broadens, and at 180 K it is seen to split into two distinct resonances at $\delta$ 3.04 and 3.06 ppm (Figure 4.1b). Even at the lowest attainable temperature obtainable in this solvent (ca. 175 K) no $^{117/119}\text{Sn}$ satellites are observed. These satellites were observed at 180 K for the analogous selenoether system allowing them to be assigned as the two possible geometric isomers. However, the two species
here have relative intensity 1:2, and are tentatively assigned as the *cis* and *trans* isomers for this SnCl₄L₂ system (δ for free Me₂Te is 1.90 ppm).

For a solution of [SnCl₄(Me₂Te)₂] with excess Me₂Te only one single resonance is observed over the entire temperature range studied (175 – 300 K). This is consistent with fast exchange between free and coordinated telluroether and also with the observed trend of weaker binding to hard acceptors as group 16 is descended.

The ¹H NMR spectra of [SnBr₄(Me₂Te)₂] studied over the same temperature range (175 – 300 K) exhibits a single resonance at δ 3.25 ppm. No splitting indicative of the presence of *cis* and *trans* isomers is observed at any temperature again consistent with the observed trend from chapters 2 and 3 that the complex is more labile when the Lewis acid is SnBr₄. The experiment was also run in the presence of excess ligand, again a single resonance is observed at all temperatures with fast exchange between free and co-ordinated telluroether.

A product was isolated for the reaction of SnI₄ with Me₂Te, but proved too hydrolytically unstable in solution to observe the species in the ¹H NMR spectrum.

### Table 4.1. Variable Temperature ¹H NMR Spectroscopic Data

<table>
<thead>
<tr>
<th></th>
<th>δ(Me)ᵃ</th>
<th>300K</th>
<th>180 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄(Me₂Te)₂]</td>
<td>3.0</td>
<td>3.04, 3.06 (1:2)</td>
<td></td>
</tr>
<tr>
<td>[SnBr₄(Me₂Te)₂]</td>
<td>3.25</td>
<td>3.17</td>
<td></td>
</tr>
<tr>
<td>[SnI₄(Me₂Te)₂]</td>
<td>n.o.ᵇ</td>
<td>n.o.ᵇ</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ In CD₂Cl₂, approximate *cis/trans* ratios in parentheses. ᵇ n.o. = not observed

### 4.2.3. Variable Temperature ¹¹⁹Sn-{¹H} and ¹²⁵Te-{¹H} NMR Spectroscopy

A solution of [SnCl₄(Me₂Te)₂] in CH₂Cl₂ solution with ca. 10% CD₂Cl₂ exhibited no resonances in either the ¹¹⁹Sn-{¹H} or ¹²⁵Te-{¹H} NMR spectra at any temperature. Significantly, when the ¹²⁵Te-{¹H} NMR spectra were recollected with approximately a two-fold excess of Me₂Te present, no resonance was observed for either free or co-ordinated telluroether, confirming exchange in solution that is so rapid.
that the NMR resonances are broadened and not observed. In contrast, the analogous selenoether complex with excess ligand displayed two resonances in the $^{77}\text{Se}-\{^1\text{H}\}$ and $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectra at 300 K with the resonances for the adduct seen to split below ca. 250 K to two distinct resonances for cis and trans isomers. These observations are again consistent with weakening Sn-L binding, Te < Se.

As expected for the weakening Lewis acids, no resonances were observed for the analogous SnBr$_4$ or SnI$_4$ complexes in either the $^{119}\text{Sn}-\{^1\text{H}\}$ or $^{125}\text{Te}-\{^1\text{H}\}$ NMR spectra.

Figure 4.1. $^1\text{H}$ NMR spectrum of [SnCl$_4$(Me$_2$Te)$_2$] in CD$_2$Cl$_2$ solution at a) 300 K and b) 180 K
4.2.4. Synthesis and Properties of Bidentate Telluroether Complexes

A range of complexes of type SnX₄L₂ (where X = Cl, Br or I; L = MeTe(CH₂)₃TeMe, PhTe(CH₂)₃TePh and o-C₆H₄(TeMe)₂) have been isolated from reaction in CH₂Cl₂. The range of telluroether ligands used is restricted since RTe(CH₂)₂TeR ligands are not known (their attempted synthesis producing only R₂Te₂). In most cases the poor solubility of the SnX₄-ditelluroether complexes meant that the products formed immediately from solution as powdered precipitates, the exception being for complexes of o-C₆H₄(TeMe)₂ where the products form gradually as a crystalline material upon slow evaporation. Due to the extreme moisture sensitivity of the tin(IV) halides and telluroethers, all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. As for the SnX₄L₂ monodentate systems these complexes prove very easily hydrolysed, rapidly turning black in moist air, and the same effect is observed over a few weeks in a dinitrogen dry box. Satisfactory microanalyses were obtained for all products isolated.

IR spectra of the SnCl₄ complexes formed all showed the expected four ν(Sn-Cl) bands (theory: 2A₁ + B₁ + B₂) in the range 300 - 340 cm⁻¹ consistent with C₂ᵥ symmetry. Similarly, the bromide systems also show four ν(Sn-Br) bands in the range 190 - 230 cm⁻¹ consistent with C₂ᵥ symmetry in these products as well. For the iodide systems the ν(Sn-I) bands are below the cut-off point of the spectrometer used (> 180 cm⁻¹) but the IR spectra show bands attributable to the telluroethers similar to those observed in previously studied Pdᴵᴵ and Ptᴵᴵ telluroether systems.³

The iodide complexes were isolated and satisfactory microanalyses were obtained. However, they prove too unstable in solution with hydrolysis the principal problem. Though even in high purity solvent the complexes are still seen to decompose in solution.
4.2.5. Single Crystal X-ray Diffraction Studies

Prior to this study there were no structurally characterised examples of telluroether complexes of any tin(IV) halides. In order to attempt to identify trends in their geometric parameters, single crystal X-ray structure analyses on [SnCl₄{ω-C₆H₄(TeMe)₂}] and [SnBr₄{ω-C₆H₄(TeMe)₂}] were undertaken.

Figure 4.2. View of the structure of [SnCl₄{ω-C₆H₄(TeMe)₂}] with the numbering scheme adopted. Ellipsoids are shown at 40% probability.
The structures for \([\text{SnCl}_4\{\omega-\text{C}_6\text{H}_4(\text{TeMe})_2\}]\) and \([\text{SnBr}_4\{\omega-\text{C}_6\text{H}_4(\text{TeMe})_2\}]\) are shown in Figures 4.2 and 4.3 respectively. Selected bond distances (Å) are presented in Tables 4.2 and angles (°) for \([\text{SnX}_4\{\omega-\text{C}_6\text{H}_4(\text{TeMe})_2\}]\) are presented in Tables 4.3 (X = Cl) and 4.4 (X = Br). In each case the structure shows a discrete tin(IV) species involving a chelating \(\omega-\text{C}_6\text{H}_4(\text{TeMe})_2\) ligand, giving a distorted octahedral molecule as was observed previously in the cases of the thioether and selenoether analogues. As with the analogous thio- and selenoether systems the distortion has the axial halides bending towards the bidentate donor set. An alternative rationalisation might be distortion towards the tetrahedral geometry of the free \(\text{SnX}_4\), arising from the weakened binding to the ditelluroether over halide atoms. In both compounds the ligand adopts a meso arrangement, with both methyl substituents directed to the same side of the \(\text{SnX}_4\text{Te}_2\) plane. In the case of the bromide species, \([\text{SnBr}_4\{\omega-\text{C}_6\text{H}_4(\text{TeMe})_2\}]\), only half the molecule is found in the asymmetric cell, the second half generated by a mirror plane \((x, \frac{1}{2} - y, z)\) upon which the tin atom and two axial halide atoms lie. This is isostructural with the selenoether analogue, \([\text{SnBr}_4\{\omega-\text{C}_6\text{H}_4(\text{SeMe})_2\}]\).

No other tin(IV) halide-telluroether complexes are known and thus there are no data with which to compare bond distances. However, the Sn-Te bond distances observed \((2.908(1) - 2.981(2) \text{ Å})\) are approximately 0.1 Å longer than the analogous Sn-Se bond distances \((2.749(1) - 2.841(2) \text{ Å})\), consistent with the larger radius of Te over Se. A similar difference was observed between the selenoether and thioether systems.

Once again variations are observed in the Sn-X bond distances (Table 4.2). In all cases \(d(\text{Sn-X})\) for \(X\) trans to X are longer than those for \(X\) trans to Te, again suggesting that the trans influence of the halide atoms in these hard SnX4 adducts is greater than that of the telluroether donor. This is in contrast with the usual trend observed in transition-metal complexes involving these ligands where the telluroether function exerts a greater trans influence than halogen atoms.
Table 4.2. Selected Bond Distances (Å) for [SnCl₄{η-C₆H₄(TeMe)₂}] and [SnBr₄{η-C₆H₄(TeMe)₂}]

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>[SnCl₄{η-C₆H₄(TeMe)₂}]</th>
<th>[SnBr₄{η-C₆H₄(TeMe)₂}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-Te(1)</td>
<td>2.908(1)</td>
<td>2.981(2)²</td>
</tr>
<tr>
<td>Sn-Te(2)</td>
<td>2.9222(8)</td>
<td></td>
</tr>
<tr>
<td>Sn-X(1)</td>
<td>2.457(2)</td>
<td>2.567(2)</td>
</tr>
<tr>
<td>Sn-X(2)</td>
<td>2.433(2)</td>
<td>2.622(2)</td>
</tr>
<tr>
<td>Sn-X(3)</td>
<td>2.384(2)</td>
<td>2.526(2)²</td>
</tr>
<tr>
<td>Sn-X(4)</td>
<td>2.390(2)</td>
<td></td>
</tr>
</tbody>
</table>

a. Second atom generated by crystallographic mirror plane, (x, ½ - y, z)

Figure 4.3. View of the structure of [SnBr₄{η-C₆H₄(TeMe)₂}] with the numbering scheme adopted. Ellipsoids are shown at 40 % probability and atoms marked with an asterisk are related by a crystallographic mirror plane (x, ½ - y, z)
The Sn-Te bond distances (Table 4.2) are also markedly different for the two structures studied. $d$(Sn-Te) for the bromide system is approximately 0.6 Å longer than that of the chloride system. This is consistent with the observed trends of the analogous thio- and selenoether systems, but whether this is as a result of the weaker Lewis acid or largely a steric effect is not known. This also has the effect of creating a more strained chelate-ring (Table 4.3). Angles of 81.67(2) and 74.99(7)$^\circ$, for the chloro and bromo species respectively, show that the shorter Sn-Te distances present within the chloro complexes creates a less strained arrangement within the five-membered chelate-ring compared to the bromo species, and hence a smaller distortion from the ideal 90$^\circ$.

Table 4.3. Selected Bond Angles (°) for $[\text{SnCl}_4\{o-C_6\text{H}_4(\text{TeMe})_2\}]$

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Value (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te(1)-Sn-Te(2)</td>
<td>81.67(2)</td>
</tr>
<tr>
<td>Te(1)-Sn-Cl(1)</td>
<td>88.55(5)</td>
</tr>
<tr>
<td>Te(1)-Sn-Cl(2)</td>
<td>90.53(5)</td>
</tr>
<tr>
<td>Te(1)-Sn-Cl(3)</td>
<td>174.10(6)</td>
</tr>
<tr>
<td>Te(1)-Sn-Cl(4)</td>
<td>87.51(6)</td>
</tr>
<tr>
<td>Te(2)-Sn-Cl(1)</td>
<td>86.54(5)</td>
</tr>
<tr>
<td>Te(2)-Sn-Cl(2)</td>
<td>91.30(5)</td>
</tr>
<tr>
<td>Te(2)-Sn-Cl(3)</td>
<td>92.73(6)</td>
</tr>
<tr>
<td>Te(2)-Sn-Cl(4)</td>
<td>168.44(6)</td>
</tr>
<tr>
<td>Cl(1)-Sn-Cl(2)</td>
<td>177.75(7)</td>
</tr>
<tr>
<td>Cl(1)-Sn-Cl(3)</td>
<td>89.25(7)</td>
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<tr>
<td>Cl(1)-Sn-Cl(4)</td>
<td>89.13(7)</td>
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<tr>
<td>Cl(2)-Sn-Cl(3)</td>
<td>91.47(8)</td>
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<tr>
<td>Cl(2)-Sn-Cl(4)</td>
<td>92.88(7)</td>
</tr>
<tr>
<td>Cl(3)-Sn-Cl(4)</td>
<td>97.93(8)</td>
</tr>
</tbody>
</table>
Table 4.4. Selected Bond Angles (°) for \([\text{SnBr}_4\{\text{o-C}_6\text{H}_4(\text{TeMe})_2\}]\)

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te(1)-Sn-Te(1*)</td>
<td>74.99(7)</td>
</tr>
<tr>
<td>Te(1)-Sn-Br(1)</td>
<td>84.36(7)</td>
</tr>
<tr>
<td>Te(1)-Sn-Br(2)</td>
<td>88.96(7)</td>
</tr>
<tr>
<td>Te(1)-Sn-Br(3)</td>
<td>92.66(7)</td>
</tr>
<tr>
<td>Te(1*)-Sn-Br(3)</td>
<td>167.64(4)*</td>
</tr>
<tr>
<td>Br(1)-Sn-Br(2)</td>
<td>171.58(7)</td>
</tr>
<tr>
<td>Br(1)-Sn-Br(3)</td>
<td>93.91(7)</td>
</tr>
<tr>
<td>Br(2)-Sn-Br(3)</td>
<td>91.51(6)</td>
</tr>
<tr>
<td>Br(3)-Sn-Br(3*)</td>
<td>99.68(9)*</td>
</tr>
</tbody>
</table>

a. Atom generated by \((x, \frac{1}{2} - y, z)\) mirror plane
4.2.6 Variable Temperature NMR Spectroscopy

As described in section 4.2.4 these complexes exhibit very poor solubility in chlorocarbon solvents, and it is only the complexes [SnX₄{η-C₆H₄(TeMe)₂}] which dissolve sparingly in CH₂Cl₂. [SnX₄{RTe(CH₂)₃TeR}], especially when R = Me, prove insoluble in chlorocarbons, and this continues the trend observed in the thio- and selenoether systems of decreasing solubility for [SnX₄{MeE(CH₂)₃EMe}] (S > Se). It is this low solubility, rather than increased stability, that leads to the isolation of complexes such as [SnBr₄{PhTe(CH₂)₃TePh}] and SnI₄ complexes which had not been isolable for the thio- or selenoether analogous systems. Solubility is higher in dry acetone or tetrahydrofuran, but it is likely that the O-donor solvent partially displaces the tellurium ligand, since the ¹H NMR spectra of such solutions reveal several species present.

This poor solubility in chlorocarbon solvents means that no useful data could be obtained for the [SnX₄{RTe(CH₂)₃TeR}] species in either the ¹H, ¹¹¹Sn-¹H or ¹²²Te-¹H NMR spectra. Resonances were observed for [SnCl₄{η-C₆H₄(TeMe)₂}] in CD₂Cl₂ though the poor solubility meant the spectra (Figure 4.4) were not well refined. Longer accumulation periods were not available to allow for the solubility problem. At 300 K the ¹H NMR spectrum shows a single δ(Me) at 2.45 ppm (Figure 4.4a) which broadens on cooling and, at 180 K, two distinct resonances δ 2.61 and 2.71 ppm were present in a ratio ca. 3:1 (Figure 4.4b). These are attributable to the meso and DL diastereoisomers, showing that for this system reversible ring opening and pyramidal inversion is slowed sufficiently at this temperature. The solubility of the complex means that even at 180 K the signal-to-noise ratio was relatively poor and ¹¹¹⁷/¹¹¹⁹Sn satellites were not observed. The ¹H NMR spectra of [SnBr₄{η-C₆H₄(TeMe)₂}] only shows a singlet δ(Me) resonance over the range 180 – 300 K, consistent with the weaker Lewis acid leading to increased lability.

Neither of the [SnX₄{η-C₆H₄(TeMe)₂}] systems exhibits any resonances in the ¹¹¹Sn-¹H or ¹²²Te-¹H NMR spectra at any temperature studied. Whilst the poor solubility of these complexes would make observation of these nuclei very difficult, separate experiments in which mixtures of [SnCl₄{η-C₆H₄(TeMe)₂}] and η-C₆H₄(TeMe)₂ were studied failed to show any ¹²²Te-¹H resonance, even for the readily soluble free ditelluroether, demonstrating that fast exchange on the NMR timescale is resulting in the resonances becoming unobservably broad. Although similar
exchange occurs in the analogous thio- and selenoether systems at 300 K, the exchange is slowed on cooling and $^{117/119}\text{Sn} \cdot ^1\text{H}$ or $^{77}\text{Se} \cdot ^1\text{H}$ resonances are easily observed at lower temperatures. The fact that this is not possible for the telluroether systems is consistent with these being poorer donors to Sn(IV) and hence leading to more labile systems.

Figure 4.4. $^1\text{H}$ NMR spectra for $[\text{SnCl}_4\{\text{o-C}_6\text{H}_4(\text{TeMe})_2\}]$ in CD$_2$Cl$_2$ solution at a) 300 K and b) 180 K
4.3. Conclusions

The products $[\text{SnX}_4(\text{Me}_2\text{Te})_2]$ (where $X = \text{Cl}$, $\text{Br}$ or $\text{I}$) arising from the reactions of $\text{SnX}_4$ with $\text{Me}_2\text{Te}$ and those with bidentate telluroethers, $[\text{SnX}_4(\text{MeTe(CH}_2)_3\text{TeMe})]$, $[\text{SnX}_4(\text{PhTe(CH}_2)_3\text{TePh})]$ and $[\text{SnX}_4(\sigma-\text{C}_6\text{H}_4(\text{TeMe})_2)]$ have been prepared. A detailed examination of the variable temperature $^1\text{H}$, $^{119}\text{Sn}$-$^1\text{H}$ and $^{125}\text{Te}$-$^1\text{H}$ NMR spectroscopy over the temperature range 300 – 180 K has been presented. These complexes are found to be poorly soluble, leading to the isolation of products that were not seen for the analogous thio- or selenoether systems. Conversely poor solubility means that very little NMR data were obtainable, although for $[\text{SnCl}_4(\sigma-\text{C}_6\text{H}_4(\text{TeMe})_2)]$ meso and DL diastereoisomers were observed at 180 K. The lack of data means that it is difficult to make qualitative observations, though it is still clear that the stability of these systems decreases with weakening Lewis acid, $\text{Cl} > \text{Br} > \text{I}$, and also that the telluroether complexes are less stable than the corresponding selenoethers.
4.4. **Observed Trends for Group 16 Complexes of Tin(IV) Halides**

In chapters 2, 3 and 4 a detailed study of the solution and solid state behaviours of the thio-, seleno- and telluro-ether complexes of the tin(IV) halides has been presented. As a consequence several trends become apparent.

Firstly no reaction was observed for any ligand with SnF$_4$. SnF$_4$ is a polymer consisting of SnF$_6$ octahedra with opposite trans edges shared, and shows poor solubility in non-coordinating solvents. The apparent lack of reactivity may therefore be attributed to kinetic factors or may be a consequence of the preference of the hard tin centre for bridging fluoride rather than the group 16 donors. It does react with some hard O- and N-donor ligands.\(^5\) We have shown that O-donor solvents such as Me$_2$CO or thf react with [SnCl$_4$(dithioether)], for example by partial displacement of the thioether donors. Of the five structurally characterised examples, three feature a retention of the SnF$_6$ octahedra observed for the free halide\(^6\) with only one uncharged octahedral complex with 2,2'-bipyridine.\(^9\)

The other three tin(IV) tetrahalides are molecular tetrahedra and thus react easily with donor ligands in non-coordinating solvents. The literature data on the coordination chemistry of these SnX$_4$ units show a clear trend in Lewis acidity: Cl > Br > I,\(^10\) and consequently relatively few complexes of SnI$_4$ are known. Indeed a search of the CCDB for structurally characterised examples found only six examples,\(^11\)-\(^16\) of which one is the sulfoxide discussed in chapter 2 of this study,\(^16\) and all feature harder N- or O-donors. Our solution and solid state data on the thio-, seleno- and telluro-ether adducts clearly supports this trend and demonstrates that the Sn-E (E = S, Se or Te) interactions become weaker as the halogen becomes heavier.

Turning to trends with changes of the group 16 donors. The solution NMR spectroscopic data shows the Sn-E interaction is strongest in thioether adducts, rather weaker in selenoethers, while the telluroether complexes are extensively dissociated in solution. Indeed, as discussed above, it appears that it is the poor solubility of certain [SnX$_4$(ditelluroether)] species which permits their isolation as solids.

Examination of the effect of varying the ligand architecture shows that, as expected, the phenyl substituted ligands are weaker donors than their methyl substituted analogues. A similar conclusion was drawn for R$_2$E complexes of SnX$_4$ by Merbach et al.\(^17\) and Abel et al.\(^18\)

The interdonor linkage also influences the solution characteristics of the SnX$_4$ adducts and, as discussed above, the complexes involving aliphatic linkages show...
decreasing stability with chelate ring-size: $5 > 6 > 4$, and thus the successful isolation of complexes involving four membered chelate rings was unexpected and analogous species have not been identified in transition metal chemistry. The $\alpha$-phenylene linkage allows relatively straightforward isolation of adducts and this may be attributed to the $\alpha$-phenylene effect. Additionally these ligands facilitate increased solubility of the adducts and hence allow easier crystallisation of the products.

The variable temperature NMR spectroscopic studies have shown that at room temperature reversible ligand dissociation is rapid on the NMR timescales, and presumably occurs via reversible ring-opening. Experiments with added ligand show rapid intermolecular exchange. At low temperatures the NMR spectra of certain systems show exchange is slow. In these systems at low temperature we also observe slow pyramidal inversion and separate resonances for the invertomers for the invertomers are clearly evident. Upon warming these solutions it appears that onset of rapid pyramidal inversion and dissociation occurs within similar temperature ranges and hence quantitative measurements of these processes are not possible.
4.5. Experimental

The tin(IV) chloride, bromide and iodide were purchased from Aldrich Chemicals. The ligands Me₂Te, MeTe(CH₂)₃TeMe, PhTe(CH₂)₃TePh and o-C₆H₄(TeMe)₂ were prepared by following literature methods.²²

Tin(IV) halides and telluroether compounds are extremely moisture sensitive, therefore all of the reactions were carried out under an atmosphere of dry nitrogen, using standard Schlenk, vacuum-line and dry box techniques.

Single Crystal X-ray Diffraction

Single crystals of [SnCl₄{o-C₆H₄(TeMe)₂}] and [SnBr₄{o-C₆H₄(TeMe)₂}] were obtained from a solution of the appropriate complex in CH₂Cl₂. The compounds were extremely sensitive to hydrolysis on exposure to moist air. Therefore, in each case the selected crystal was coated with mineral oil, mounted on a glass fibre using silicone grease as adhesive, and immediately placed in a stream of cold nitrogen gas. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low temperature attachment operating at 150 K, using graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å), T = 150 K, ω-2θ scans. The intensities of three standard reflections were monitored every 150 reflections. No significant crystal decay or movement was observed. As there were no identifiable faces for [SnCl₄{o-C₆H₄(TeMe)₂}] the raw data were corrected for absorption using psi-scans. The weighting scheme \( w^{-1} = σ^2(F) \) gave satisfactory agreement analyses in each case.

The structures were solved by direct methods,²¹ and then developed by iterative cycles of full-matrix least-squares refinement (based on \( F \)) and difference Fourier syntheses which located all non-H atoms in the asymmetric unit.²² For [SnBr₄{o-C₆H₄(TeMe)₂}] an empirical absorption correction using DIFABS²³ was applied to the raw data at isotropic convergence, as psi scans did not provide a satisfactory absorption correction. All non-H atoms in the structures were refined anisotropically (with the exception of [SnBr₄{o-C₆H₄(TeMe)₂}] for which C(4) was refined isotropically since anisotropic refinement resulted in this atom becoming non-positive definite, probably a result of an imperfect absorption correction), and H atoms were placed in fixed, calculated positions with \( d(C-H) = 0.96 \) Å. Crystallographic data are presented in Table 4.5.
### Table 4.5. Crystallographic Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$[\text{SnCl}_4{\text{Q-C}_6\text{H}_4(\text{TeMe})_2}}]$</th>
<th>$[\text{SnBr}_4{\text{Q-C}_6\text{H}_4(\text{TeMe})_2}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{CsH}_2\text{SnTe}_2$</td>
<td>$\text{CsH}_2\text{Br}_2\text{SnTe}_2$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>621.87</td>
<td>799.67</td>
</tr>
<tr>
<td>Colour, morphology</td>
<td>Yellow, column</td>
<td>Red-brown, block</td>
</tr>
<tr>
<td>Crystal dimensions/mm</td>
<td>0.40 x 0.15 x 0.10</td>
<td>0.30 x 0.20 x 0.20</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
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<td>$\text{P2}_1/\text{m}$</td>
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<tr>
<td>$a/\text{Å}$</td>
<td>8.064(3)</td>
<td>6.829(9)</td>
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<tr>
<td>$b/\text{Å}$</td>
<td>14.362(2)</td>
<td>11.50(1)</td>
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<tr>
<td>$c/\text{Å}$</td>
<td>13.549(2)</td>
<td>10.23(1)</td>
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<tr>
<td>$\beta/\text{°}$</td>
<td>102.10(1)</td>
<td>100.5(1)</td>
</tr>
<tr>
<td>$U/\text{Å}^3$</td>
<td>1534.3(6)</td>
<td>790(1)</td>
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<td>$Z$</td>
<td>4</td>
<td>2</td>
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<td>HKL limits</td>
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<td>$F(000)$</td>
<td>1120</td>
<td>704</td>
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<tr>
<td>$D_2/\text{g cm}^{-3}$</td>
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<td>$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$</td>
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<td>153.52</td>
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<td>Transmission factors</td>
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<td>1.000, 0.410</td>
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<td>(max. and min.)</td>
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<tr>
<td>No. of unique obs. reflections</td>
<td>2834</td>
<td>1482</td>
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<tr>
<td>$R_{\text{int}}$ (based on $F^2$)</td>
<td>0.028</td>
<td>0.051</td>
</tr>
<tr>
<td>Unique obs. reflections with $</td>
<td>F_o</td>
<td>&gt; 2.0\sigma(</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>136</td>
<td>68</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.33</td>
<td>2.67</td>
</tr>
<tr>
<td>$R(F_o)$</td>
<td>0.031</td>
<td>0.039</td>
</tr>
<tr>
<td>$R_w(F_o)$</td>
<td>0.035</td>
<td>0.043</td>
</tr>
<tr>
<td>Max. residual peak/eÅ$^{-3}$</td>
<td>1.60</td>
<td>1.70</td>
</tr>
<tr>
<td>Max. residual trough/eÅ$^{-3}$</td>
<td>-0.84</td>
<td>-1.90</td>
</tr>
</tbody>
</table>

\[
R = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)/\sum |F_{\text{obs}}|}{\sum |F_{\text{obs}}|}
\]
\[
R_w = \frac{\sqrt{\sum w_i(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}/\sum w_i|F_{\text{obs}}|^2}}{\sum w_i|F_{\text{obs}}|^2}
\]
\[
\text{GOF} = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)/\sigma_i^2}{(n - m) \approx 1}
\]
Complex Synthesis

**[SnCl₄(Me₂Te)₂]**

Dimethyl telluride (0.32 g, 2 mmol) was dissolved in anhydrous, degassed CH₂Cl₂ (5 cm³) in a 3-neck RB flask under an atmosphere of dry N₂ and the solution further degassed. Addition of SnCl₄ (0.26 g, 1 mmol) to the solution gave immediate formation of a yellow precipitate which was filtered off and dried in vacuo. Found: C, 8.6; H, 2.3. Calculated for C₄H₁₂Cl₄Te₂Sn: C, 8.3; H, 2.1 %. IR spectrum (nujol mull) v/cm⁻¹ (Sn-Cl): 312. ¹H NMR (CD₂Cl₂): δ 3.0 (s) (300 K); 3.04, 3.06 (180 K).

**[SnBr₄(Me₂Te)₂]**

A saturated solution of SnBr₄ (0.44 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³) was added dropwise to a solution of dimethyl telluride (0.32 g, 2 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³). The complex formed as a fawn powder which was filtered off and dried in vacuo. Found: C, 6.7; H, 1.7. Calculated for C₄H₁₂Br₄Te₂Sn: C, 6.4; H, 1.6 %. IR spectrum (nujol mull) v/cm⁻¹ (Sn-Br): 220. ¹H NMR (CD₂Cl₂, 300 K): δ 2.8 (s).

**[SnCl₄{MeTe(CH₂)₃TeMe}]**

SnCl₄ (0.26 g, 1 mmol) was added to a solution of MeTe(CH₂)₃TeMe (0.32 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (10 cm³). The complex precipitated immediately as a yellow powder which was filtered off and dried in vacuo. Found: C, 9.9; H, 2.0. Calculated for C₅H₁₃Cl₄Te₂Sn: C, 10.2; H, 2.0 %. IR spectrum (nujol mull) v/cm⁻¹ (Sn-Cl): 317, 313, 309 and 305.

**[SnCl₄{PhTe(CH₂)₃TePh}]**

SnCl₄ (0.26 g, 1 mmol) was added to a solution of PhTe(CH₂)₃TePh (0.45 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (10 cm³). The complex precipitated immediately as a red-brown powder which was filtered off and dried in vacuo. Found: C, 25.7; H, 2.5. Calculated for C₁₅H₁₆Cl₄Te₂Sn: C, 25.5; H, 2.3 %. IR spectrum (nujol mull) v/cm⁻¹ (Sn-Cl): 332, 321, 314 and 309.
Chapter 4  

Group 14 Halide Complexes With Mono- and Bidentate Telluroethers

\[ \text{[SnCl}_4\{\sigma-\text{C}_6\text{H}_4\text{(TeMe)}_2\}] \]

SnCl\(_4\) (0.26 g, 1 mmol) was added to a solution of \(\sigma-\text{C}_6\text{H}_4\text{(TeMe)}_2\) (0.36 g, 1 mmol) in anhydrous, degassed CH\(_2\)Cl\(_2\) (10 cm\(^3\)). The complex formed as a white crystalline precipitate which was filtered off and dried \textit{in vacuo}. Found: C, 15.4; H, 1.7. Calculated for C\(_8\)H\(_{10}\)Cl\(_4\)Te\(_2\)Sn: C, 15.4; H, 1.6 %. IR spectrum (nujol mull) v/cm\(^{-1}\) (Sn-Cl): 315, 304, 296 and 284. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 2.45 (s, 3 H), 7.3, 7.7 (2 H) (300 K); 2.61, 2.71, 7.0-7.7 (180 K).

\[ \text{[SnBr}_4\{\text{MeTe(CH}_2)_3\text{TeMe}\}] \]

A saturated solution of SnBr\(_4\) (0.44 g, 1 mmol) in anhydrous, degassed CH\(_2\)Cl\(_2\) (5 cm\(^3\)) was added dropwise to a solution of MeTe(CH\(_2\)_3TeMe (0.32 g, 1 mmol) in anhydrous, degassed CH\(_2\)Cl\(_2\) (5 cm\(^3\)). The complex precipitated immediately as a yellow powder which was filtered off and dried \textit{in vacuo}. Found: C, 8.1; H, 2.2; Br, 42.1. Calculated for C\(_5\)H\(_{14}\)Br\(_4\)Te\(_2\)Sn: C, 7.9; H, 1.6; Br, 41.7 %. IR spectrum (nujol mull) v/cm\(^{-1}\) (Sn-Br): 219, 217, 212 and 210.

\[ \text{[SnBr}_4\{\text{PhTe(CH}_2)_3\text{TePh}\}] \]

A saturated solution of SnBr\(_4\) (0.44 g, 1 mmol) in anhydrous, degassed CH\(_2\)Cl\(_2\) (5 cm\(^3\)) was added dropwise to a solution of PhTe(CH\(_2\)_3TePh (0.45 g, 1 mmol) in anhydrous, degassed CH\(_2\)Cl\(_2\) (5 cm\(^3\)). The complex precipitated immediately as a brown powder which was filtered off and dried \textit{in vacuo}. Found: C, 19.9; H, 1.9; Br, 37.2. Calculated for C\(_{15}\)H\(_{16}\)Br\(_4\)Te\(_2\)Sn: C, 20.4; H, 1.8; Br, 36.0 %. IR spectrum (nujol mull) v/cm\(^{-1}\) (Sn-Br): 218, 215, 213 and 207.

\[ \text{[SnBr}_4\{\sigma-\text{C}_6\text{H}_4\text{(TeMe)}_2\}] \]

A saturated solution of SnBr\(_4\) (0.44 g, 1 mmol) in anhydrous, degassed CH\(_2\)Cl\(_2\) (5 cm\(^3\)) was added dropwise to a solution of \(\sigma-\text{C}_6\text{H}_4\text{(TeMe)}_2\) (0.36 g, 1 mmol) in anhydrous, degassed CH\(_2\)Cl\(_2\) (5 cm\(^3\)). The complex formed as a dark brown crystalline precipitate which was filtered off and dried \textit{in vacuo}. Found: C, 12.3; H, 1.5; Br, 40.3. Calculated for C\(_8\)H\(_{10}\)Br\(_4\)Te\(_2\)Sn: C, 12.3; H, 1.3; Br, 39.9 %. IR spectrum (nujol mull) v/cm\(^{-1}\) (Sn-Br): 218, 216, 214 and 207. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 2.4 (13 H), 7.3, 7.7 (2 H) (300 K); 2.6, 7.5, 7.65 (180 K).
Chapter 4  Group 14 Halide Complexes With Mono- and Bidentate Telluroethers

[SnI₄{MeTe(CH₂)₃TeMe}]

A saturated solution of SnI₄ (0.63 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³) was added dropwise to a solution of MeTe(CH₂)₃TeMe (0.32 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³). The complex precipitated immediately as a brown powder which was filtered off and dried \textit{in vacuo}. Found: C, 6.5; H, 1.5; I, 51.42. Calculated for C₅H₁₂I₄Te₂Sn: C, 6.3; H, 1.27; I, 53.23 %.

[SnI₄{PhTe(CH₂)₃TePh}]

A saturated solution of SnI₄ (0.63 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³) was added dropwise to a solution of PhTe(CH₂)₃TePh (0.45 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³). A pale brown precipitate forms immediately, which was filtered off and dried \textit{in vacuo}. Found: C, 17.1; H, 1.7. Calculated for C₁₅H₁₆I₄Te₂Sn: C, 16.8; H, 1.3 %.

[SnI₄{o-C₆H₄(TeMe)₂}]

A saturated solution of SnI₄ (0.63 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³) was added dropwise to a solution of o-C₆H₄(TeMe)₂ (0.36 g, 1 mmol) in anhydrous, degassed CH₂Cl₂ (5 cm³). A fawn coloured precipitate forms immediately. Further precipitate is formed on reducing the volume \textit{in vacuo} and this is filtered off and dried \textit{in vacuo}. Found: C, 10.1; H, 1.3. Calculated for C₉H₁₀I₄Te₂Sn: C, 9.72; H, 1.01 %.
References


22 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.

Chapter 5

Tin(IV) Halide Complexes of Phosphine, Arsine and Phosphine Oxide Ligands
5.1. Introduction

In chapters 2, 3 and 4 the first detailed studies of group 14 halide complexes of mono- and bidentate thio-, seleno- and telluroether ligands were described. In contrast the complexes formed with the group 15 ligands has been studied more extensively.

Tin(IV) halide complexes of group 15 donors have been known for over 50 years.\(^1\)\(^-\)\(^9\) A range of phosphine and diphosphine complexes have been prepared and characterised by vibrational and Mössbauer spectroscopy and X-ray crystallography.\(^1\)\(^-\)\(^9\) As might be expected by analogy with the results of our studies of the tin(IV) complexes of the group 16 donors, complexes are formed easily with the stronger σ-donor phosphines. Direct reaction of SnX\(_4\) (where X = Cl or Br) with ligands of the type R\(_3\)P in solution readily forms the 1:2 [SnX\(_4\)(R\(_3\)P)\(_2\)] complex. Vibrational spectroscopic studies concluded\(^10\) that the complexes existed primarily as the trans isomers in the solid state. This assignment was confirmed by the single crystal X-ray diffraction analysis of trans-[SnCl\(_4\)(Et\(_3\)P)\(_2\)]\(^11\) (Figure 5.1).

Figure 5.1 View of the molecular structure of trans-[SnCl\(_4\)(Et\(_3\)P)\(_2\)] (taken from ref. 11)
The studies also showed that while complexes of SnI₄ were formed they were too unstable to isolate from these reactions. The air sensitive complex trans-[SnI₄(Pr₃P)₂] (Figure 5.2) has been isolated and structurally characterised, but from the reaction of tin powder with Pr₃PI₂ in diethyl ether. These findings are consistent with the trend in SnX₄ Lewis acidity: Cl > Br > I, seen in chapters 2, 3 and 4 and literature data.

Figure 5.2 View of the molecular structure of trans-[SnI₄(Pr₃P)₂] (taken from ref. 7)

Surprisingly few studies have reported multinuclear NMR spectroscopic data. The 1:2 tin(IV) halide complexes with monodentate phosphines have been examined by $^{31}$P-{¹H} and $^{119}$Sn-{¹H} NMR spectroscopy by Colton et al. and McFarlane et al. and Malone et al. All studies conclude that the trans isomer is the predominant species in solution. Malone and Mann note that the observed trend of a large $^2J(^{31}P-^{31}P)$ for trans configurations...
of transition metal complexes with phosphines does not extend to these octahedral tin(IV) complexes. Further to this, McFarlane et al.\textsuperscript{15} also note that the trans coupling for tin(IV) complexes is of opposite sign to that usually found in the transition metal case. They also found that while for transition metal complexes the $\mathcal{J}(M-31P)$ is determined by the trans influence of groups trans to the phosphorus donor, for these octahedral tin(IV) complexes it is the nature of the groups cis to the phosphorus donor which governs the size of the coupling.

The complexes of bidentate phosphines of the tin(IV) halides, analogous to the group 16 systems studied in chapters 2, 3 and 4, have not been studied in as much detail as the monodentate systems. In the solid state Sarikhaya\textsuperscript{9} has used vibration spectroscopy to examine a range of SnX$_4$ complexes with bidentate phosphines, R$_2$P(CH$_2$)$_n$PR$_2$ (where R = Me, Et or Ph for n = 2; R = Me or Et for n = 3). The IR spectra of these species exhibit four Sn-X bands consistent with $C_{2v}$ symmetry and are analogous to the chelate structures seen for the equivalent group 16 bidentate ligand complexes in chapter 2, 3 and 4. The single crystal X-ray analysis of cis-[SnCl$_4$(dppe)] (where dppe = 1,2-bis(diphenylphosphino)ethane) by Kunkel and Dehnicke\textsuperscript{8} confirms this assignment. Dakternieks et al.\textsuperscript{18} have also examined the complex formed between Ph$_2$PCH$_2$PPh$_2$ (dppm) and SnCl$_4$ and found that a chelate is not formed but rather the 1:2 complex is formed with two mutually trans dppm ligands. The $^{31}$P-{$^1$H} NMR spectra of various mixtures of SnX$_4$ (X = Cl or Br) and Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1 - 4) have been studied \textit{in situ} by Petrosyan \textit{et al.}\textsuperscript{14} but a number of their results would suggest decomposition of the complexes with the formation of phosphine oxides. Complexes of SnI$_4$ with group 15 bidentate ligands have been produced \textit{in situ}\textsuperscript{5} but have proved too unstable to be isolated as solids.

As for the phosphines a good deal of work has been done examining the complexes of the tin(IV) halides with monodentate arsines\textsuperscript{1,5,6,19,20} using a combination of IR and $^{119}$Sn Mössbauer spectroscopic techniques. The results of these studies again confirm the expected trans isomer as the predominant species in the 1:2 [SnX$_4$(R$_3$As)$_2$] systems. Very few examples of bidentate arsine complexes with SnX$_4$ have been reported. Both involve $\sigma$-phenylene backboned ligands, $\sigma$-C$_6$H$_4$(AsMe$_2$)$_2$\textsuperscript{1} and $\sigma$-C$_6$H$_4$(AsEt$_2$)$_2$,\textsuperscript{21} and are assigned as cis coordinated chelates on the basis of vibrational spectroscopy. No structural analyses have been carried out on either the mono- or bidentate arsine complexes.
5.2 Results & Discussion

5.2.1 Synthesis and Properties of Me₃P Complexes of SnX₄

The complexes [SnX₄(Me₃P)₂] (X = Cl, Br or I) have been prepared by reaction of the appropriate SnX₄ with two molar equivalents of Me₃P in thoroughly degassed, anhydrous CH₂Cl₂. The solids formed are hydrolysed easily, even the briefest exposure to the laboratory atmosphere causes oxidation forming the phosphine oxide complex. All complexes were therefore stored and handled in a dinitrogen filled dry-box. The far-IR spectrum of the chloride complex shows one broad peak at 321 cm⁻¹ for v(SnCl) probably corresponding to the trans isomer (D₄h) being the principal isomer present in the solid state, consistent with the conclusions of previous studies on this compounds.⁹ The same observation is made for the bromide species with a broad band observed at 220 cm⁻¹, again in agreement with previous studies.⁹ Satisfactory elemental analyses were obtained for all species. IR spectroscopic and analytical data are presented in Table 5.1.

Table 5.1. Analytical and Spectroscopic data for [SnX₄(Me₃P)₂] complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>%C ⁸</th>
<th>%H ⁸</th>
<th>v(Sn-X) (cm⁻¹)</th>
<th>¹H NMR ⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄(Me₃P)₂]</td>
<td>White</td>
<td>17.1(17.5)</td>
<td>4.3(4.4)</td>
<td>321</td>
<td>1.83(m)</td>
</tr>
<tr>
<td>[SnBr₄(Me₃P)₂]</td>
<td>Pale yellow</td>
<td>11.9(12.2)</td>
<td>3.2(3.1)</td>
<td>220</td>
<td>1.50(m)</td>
</tr>
<tr>
<td>[SnI₄(Me₃P)₂]</td>
<td>Deep yellow</td>
<td>9.1(9.3)</td>
<td>2.5(2.3)</td>
<td>-</td>
<td>1.56(m)</td>
</tr>
</tbody>
</table>

⁸ Calculated values in parentheses
⁹ Nujol mulls.
  c. CDCl₃ solution at 300 K
5.2.2 Variable Temperature $^{31}\text{P}-\{^1\text{H}\}$ and $^{119}\text{Sn}-\{^1\text{H}\}$ NMR Spectroscopy

The complexes proved poorly soluble in CD$_2$Cl$_2$ necessitating long accumulation times. $^1\text{H}$ NMR spectroscopic data are presented in Table 1, $^{31}\text{P}-\{^1\text{H}\}$ and $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectroscopic data are presented in Table 5.2. [SnCl$_4$(Me$_3$P)$_2$] exhibits a single resonance in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum (Figure 5.3a, $\delta = 6.8$ ppm, $^1J(31\text{P}-117/119\text{Sn}) = 2720$ Hz) indicating that only a single isomer is present in solution. As in the cases of the analogous group 16 ligands coordinating solvents were not used as they were found to partially displace the ligands in solution.$^{22}$ However, in a freshly prepared MeNO$_2$ solution of [SnCl$_4$(Me$_3$P)$_2$] the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum (Figure 5.3b) revealed two isomers in the approximate ratio 1:2, the minor isomer has $\delta = 8.0$ and the major isomer $\delta = 3.6$ ppm. Significantly, the minor isomer has a $^1J(31\text{P}-117/119\text{Sn})$ coupling of the same values to that observed in CD$_2$Cl$_2$, 2720 Hz, and is therefore assigned as the same form. The same MeNO$_2$ solution in the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectrum has two triplets at $\delta -646$ and $-630$ ppm which have $^1J(119\text{Sn}-31\text{P})$ couplings which can be correlated with those in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum. On standing the resonance of the isomer with $\delta = 8.0$ diminishes and a new resonance at $\delta = 39.5$ appears, assigned to the formation of the phosphine oxide. The two resonances are assigned as trans and cis geometrical isomers based on the relative magnitude of the coupling constants.$^{15}$ Cis-trans isomerisation appears slow at 300 K on the NMR timescale. The fact that two isomers are observed for the solution in MeNO$_2$ and only the trans isomer in CH$_2$Cl$_2$ may be due to solvent dependent isomerisation, but is more likely a consequence of the poor solubility of the cis isomer in chlorocarbon solvents.

This poor solubility is also found for the SnBr$_4$ complex, [SnBr$_4$(Me$_3$P)$_2$], in CH$_2$Cl$_2$ but far better solubility is again achieved in MeNO$_2$. At 300 K a single resonance is seen in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum at $\delta -3.0$ ppm with no evident $^{117/119}\text{Sn}$ satellites. Cooling the solution to 250 K resulted in only a slight shift to $\delta -2.6$ ppm due to temperature effects and still no $^{117/119}\text{Sn}$ satellites observed. No resonances are observed over the same range in the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectrum. It seems likely that the observed resonance in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum arises from the trans isomer, and the absence of $^1J(31\text{P}-119\text{Sn})$ couplings or any resonances in the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectrum reflects rapid reversible ligand dissociation. The limited temperature range of MeNO$_2$ (m.p. $-29$ °C) prevents the lower temperature studies that proved effective for studying the analogous group 16 donor systems (chapters 2-4).
Figure 5.3. 

$^3$P-¹H] NMR Spectra of $[SnCl_4(Me_3P)_2]$ at 300 K in a) CDCl$_3$/CH$_2$Cl$_2$ and b) (CD$_3$)$_2$CO/MeNO$_2$ solution.
Table 5.2. $^{31}$P-{$^1$H} and $^{119}$Sn-{$^1$H} NMR data for [SnX₄(Me₃P)₂] complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ($^{31}$P-{$^1$H})</th>
<th>δ($^{119}$Sn-{$^1$H})</th>
<th>$^1J(^{119}$Sn-$^{31}$P)</th>
<th>Solvent</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄(Me₃P)₂]</td>
<td>(trans) 6.8 ppm</td>
<td>n.o.</td>
<td>2720 Hz</td>
<td>CH₂Cl₂</td>
<td>300 K</td>
</tr>
<tr>
<td>[SnCl₄(Me₃P)₂]</td>
<td>(cis) 3.6 ppm</td>
<td>-630 ppm</td>
<td>2190 Hz</td>
<td>MeNO₂</td>
<td>300 (Sn at 250 K)</td>
</tr>
<tr>
<td>[SnBr₄(Me₃P)₂]</td>
<td>(trans) -3.0 ppm</td>
<td>n.o.</td>
<td>2768 Hz</td>
<td>MeNO₂</td>
<td>300 (Sn at 250 K)</td>
</tr>
<tr>
<td>[SnI₄(Me₃P)₂]</td>
<td>(trans) -3.7 ppm</td>
<td>n.o.</td>
<td>n.o.</td>
<td>MeNO₂</td>
<td>300</td>
</tr>
</tbody>
</table>

a. Samples made up in dried solvents and run immediately.
b. Relative to neat external 85 % H₃PO₄.
c. Relative to neat external SnMe₄.
d. ± 6 Hz.

Similar results were observed for [SnI₄(Me₃P)₂] with a single resonance observed at δ -3.5 ppm in the $^{31}$P-{$^1$H} NMR spectrum (Figure 5.4), but no resonances in the $^{119}$Sn-{$^1$H} NMR spectrum in the range studied (300-250 K). A second resonance was present in the $^{31}$P-{$^1$H} NMR spectrum at δ 59 ppm, attributed to the formation of the phosphine oxide. This resonance was observed to grow rapidly with time as the complex decomposed.
Figure 5.4. $^{31}$P-$^1$H NMR spectrum of [SnI$_4$(Me$_3$P)$_2$] in CDCl$_3$/MeNO$_2$ solution at 300 K
5.2.3. Synthesis and Properties of Bidentate Phosphine Complexes of SnX₄

A range of complexes of type [SnX₄(L-L)] (where X = Cl, Br or I; L-L = \(\text{Me}_2\text{P(CH}_2\text{)}_2\text{PMe}_2\) (dmpe), \(\text{Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2\) (dppe) and \(\alpha\text{-C}_6\text{H}_4\text{(PPh}_2\text{)}_2\)) have been isolated from reaction in \(\text{CH}_2\text{Cl}_2\). In most cases the poor solubility of the SnX₄-diphosphine complexes meant that the products formed immediately from solution as powdered precipitates, the exception being for the SnI₄ complex of \(\alpha\text{-C}_6\text{H}_4\text{(PPh}_2\text{)}_2\) where the reaction formed a dark red solution with a solid isolated by removal of the solvent \textit{in vacuo}. Due to the extreme moisture sensitivity of the tin(IV) halides and phosphines when in solution, all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. As for the [SnX₄L₂] systems these complexes prove very easily hydrolysed.

IR spectra of the SnCl₄ complexes formed all showed the expected four \(\nu\) (Sn-Cl) bands (theory: \(2A_1 + B_1 + B_2\)) in the range 300 - 340 cm\(^{-1}\) consistent with \(C_{2v}\) symmetry.\(^9\) Similarly, the bromide systems also show four \(\nu\) (Sn-Br) bands in the range 190 – 230 cm\(^{-1}\).\(^9\) Satisfactory microanalyses were obtained for all products isolated. Analytical and spectroscopic data are presented in Table 5.3. Solids were also isolated from the reactions of \(\text{Ph}_2\text{PCH}_2\text{PPh}_2\) (dppm) and \(\text{Ph}_2\text{P(CH}_2\text{)}_3\text{PPh}_2\) (dppp) with SnX₄ (X = Cl or Br). However, while the solids are relatively stable once isolated, with microanalyses and IR spectra confirming 1:1 adduct formation, they proved extremely susceptible to oxidation in solution, with resonances in the \(^{31}\text{P}-\{^1\text{H}\}\) spectra only observed for decomposition products, and hence these complexes were not studied further.
### Table 5.3. Analytical and Spectroscopic data for [SnX₄(diphosphine)] complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>%Cᵃ</th>
<th>%H</th>
<th>ν(Sn-X)ᵇ (cm⁻¹)</th>
<th>¹H NMRᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄(dmpe)]</td>
<td>White</td>
<td>17.4(17.6)</td>
<td>4.1(3.9)</td>
<td>325, 310, 299, 283</td>
<td>2.18(m), 1.57(m)</td>
</tr>
<tr>
<td>[SnBr₄(dmpe)]</td>
<td>Yellow</td>
<td>12.0(12.3)</td>
<td>2.6(2.7)</td>
<td>206, 199, 196, 193</td>
<td>2.21(m), 1.60(m)</td>
</tr>
<tr>
<td>[SnI₄(dmpe)]</td>
<td>Dark red</td>
<td>9.3(9.3)</td>
<td>2.1(2.1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[SnCl₄(dppe)]</td>
<td>White</td>
<td>47.1(47.4)</td>
<td>3.8(3.7)</td>
<td>322, 313, 299, 294</td>
<td>2.2(m), 7.2-7.9(m)</td>
</tr>
<tr>
<td>[SnBr₄(dppe)]</td>
<td>Yellow</td>
<td>37.5(37.2)</td>
<td>2.7(2.9)</td>
<td>220, 217, 208, 205</td>
<td>2.2(m), 7.3-8.0(m)</td>
</tr>
<tr>
<td>[SnI₄(dppe)]</td>
<td>Dark red</td>
<td>30.3(30.5)</td>
<td>2.5(2.4)</td>
<td>-</td>
<td>2.25(m), 7.3-7.9(m)</td>
</tr>
<tr>
<td>[SnCl₄{α-C₆H₄(PPh₂)₂}]</td>
<td>White</td>
<td>51.1(51.0)</td>
<td>3.5(3.4)</td>
<td>320, 313, 310, 300</td>
<td>-</td>
</tr>
<tr>
<td>[SnBr₄{α-C₆H₄(PPh₂)₂}]</td>
<td>Yellow</td>
<td>40.3(40.6)</td>
<td>3.0(3.0)</td>
<td>217, 212, 208, 195</td>
<td>-</td>
</tr>
<tr>
<td>[SnI₄{α-C₆H₄(PPh₂)₂}]</td>
<td>Dark red</td>
<td>33.3(33.6)</td>
<td>2.4(2.3)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

ᵃ. Calculated value in parentheses
ᵇ. Nujol mulls.
ᶜ. CDCl₃ solution 300 K.
5.2.4. Variable Temperature $^{31}P-\{^1H\}$ and $^{119}Sn-\{^1H\}$ NMR Spectroscopy

$^{31}P-\{^1H\}$ and $^{119}Sn-\{^1H\}$ NMR spectroscopic data are presented in Table 5.4. $^1H$ NMR spectra were also collected for all the adducts formed but were relatively uninformative.

### Table 5.4. $^{119}Sn-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR data for $[SnX_4(diphosphine)]$ complexes

<table>
<thead>
<tr>
<th>Complex $^a$</th>
<th>$\delta({^1H})$</th>
<th>$\delta({^{119}Sn})$</th>
<th>$J({^{119}Sn}^{31}P)$</th>
<th>Solvent</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[SnCl_4(dmpe)]$</td>
<td>-20.9 (br)</td>
<td>-617 (t)</td>
<td>1080</td>
<td>Me$_2$CO</td>
<td>300</td>
</tr>
<tr>
<td>$[SnCl_4(dmpe)]$</td>
<td>-20.9</td>
<td>n.o.</td>
<td>1005</td>
<td>CH$_2$Cl$_2$</td>
<td>300</td>
</tr>
<tr>
<td>$[SnBr_4(dmpe)]$</td>
<td>-26.0</td>
<td>-1213 (t)</td>
<td>680</td>
<td>Me$_2$CO</td>
<td>300</td>
</tr>
<tr>
<td>$[SnBr_4(dmpe)]$</td>
<td>-28.5</td>
<td>n.o.</td>
<td>645</td>
<td>CH$_2$Cl$_2$</td>
<td>300</td>
</tr>
<tr>
<td>$[SnI_4(dmpe)]$</td>
<td>-40 (br)</td>
<td>-2425 (t)</td>
<td>n.o.</td>
<td>CH$_2$Cl$_2$</td>
<td>190</td>
</tr>
<tr>
<td>$[SnCl_4(dppe)]$</td>
<td>-18.8</td>
<td>-626 (t)</td>
<td>890</td>
<td>CH$_2$Cl$_2$</td>
<td>300</td>
</tr>
<tr>
<td>$[SnBr_4(dppe)]$</td>
<td>-31.0</td>
<td>-1212 (t)</td>
<td>460</td>
<td>CH$_2$Cl$_2$</td>
<td>250</td>
</tr>
<tr>
<td>$[SnI_4(dppe)]$</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>CH$_2$Cl$_2$</td>
<td>190</td>
</tr>
<tr>
<td>$[SnCl_4(\omega-C_6H_4(PPh_2)_2)]$</td>
<td>-13.9</td>
<td>-607.5 (t)</td>
<td>717</td>
<td>CH$_2$Cl$_2$</td>
<td>300</td>
</tr>
<tr>
<td>$[SnBr_4(\omega-C_6H_4(PPh_2)_2)]$</td>
<td>-24.2</td>
<td>-1218 (t)</td>
<td>305</td>
<td>CH$_2$Cl$_2$</td>
<td>250</td>
</tr>
<tr>
<td>$[SnI_4(\omega-C_6H_4(PPh_2)_2)]$</td>
<td>-52.5</td>
<td>n.o.</td>
<td>n.o.</td>
<td>CH$_2$Cl$_2$</td>
<td>190</td>
</tr>
</tbody>
</table>

$^a$. Samples made up in dried solvents and run immediately.

$^b$. Relative to external 85% H$_3$PO$_4$.

$^c$. Relative to neat external SnMe$_4$.

$^d$. ± 6 Hz.

$^e$. Resonances only observed in the presence of excess of the group 15 ligand.

The $^{31}P-\{^1H\}$ NMR spectrum of $[SnCl_4(\omega-C_6H_4(PPh_2)_2)]$ in anhydrous CH$_2$Cl$_2$ solution at 300 K shows a singlet at $\delta$ -13.9 ppm (Figure 5.5a). Satellites from $^{1}J(\{^{31}P-^{117}Sn\})$ and $^{1}J(\{^{31}P-^{119}Sn\})$ coupling are also clearly visible in the spectrum with values of 690 and 717 Hz respectively. This assignment is confirmed by the ratio between these two figures, $^{1}J(\{^{31}P-^{119}Sn\})/^{1}J(\{^{31}P-^{117}Sn\}) = 1.047$, which is consistent with the ratio between the magnetogyric ratios of the two tin isotopes, $\gamma(\{^{119}Sn\})/\gamma(\{^{117}Sn\}) = 1.046$. A triplet is observed in the $^{119}Sn-\{^1H\}$ NMR spectrum (Figure 5.5b) at $\delta$ -607.5 ppm,
Figure 5.5. a) $^{31}$P-$^1$H and b) $^{195}$Sn-$^1$H NMR spectra of [SnCl$_4$(o-C$_6$H$_4$(PPh$_3$)$_2$)] in CDCl$_3$/CH$_2$Cl$_2$ solution at 300 K.
within the range observed for octahedral SnCl₄ adducts found in chapters 2-4, with the
$^1J(^{119}\text{Sn}-^3\text{P})$ coupling of the same value as that seen in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum,
717 Hz. The spectrum remains relatively unchanged on cooling the solution to 190 K.
The same behaviour is seen in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum of [SnBr₄{α-C₆H₄(PPh₂)₂}] with a resonance seen at δ = 24.2 ppm with $^1J(^{119}\text{Sn}-^{177/119}\text{Sn})$ coupling with a value of
305 Hz, the spectrum is not sufficiently resolved to distinguish the $^{117}\text{Sn}$ and $^{119}\text{Sn}$
couplings. The $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectrum exhibits a triplet at δ = -1218 with $^1J(^{119}\text{Sn}-
^3\text{P})$ coupling matching that seen in the $^3\text{P}-\{^1\text{H}\}$ NMR spectrum. Once again cooling
the sample to 190 K has little effect on the spectrum. Neither the $^{31}\text{P}-\{^1\text{H}\}$ nor the
$^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectra obtained from [SnI₄{α-C₆H₄(PPh₂)₂}] exhibited any
resonances at 300 K in CH₂Cl₂ solution. On cooling the solution to ca. 230 K a singlet
becomes apparent in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum at δ = -53 ppm which sharpens on
cooling to 190 K. Even at this temperature tin satellites are not observed. However
since the line-width at this temperature is still > 200 Hz it is possible that the couplings
are obscured since the value of the $^{117/119}\text{Sn}^{-3}\text{P}$ couplings reduce rapidly with halide
Cl > Br, and the couplings for the iodide species may therefore be very small. No
$^{119}\text{Sn}-\{^1\text{H}\}$ NMR resonance was observed over the entire temperature range examined
(300 – 190 K). Comparison between these three complexes shows that dissociation in
the chloro- and bromo-complexes is minimal allowing $^{117/119}\text{Sn}^{-3}\text{P}$ couplings to be
seen even at 300 K. In comparison the iodo-complex is extremely labile in solution at
300 K, and remains so on the NMR timescale until ca. 230 K when a signal becomes
visible in the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum. It was also observed that the iodo-complex was
more prone to oxidation in solution, turning into the phosphine oxide rapidly.

Changing the ligand architecture from the rigid α-phenylene backbone to the
more flexible dimethylene backbone results in an increased tendency of the
[SnX₄(diphosphine)] complexes to reversibly dissociate ligand in solution. This
apparent stability in the α-phenylene complexes is attributed to the α-phenylene effect
observed by Warren and Bennett¹³ where energetically the rigid backbone resists
dissociation. The [SnX₄(dmpe)] complexes were very poorly soluble in CH₂Cl₂ such
that extremely long accumulations were required. Even then the $^{31}\text{P}-\{^1\text{H}\}$ spectra were
not clear and convincing $^{119}\text{Sn}-\{^1\text{H}\}$ resonances were not observed. Acetone offered
vastly improved solubility and the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectra observed were similar to
those obtained from CH₂Cl₂ solution (allowing for small solvent shifts), and resonances
were observed in the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectra. At 300 K the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum

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Figure 5.6. a) $^3$P$_1$-H (300 K) and b) $^{119}$Sn$^{-1}$H NMR spectra (270 K) of [SnCl$_4$(dmpe)] in (CD$_3$)$_2$CO solution.
of [SnCl₄(dmpe)] in acetone (Figure 5.6a) has a resonance at δ -20.9 ppm with $^1J(^{31}P - ^{117/119}Sn)$ coupling evident with a value of 1080 Hz. The same spectrum is observed in CH₂Cl₂ solution with $^1J(^{31}P - ^{117/119}Sn)$ coupling of 1005 Hz. In CH₂Cl₂ solution no resonance is observed at any temperature (300 - 190 K) in the $^{119}Sn \cdot \{^1H\}$ NMR spectrum. However, in Me₂CO solution at 270 K a resonance is observed at δ -617 ppm (Figure 5.6b), once again consistent with the observed range for octahedral complexes of SnCl₄, and does not arise from an SnCl₄ adduct with acetone as $^1J(^{19}Sn - ^{31}P)$ couplings of equal size to those in the $^{31}P \cdot \{^1H\}$ NMR spectrum are observed. The same behaviour is observed in [SnBr₄(dmpe)] with a triplet in the $^{31}P \cdot \{^1H\}$ NMR spectrum at δ -26.0 ppm in acetone solution (δ - 28.5 ppm in CH₂Cl₂ solution) with a clearly resolved $^1J(^{31}P - ^{117/119}Sn)$ coupling of value 680 Hz (645 Hz in CH₂Cl₂). Once again the effect of changing solvent in found with no resonance observed in the $^{119}Sn \cdot \{^1H\}$ NMR spectrum of the CH₂Cl₂ due to poor solubility, but a resonance observed from acetone solution at δ -1213 ppm. This is again consistent with the assigned ranges for octahedral SnBr₄ adducts observed previously (chapters 2-4) and with $^1J(^{19}Sn - ^{31}P)$ coupling corresponding to those of the $^{31}P \cdot \{^1H\}$ NMR spectra.

Decomposition of the iodo-complex, [SnI₄(dmpe)], is extremely rapid in solution aided by the high lability of the complex. At 300 K no resonances are observed for the adduct, though several weak signals are observed for decomposition products. After a short period a yellow precipitate is formed from the brown solution. In CH₂Cl₂ solution no resonances are observed at any temperature (300 - 190 K) in either the $^{31}P \cdot \{^1H\}$ or $^{119}Sn \cdot \{^1H\}$ NMR spectra. At 190 K in a Me₂CO solution with a 5-fold excess of ligand a broad resonance is observed at δ -40 ppm in the $^{31}P \cdot \{^1H\}$ NMR spectrum and a poorly defined triplet is seen in the $^{119}Sn \cdot \{^1H\}$ NMR spectrum at δ -2425 ppm. These values are consistent with the few resonances that were observed in the studies of group 16 systems, and the $^1J(^{119}Sn - ^{31}P)$ coupling of ca. 200 Hz is consistent with this coupling not being observed in the spectra of [SnI₄{ο-C₆H₄(PPh₂)₂}]. On warming to 230 K these signals are lost but reappear on recooling the solution, consistent with ligand dissociation becoming too rapid on the NMR timescale at this temperature.

The complex [SnCl₄(dppe)] is already known to contain a chelating diphosphine from the single crystal X-ray study by Kunkel et al.⁸ and the octahedral tin(IV) centre is confirmed in the $^{119}Sn \cdot \{^1H\}$ NMR spectrum (Figure 5.7b) of a solution in CH₂Cl₂ where a resonance is observed at δ -626 ppm with clearly resolved $^1J(^{119}Sn - ^{31}P)$ coupling of value 890 Hz. In the $^{31}P \cdot \{^1H\}$ NMR spectrum (Figure 5.7b) a clear
Figure 5.7. a) $^{31}\text{P}\{^1\text{H}\}$ (300 K) and b) $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum (250 K) of [SnCl$_4$(dppe)] in CDCl$_3$/CH$_2$Cl$_2$ solution.
resonance is observed at $\delta -18.8$ ppm with coupling present to both tin nuclei, $^1J(^{31}\text{P}-^{117}\text{Sn}) = 850$ and $^1J(^{31}\text{P}-^{119}\text{Sn}) = 890$ Hz. $^1J(^{31}\text{P}-^{117}\text{Sn})/^1J(^{31}\text{P}-^{119}\text{Sn}) = 1.047$. The bromo-complex, $[\text{SnBr}_4(\text{dppe})]$, was found to be very easily decomposed to the phosphine oxide in solution. The adduct was observed in a sample cooled to ca. 250 K at $\delta -31$ ppm with tin satellites observed on further cooling to 190 K of 460 Hz. In the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectrum no resonances were seen until the solution was cooled to 190 K when a triplet at $\delta -1212$ ppm is observed with corresponding $^1J(^{119}\text{Sn}-^{31}\text{P})$ of 460 Hz. The effect of altering ligand substituent has therefore increased the lability of the bromo-complex relative to the chloro-, consistent with the observations made previously (chapters 2-4). This trend is further continued for the iodo-complex. No resonances except those of decomposition products, such as phosphine oxides (e.g. $\delta 48$ ppm), are observed at any temperature (300 -190 K) in either the $^{31}\text{P}-\{^1\text{H}\}$ or the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectra, consistent with this complex still exchanging rapidly in solution.

In chapter 3 it was observed that the chelate-ring parameter, $\Delta R$ as first formulated by Garrou,\textsuperscript{24} for the selenoethers follows the trend of large positive values for five-membered chelate-rings and negative values for the more strained six-membered chelate-rings observed for analogous transition metal complexes.\textsuperscript{25} The data collected for $\text{cis-[SnCl}_4(\text{Me}_3\text{P})_2]$ and $[\text{SnCl}_4(\text{dmpe})]$ permits a similar calculation in this study. The coordination shift, $\Delta$, for $\text{cis-[SnCl}_4(\text{Me}_3\text{P})_2]$ is 64.6 ($\delta \text{cis-[SnCl}_4(\text{Me}_3\text{P})_2]$ = -61 ($\delta \text{ free Me}_3\text{P}$)) and $\Delta$ for $[\text{SnCl}_4(\text{dmpe})]$ is 28.5 ($\delta \text{free dmpe}$) giving a chelate-ring parameter of $-36.1$ for the five-membered chelate-ring in $[\text{SnCl}_4(\text{dmpe})]$. This is the opposite to the positive value that would be expected for a five-membered chelate-ring.\textsuperscript{24,25} The reason for this is not clear but similarly unexpected observations have been made by Schmidbaur et al.\textsuperscript{26} with an upfield coordination shift in the $^{31}\text{P}$ NMR spectrum of the $\alpha$-$\text{C}_6\text{H}_4(\text{PPh}_2)_2$ complex of indium(III) chloride rather than the normal downfield shift observed on complexation.\textsuperscript{25} The value of the chelate ring parameter is well established as an aid to assignment of structures in transition metal complexes.\textsuperscript{25} From our results and those of Schmidbaur et al.,\textsuperscript{26} it is clear that different effects are operating in main group compounds. Studies of other main group systems and theoretical work are needed before this highly unexpected observation can be explained.
5.2.5. Synthesis and Properties of Bidentate Arsine Complexes of SnX₄

A range of complexes of type [SnX₄(L-L)] (X = Cl, Br or I for L-L = O-C₆H₄(AsMe₂)₂ (diars); X = Cl or Br for L-L = Ph₂As(CH₂)₂AsPh₂ (dpae)) have been isolated from reaction in CH₂Cl₂. The adducts formed proved more soluble than those of [SnX₄(diphosphine)] with only the chloro-complexes precipitating from solution. The other complexes formed were isolated by slowly removing the solvent in vacuo until a precipitate was formed, which was then filtered and dried in vacuo. Given the extreme moisture sensitivity all reactions were carried out in rigorously anhydrous solvent under an atmosphere of dry dinitrogen using standard Schlenk techniques. The arsines are known not to oxidise as readily as the phosphines and while the solids formed appear less air- or moisture-sensitive than the analogous [SnX₄(diphosphine)] complexes all complexes were still stored in a dinitrogen dry-box. IR spectroscopy of the chloro- and bromo- complexes again suggests chelate formation with four v(Sn-X) bands observed, consistent with C₂ᵥ symmetry. Satisfactory elemental analyses were obtained for all solids formed. Analytical and spectroscopic data are presented in Table 5.5.

Table 5.5 Analytical and Spectroscopic data for Tin - Diarsine Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>%C a</th>
<th>%H</th>
<th>v(Sn-X)b (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄(diars)]</td>
<td>White</td>
<td>21.8(22.0)</td>
<td>3.0(3.0)</td>
<td>323, 315, 304, 300</td>
</tr>
<tr>
<td>[SnBr₄(diars)]</td>
<td>Yellow</td>
<td>16.9(16.6)</td>
<td>2.4(2.2)</td>
<td>217, 209, 195</td>
</tr>
<tr>
<td>[SnI₄(diars)]</td>
<td>Dark red</td>
<td>13.4(13.2)</td>
<td>2.0(1.8)</td>
<td>-</td>
</tr>
<tr>
<td>[SnCl₄(dpae)]</td>
<td>White</td>
<td>42.2(41.8)</td>
<td>3.4(3.2)</td>
<td>325, 317, 310, 303</td>
</tr>
<tr>
<td>[SnBr₄(dpae)]</td>
<td>Yellow</td>
<td>34.0(33.8)</td>
<td>2.7(2.6)</td>
<td>217, 212, 195</td>
</tr>
</tbody>
</table>

a. Calculated value in parentheses.
b. Nujol mulls.
5.2.6. Variable Temperature $^1$H and $^{119}$Sn-$^1$H NMR Spectroscopy

<table>
<thead>
<tr>
<th>Complex $^a$</th>
<th>$\delta(^1H)^b$ (ppm)</th>
<th>$\delta(^{119}Sn-^1H)^c$ (ppm)</th>
<th>Solvent</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl$_4$(diars)]</td>
<td>1.89(s), 7.7(m)</td>
<td>-675</td>
<td>CH$_2$Cl$_2$</td>
<td>300</td>
</tr>
<tr>
<td>[SnBr$_4$(diars)]</td>
<td>1.8(s), 7.6(m)</td>
<td>-1354</td>
<td>CH$_2$Cl$_2$</td>
<td>270</td>
</tr>
<tr>
<td>[SnI$_4$(diars)]</td>
<td>1.6(s), 7.5(br, m)</td>
<td>-2290</td>
<td>CH$_2$Cl$_2$</td>
<td>190</td>
</tr>
<tr>
<td>[SnCl$_4$(dpae)]</td>
<td>2.15(s), 7.3-7.8(m)</td>
<td>-662</td>
<td>CH$_2$Cl$_2$</td>
<td>250</td>
</tr>
<tr>
<td>[SnBr$_4$(dpae)]</td>
<td>2.2(s), 7.3-7.7(m)</td>
<td>-1368</td>
<td>CH$_2$Cl$_2$</td>
<td>200</td>
</tr>
</tbody>
</table>

$^a$ Samples made up in dried solvent and run immediately.  
$^b$ CDCl$_3$ solution.  
$^c$ Relative to neat external SnMe$_4$.

$^1$H and $^{119}$Sn-$^1$H NMR spectroscopic data are presented in Table 5.6. In the $^1$H NMR spectrum of [SnCl$_4$(diars)] in CH$_2$Cl$_2$ a sharp $\delta$(Me) resonance at 1.89 ppm is observed which shows a significant coordination shift from the free ligand ($\delta$ 1.2 ppm). The $^{119}$Sn-$^1$H NMR spectrum (Figure 5.8) shows a single resonance at $\delta$ -674 ppm that shows only a small temperature drift on cooling the solution to 190 K. The $^1$H NMR spectrum of [SnBr$_4$(diars)] exhibits a broad resonance at $\delta$ 1.6 ppm for $\delta$(Me) and a similarly broad feature for the aromatic resonances. Both are seen to sharpen on cooling to ca. 270 K. Similarly, no $^{119}$Sn-$^1$H resonance is observed at 300 K but at ca. 270 K a singlet is observed at $\delta$ -1354 ppm. The resonance is seen to drift only slightly to high frequency on cooling to 190 K. The data are consistent with some reversible ligand dissociation at ambient temperatures, which is slowed on cooling, consistent with the bromo-complexes being more labile in solution than the chloro-complex. Continuing this trend, no resonances are observed at any temperature (300 – 190 K) in the $^{119}$Sn-$^1$H NMR spectrum for the iodo-complex, [SnI$_4$(diars)], despite the solution being a deep red-brown colour. Similarly, the $^1$H NMR spectrum only exhibits broad resonances over the same range. When a 10-fold excess of diars ligand
is added to the solution a broad $^{119}\text{Sn}-\{^1\text{H}\}$ resonance is observed at $\delta -2290$ ppm. This is tentatively assigned to $[\text{SnL}_4(\text{diars})]$ as the resonance falls within the range of previous octahedral $[\text{SnL}_4(L-L)]$ complexes. The formation of an octahedral chelate complex was confirmed by an X-ray study (section 5.2.7) of crystals obtained from a CH$_2$Cl$_2$ solution. A further study of $[\text{SnCl}_4(\text{diars})]$ with a 10-fold excess of diars showed no change in the $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectrum over the range 300 - 190 K. This indicates that in marked contrast to the formation of dodecahedral $[\text{MX}_4(\text{diars})_2]^{n+}$ by several early transition metals (e.g. Ti(IV), Mo(IV), Nb(V) or Ta(V)),$^{27}$ eight-coordinate $[\text{SnCl}_4(\text{diars})_2]$ does not form with tin(IV).

**Figure 5.8.** $^{119}\text{Sn}-\{^1\text{H}\}$ NMR spectrum of $[\text{SnCl}_4(\text{diars})]$ in CDCl$_3$/CH$_2$Cl$_2$ solution at 240 K
Examining the complexes of dpae, which has dramatically different ligand architecture, there are some immediate observations. The complexes of SnCl₄ and SnBr₄ were isolable as solids, but although a mixture of SnI₄ and the ligand forms a very dark red solution in CH₂Cl₂, on concentration of the solution in vacuo inhomogeneous products were obtained. While these may contain the complex [SnI₄(dpae)] it was not possible to isolate it as a pure product. At 300 K a solution of [SnCl₄(dpae)] in CH₂Cl₂ has no resonances in the $^{119}$Sn-{$^1$H} NMR spectrum indicative of ligand dissociation at this temperature. Cooling the solution to ca. 270 K a weak resonance at $\delta$ -662 ppm is observed which resolves and sharpens at 250 K (Figure 5.9). Again consistent with previous results the bromo-complex, [SnBr₄(dpae)], was found to be more labile in solution such that no resonance is observed in the $^{119}$Sn-{$^1$H} NMR spectrum until ca. 200 K when a resonance is observed at $\delta$ -1368 ppm.

Figure 5.9. $^{119}$Sn-{$^1$H} NMR spectrum of [SnCl₄(dpae)] in CDCl₃/CH₂Cl₂ solution at 250 K
Red-brown crystals of [SnI₄(diars)] were obtained by slow evaporation of a CH₂Cl₂ solution. The structure is shown in Figure 5.10 and selected bond lengths (Å) and angles (°) are presented in Tables 5.7 and 5.8 respectively. The structure shows a distorted octahedral geometry at the tin composed of chelating diarsine and four iodines. All the (cis) I-Sn-I angles are greater than 90° (range 92.59(6) – 100.14(6)°) with the As-Sn-As angles of the chelate constrained to 78.47(7)°. This distortion is the same as was observed with the chelates of group 16 ligands (chapters 2-4) and common to all SnX₄ systems where the cis isomer is present. A search of the CCDC showed that this was the first structurally characterised example of a tin-arsine complex, and that prior to this structure only six other examples of SnI₄ adducts had been reported with one structure, cis-[SnI₄{η¹-O-MeS(O)(CH₂)₃SMe}₂], featuring previously in
this study (chapter 2). All the previous structures reported have featured harder O-,
N- or P-donors.\(^7\) The Sn-I distances present within this tin-arsine complex
(Sn-I\(_{trans}\) = 2.817(2), 2.860(2) \(\text{Å}\), Sn-I\(_{transAs}\) = 2.792(2), 2.787(2) \(\text{Å}\)) may be compared
with those in \textit{trans}-[SnI\(_4\)(Pr\(_3\)P)\(_2\)]\(^7\) (2.863(3), 2.872(3) \(\text{Å}\)), in \textit{cis}-[SnI\(_4\)(Ph\(_3\)PO)\(_2\)]\(^{30}\) (Sn-
I\(_{trans}\) 2.781(-), 2.810(-), Sn-I\(_{transO}\) 2.780(-), 2.861(-) \(\text{Å}\)), and in \textit{cis}-[SnI\(_4\){\(\eta^1\)-O-
MeS(O)(CH\(_2\))\(_3\)SMe}\(_2\)]\(^{32}\) (Sn-I\(_{trans}\) 2.762(2), 2.802(2), Sn-I\(_{transO}\) 2.788(2), 2.780(2) \(\text{Å}\)).

While no previous examples of tin-arsine complexes have been structurally
characterised to allow comparison of Sn-As distances, the Sn-As distances (2.716(2)
and 2.752(2) \(\text{Å}\)) are seen to be longer than the Sn-P distances of characterised tin-
phosphine complexes ([SnCl\(_4\){Ph\(_2\)P(CH\(_2\))\(_2\)PPh\(_2\)}],\(^8\) Sn-P = 2.679(2) and 2.653(2) \(\text{Å}\))
consistent with the increased radius of As over P. For example the same trend is
observed in Ni(III) systems with \(\omega\)-C\(_6\)H\(_4\)(PMe)\(_2\) (diphos)\(^{33}\) and diars.\(^{34}\) In
[NiCl\(_2\)(diars)\(_2\)][Cl]\(^{33}\) the Ni-As distances (2.340 and 2.345 \(\text{Å}\)) are seen to be \textit{ca.} 0.1 \(\text{Å}\)
longer than the Sn-P distances observed in [NiCl\(_2\)(diphos)\(_2\)][PF\(_6\)]\(^{34}\) (Ni-P = 2.255 \(\text{Å}\)).

\begin{table}[h]
\centering
\begin{tabular}{llllll}
I(1) & Sn & 2.859(2) & I(2) & Sn & 2.818(2) \\
I(3) & Sn & 2.792(2) & I(4) & Sn & 2.787(2) \\
Sn & As(1) & 2.716(2) & Sn & As(2) & 2.752(2) \\
As(1) & C(1) & 1.90(2) & As(1) & C(2) & 1.87(2) \\
As(1) & C(3) & 1.93(2) & As(2) & C(8) & 1.99(2) \\
As(2) & C(9) & 1.92(3) & As(2) & C(10) & 1.98(2) \\
\end{tabular}
\caption{Selected bond lengths (\(\text{Å}\)) with e.s.d.s for [SnI\(_4\)(diars)]}
\end{table}
Table 5.8. Selected bond angles (°) with e.s.d.s for [SnI₄(diars)]

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
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<td>I(1)</td>
<td>Sn</td>
<td>I(2)</td>
<td>169.76(6)</td>
<td>I(1)</td>
<td>Sn</td>
<td>I(3)</td>
<td>94.59(6)</td>
</tr>
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<td>Sn</td>
<td>I(4)</td>
<td>92.62(5)</td>
<td>I(1)</td>
<td>Sn</td>
<td>As(1)</td>
<td>85.97(6)</td>
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<td>Sn</td>
<td>As(2)</td>
<td>84.89(7)</td>
<td>I(2)</td>
<td>Sn</td>
<td>I(3)</td>
<td>93.17(6)</td>
</tr>
<tr>
<td>I(2)</td>
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<td>I(4)</td>
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<td>Sn</td>
<td>As(1)</td>
<td>87.77(6)</td>
</tr>
<tr>
<td>I(2)</td>
<td>Sn</td>
<td>As(2)</td>
<td>85.93(6)</td>
<td>I(3)</td>
<td>Sn</td>
<td>I(4)</td>
<td>100.15(6)</td>
</tr>
<tr>
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<td>Sn</td>
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<td>87.18(6)</td>
<td>I(3)</td>
<td>Sn</td>
<td>As(2)</td>
<td>165.61(7)</td>
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<tr>
<td>I(4)</td>
<td>Sn</td>
<td>As(1)</td>
<td>172.63(8)</td>
<td>I(4)</td>
<td>Sn</td>
<td>As(2)</td>
<td>94.24(7)</td>
</tr>
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<td>As(1)</td>
<td>C(1)</td>
<td>117.0(7)</td>
</tr>
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<td>C(2)</td>
<td>116.4(7)</td>
<td>Sn</td>
<td>As(1)</td>
<td>C(3)</td>
<td>108.8(5)</td>
</tr>
<tr>
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<td>As(2)</td>
<td>C(8)</td>
<td>107.1(6)</td>
<td>Sn</td>
<td>As(2)</td>
<td>C(9)</td>
<td>120.1(7)</td>
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<tr>
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<td>C(10)</td>
<td>116.2(7)</td>
<td></td>
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</tr>
</tbody>
</table>

5.2.8. Synthesis and Properties of o-C₆H₄(P(O)Ph₂)₂ Complexes of SnX₄

To verify that the complexes isolated with o-C₆H₄(PPh₂)₂ were not phosphine oxide complexes, the complexes of o-C₆H₄(P(O)Ph₂)₂ with SnX₄ (X = Cl, Br or I) were prepared. The ligand was easily obtained by iodine oxidation of the diphosphine, o-C₆H₄(PPh₂)₂, followed by base hydrolysis. The phosphine oxide is a white, air-stable solid which exhibits ν(P=O) as a very strong broad feature at 1200 cm⁻¹ and δ³¹P-{¹H} at 33.6 ppm in CH₂Cl₂ solution. The complexes were formed from direct reaction of ligand in CH₂Cl₂ solution with an equimolar solution of SnX₄. The chloro- and bromo-complexes, [SnX₄{o-C₆H₄(P(O)Ph₂)₂}] (X = Cl or Br), formed immediately as white and pale yellow precipitates respectively. The reaction of ligand with SnI₄ formed a dark red solution with the solid, [SnI₄{o-C₆H₄(P(O)Ph₂)₂}], isolated on removal of CH₂Cl₂ in vacuo. The effect of coordination to an SnX₄ acceptor is to lower ν(P=O) by
ca. 50-60 cm⁻¹. Satisfactory elemental analyses were obtained for all solids formed. Analytical and spectroscopic data are presented in Table 5.9.

Table 5.9. Analytical and Spectroscopic data for [SnX₄{o-C₆H₄(P(O)Ph₂)₂}] complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>%C</th>
<th>%H</th>
<th>v(Sn-X)ᵇ</th>
<th>v(P-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SnCl₄{o-C₆H₄(P(O)Ph₂)₂}]</td>
<td>White</td>
<td>49.0</td>
<td>3.2</td>
<td>318, 325(sh)</td>
<td>1152</td>
</tr>
<tr>
<td>[SnBr₄{o-C₆H₄(P(O)Ph₂)₂}]</td>
<td>Pale yellow</td>
<td>38.9</td>
<td>2.7</td>
<td>214(br)</td>
<td>1152</td>
</tr>
<tr>
<td>[SnI₄{o-C₆H₄(P(O)Ph₂)₂}]</td>
<td>Orange-red</td>
<td>32.8</td>
<td>2.3</td>
<td>-</td>
<td>1138</td>
</tr>
</tbody>
</table>

a. Calculated value in parentheses.

The problems of poor solubility associated with group 16 complexes of SnX₄ which had hindered the solution studies previously proved to be a problem again. The poor solubility of the chloro- and bromo-complexes meant long accumulations were necessary for the ³¹P-{¹H} NMR spectroscopic studies. ³¹P-{¹H} and ¹¹⁹Sn-{¹H} NMR spectroscopic data are presented in Table 5.10. At 300 K resonances at δ 41.6 and 42.4 ppm are observed in the ³¹P-{¹H} NMR spectra CH₂Cl₂ solutions of the chloro- and bromo-complexes respectively. Low temperature studies were precluded by precipitation of the complexes on cooling. The poor solubility also prevented ¹¹⁹Sn-{¹H} NMR spectra from being recorded. In contrast, the iodo-complex was found to be extremely soluble in CH₂Cl₂ and a resonance at δ 39.8 ppm is observed in the ³¹P-{¹H} NMR spectrum which is essentially unchanged on cooling the solution to 190 K. Even at this lowest temperature no ³¹P-¹¹⁷/¹¹⁹Sn satellites are observed about the ³¹P-{¹H} resonance and attempts to record ¹¹⁹Sn-{¹H} NMR spectra were unsuccessful. This almost certainly indicates that in solution reversible ring opening and/or dissociation are occurring at a rate too rapid to be observed on the NMR timescale. The results of the ³¹P-{¹H} NMR study that were obtained are sufficient to confirm the assignments made for the phosphine complexes were not for phosphine-oxide resonances. They
also confirm that it is these phosphine oxides that are formed when decomposition as a result of oxidation occurs in solution.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta(^{31}P{^1H})^a$ (ppm)</th>
<th>$\delta(^{19}Sn{^1H})$ (ppm)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[SnCl_4{\sigma-C_6H_4(P(O)Ph_2)}_2]$</td>
<td>42.4</td>
<td>n.o.</td>
<td>CDCl_3/CH_2Cl_2</td>
</tr>
<tr>
<td>$[SnBr_4{\sigma-C_6H_4(P(O)Ph_2)}_2]$</td>
<td>41.6</td>
<td>n.o.</td>
<td>CDCl_3/CH_2Cl_2</td>
</tr>
<tr>
<td>$[SnI_4{\sigma-C_6H_4(P(O)Ph_2)}_2]$</td>
<td>39.8</td>
<td>n.o.</td>
<td>CDCl_3/CH_2Cl_2</td>
</tr>
</tbody>
</table>

a. Relative to external 85 % H_3PO_4.

5.2.9. X-ray Structure of $[SnI_4\{\sigma-C_6H_4(P(O)Ph_2)\}_2]$]

Crystals of $[SnI_4\{\sigma-C_6H_4(P(O)Ph_2)\}_2]$ were first obtained by slow evaporation of a CH_2Cl_2 solution of $[SnI_4\{\sigma-C_6H_4(PPh_2)\}_2]$. The solution was prepared and stored inside a dinitrogen dry-box illustrating the extreme sensitivity of these complexes. The crystals were identified as phosphine oxide by comparison of the IR and $^{31}P\{^1H\}$ NMR spectra with those of the genuine complex prepared directly from $\sigma$-C_6H_4(P(O)Ph_2).

Two different crystalline forms of $[SnI_4\{\sigma-C_6H_4(P(O)Ph_2)\}_2]$ were obtained. Slow evaporation of the CH_2Cl_2 solution producing red crystals of the diphosphine dioxide complex as a 1:1 CH_2Cl_2 solvate (Figure 5.11) which had a monoclinic cell (P2_1/c). A similar CH_2Cl_2 solution of $[SnI_4\{\sigma-C_6H_4(PPh_2)\}_2]$ layered with n-hexane produced red crystals that were characterised as an unsolvated orthorhombic form (C222_1) of $[SnI_4\{\sigma-C_6H_4(P(O)Ph_2)\}_2]$. The geometries of the two forms showed no significant differences in bond lengths or angles so the distances quoted are for the solvated form that was the higher quality structure. Selected bond lengths (Å) and angles (°) are presented in Tables 5.11 and 5.12 respectively. The Sn-I_
trans distances, 2.7759(7) and 2.2976(7) Å and Sn-I_
transO distances, 2.7839(8) and 2.7796(8) Å, are in
Table 5.11. Selected bond lengths (Å) with e.s.d's for [SnI₄{o-C₆H₄(P(O)Ph₂)₂}]

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>I(1) Sn</td>
<td>2.7759(7)</td>
<td>I(2) Sn</td>
<td>2.7976(7)</td>
</tr>
<tr>
<td>I(3) Sn</td>
<td>2.7839(8)</td>
<td>I(4) Sn</td>
<td>2.7796(8)</td>
</tr>
<tr>
<td>Sn O(1)</td>
<td>2.120(5)</td>
<td>Sn O(2)</td>
<td>2.138(5)</td>
</tr>
<tr>
<td>P(1) O(1)</td>
<td>1.509(6)</td>
<td>P(1) C(1)</td>
<td>1.823(8)</td>
</tr>
<tr>
<td>P(1) C(7)</td>
<td>1.793(8)</td>
<td>P(1) C(13)</td>
<td>1.788(8)</td>
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<tr>
<td>P(2) O(2)</td>
<td>1.513(5)</td>
<td>P(2) C(6)</td>
<td>1.808(7)</td>
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<tr>
<td>P(2) C(19)</td>
<td>1.810(8)</td>
<td>P(2) C(25)</td>
<td>1.787(8)</td>
</tr>
<tr>
<td>C(1) C(6)</td>
<td>1.42(1)</td>
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</tbody>
</table>

Figure 5.11. View of the structure of [SnI₄{o-C₆H₄(P(O)Ph₂)₂}] (monoclinic form [P2₁/c]) with numbering scheme adopted. Ellipsoids are drawn at 40 % and H atoms and the CH₂Cl₂ solvate are omitted for clarity.
good agreement with the previous structurally characterised example of oxide complexes of SnI$_4$.\textsuperscript{29,30,32} The Sn-O distances, 2.120(5) and 2.138(5) Å, are similar to those in cis-[SnI$_4$(Ph$_3$PO)$_2$],\textsuperscript{30} 2.148(-) and 2.119(-)Å. From a study of the CCDB this structure appears to be the first reported example of a complex of this diphosphine dioxide and features an unusual seven-member chelate-ring. The ring itself appears to be relatively unstrained with O-Sn-O angles of 79.6(2) and 80.6(4)$^\circ$ for the solvated and unsolvated forms. Seven-membered chelate-rings of this variety have been observed previously for [Cu{ω-C$_6$H$_4$(P(0)Ph$_2$)$_2$Cl}[CuCl$_4$].\textsuperscript{36} The angles within this complex are comparable, 84.6(4)$^\circ$, and also relatively unstrained.

Table 5.12. Selected bond angles (°) with e.s.d's for [SnI$_4${ω-C$_6$H$_4$(P(0)Ph$_2$)$_2$}]

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Value</th>
<th>Bond Angles</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(1) Sn I(2)</td>
<td>172.42(3)</td>
<td>I(1) Sn I(3)</td>
<td>92.25(2)</td>
</tr>
<tr>
<td>I(1) Sn I(4)</td>
<td>92.90(2)</td>
<td>I(1) Sn O(1)</td>
<td>87.0(1)</td>
</tr>
<tr>
<td>I(1) Sn O(2)</td>
<td>91.6(1)</td>
<td>I(2) Sn I(3)</td>
<td>91.67(2)</td>
</tr>
<tr>
<td>I(2) Sn I(4)</td>
<td>92.89(2)</td>
<td>I(2) Sn O(1)</td>
<td>86.4(1)</td>
</tr>
<tr>
<td>I(2) Sn O(2)</td>
<td>83.6(1)</td>
<td>I(3) Sn I(4)</td>
<td>98.93(3)</td>
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<tr>
<td>I(3) Sn O(1)</td>
<td>92.3(1)</td>
<td>I(3) Sn O(2)</td>
<td>170.8(1)</td>
</tr>
<tr>
<td>I(4) Sn O(1)</td>
<td>168.8(1)</td>
<td>I(4) Sn O(2)</td>
<td>89.2(1)</td>
</tr>
<tr>
<td>Sn O(1) P(1)</td>
<td>147.7(3)</td>
<td>Sn O(2) P(2)</td>
<td>149.1(3)</td>
</tr>
<tr>
<td>P(1) C(1) C(6)</td>
<td>126.4(6)</td>
<td>P(2) C(6) C(1)</td>
<td>124.7(6)</td>
</tr>
<tr>
<td>O(1) Sn O(2)</td>
<td>79.6(2)</td>
<td>O(1) P(1) C(1)</td>
<td>115.3(3)</td>
</tr>
<tr>
<td>O(1) P(1) C(7)</td>
<td>107.7(3)</td>
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<td>O(2) P(2) C(6)</td>
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<td>105.6(3)</td>
</tr>
<tr>
<td>C(1) P(1) C(13)</td>
<td>108.7(3)</td>
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<td>C(19) P(2) C(25)</td>
<td>108.3(3)</td>
<td></td>
<td></td>
</tr>
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</table>
5.3. Conclusions

The products \([\text{SnX}_4(\text{Me}_3\text{P})_2]\) (where \(X = \text{Cl}, \text{Br} \) or \(I\)) arising from the reactions of \(\text{SnX}_4\) with \(\text{Me}_3\text{P}\) and those with bidentate phosphines, \([\text{SnX}_4\{\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2\}\}\) (where \(X = \text{Cl}, \text{Br}\) or \(I\); \(R = \text{Me} \) or \(\text{Ph}\)) and \([\text{SnX}_4\{\text{o-C}_6\text{H}_4(\text{PPh}_2)_2\}\}\) \((X = \text{Cl}, \text{Br}\) or \(I\)) have been prepared in high yield. For comparison the complexes \([\text{SnX}_4\{\text{o-C}_6\text{H}_4(\text{P(0)Ph}_2)_2\}\}\) \((X = \text{Cl}, \text{Br}\) or \(I\)) have also been prepared in high yield. A detailed examination of the variable temperature \(^{119}\text{Sn}\{-^1\text{H}\}\) and \(^{31}\text{P}\{-^1\text{H}\}\) NMR spectroscopy over the temperature range 300 – 190 K has been presented. Of interest in the variable temperature NMR spectroscopic studies are the reversible ligand dissociation in solution, including ring opening for chelate complexes. The results were complicated by the easy oxidation of the phosphine ligands, but the studies do show that the phosphine complexes are more stable than the arsine complexes in strictly anhydrous, oxygen free conditions. The effects of altering the ligand architecture is clear, with methyl substituted ligands forming more stable complexes than those of the phenyl substituted ligands. It is clear that complexes involving a five-membered chelate-ring are typically more stable that those featuring four- or six-membered chelate-rings. The results also clearly illustrate that the stability of the complexes formed decreases with the \(\text{SnX}_4\) acceptor: \(X = \text{Cl} > \text{Br} >> I\) consistent with previous studies.\(^{12}\) It is also apparent that these better \(\sigma\)-donor group 15 ligands form more stable complexes than the equivalent group 16 ligands. X-ray studies have been used to structurally characterise the first example of a tin-arsine complex, and also \([\text{SnI}_4\{\text{o-C}_6\text{H}_4(\text{P(O)Ph}_2)_2\}\}.\text{CH}_2\text{Cl}_2\) and \([\text{SnI}_4\{\text{o-C}_6\text{H}_4(\text{P(0)Ph}_2)_2\}\], featuring highly unusual seven-member chelate-rings that appear unstrained.
5.4. Experimental

The tin(IV) chloride, bromide and iodide and the ligands Me₃P, Me₂P(CH₂)₂PMe (dmpe) and Ph₂P(CH₂)₂PPh₂ (dppe), were purchased from Aldrich Chemicals. The ligands o-C₆H₄(PPh₂)₂,³⁷ Ph₂As(CH₂)₂AsPh₂ (dpae)³⁸ and o-C₆H₄(AsMe₂)₂ (diars)³⁹ were all prepared by following literature methods.

All of the reactions were carried out under an atmosphere of dry nitrogen in dry solvents purchased from Aldrich Chemicals, using standard Schlenk, vacuum-line and dry box techniques.

Single Crystal X-ray Diffraction

Single crystals of [SnI₄{o-C₆H₄(AsMe₂)₂}] and [SnI₄{o-C₆H₄(PPh₂)₂}].CH₂Cl₂ and [SnI₄{o-C₆H₄(P(O)Ph₂)₂}] were obtained from a solution of the appropriate complex in CH₂Cl₂. Crystals of [SnI₄{o-C₆H₄(P(O)Ph₂)₂}] were obtained from a CH₂Cl₂ solution of the complex layered with n-hexane. It was assumed that the crystals were moisture sensitive and therefore in each case the selected crystal was coated with mineral oil, mounted on a glass fibre using silicone grease as adhesive, and immediately placed in a stream of cold nitrogen gas. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low temperature attachment operating at 150 K, using graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å), ω-2θ scans. The intensities of three standard reflections were monitored every 150 reflections. No significant crystal decay or movement was observed. As there were no identifiable faces for [SnI₄{o-C₆H₄(P(O)Ph₂)₂}] and [SnI₄{o-C₆H₄(P(O)Ph₂)₂}].CH₂Cl₂ the raw data were corrected for absorption using psi-scans. The weighting scheme \( w^{-1} = σ²(F) \) gave satisfactory agreement analyses in each case.

The structures were solved by direct methods,⁴⁰ and then developed by iterative cycles of full-matrix least-squares refinement (based on \( F \)) and difference Fourier syntheses which located all non-H atoms in the asymmetric unit.⁴¹ For [SnI₄{o-C₆H₄(AsMe₂)₂}] an empirical absorption correction using DIFABS⁴² was applied to the raw data at isotropic convergence, as psi scans did not provide a satisfactory absorption correction. All non-H atoms in the structures were refined anisotropically and H atoms were placed in fixed, calculated positions with \( d(C-H) = 0.96 \) Å for [SnI₄{o-C₆H₄(P(O)Ph₂)₂}] and [SnI₄{o-C₆H₄(P(O)Ph₂)₂}].CH₂Cl₂. Only Sn, I and As atoms
were refined anisotropically, C atoms were refined isotropically as they turn non-positive definite when refined anisotropically, probably a result of an imperfect absorption correction. For \([\text{SnI}_4 \{\ell\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]\) and \([\text{SnI}_4 \{\ell\text{-C}_6\text{H}_4(\text{P(0)}\text{Ph}_2)_2\}]\) the Flack parameter was refined and indicated the correct enantiomorph in each case.

Crystallographic data for these structures are presented in Table 5.13.
Table 5.13. Crystallographic data

<table>
<thead>
<tr>
<th>Compound</th>
<th>[SnI₄(η-C₆H₄AsMe₂)₂]</th>
<th>[SnI₄(η-C₆H₄(P(0)Ph₂)₂)]</th>
<th>[SnI₄(η-C₆H₄(P(0)Ph₂)₂)]CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₀H₉As₂SnI₄</td>
<td>C₃₁H₄₇Cl₄O₂P₂SnI₄</td>
<td>C₃₀H₄₉O₂P₂SnI₄</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>912.39</td>
<td>1189.71</td>
<td>1104.77</td>
</tr>
<tr>
<td>Colour, morphology</td>
<td>Red, plate</td>
<td>Red, block</td>
<td>Red, block</td>
</tr>
<tr>
<td>Crystal dimensions/mm</td>
<td>0.80 x 0.45 x 0.15</td>
<td>0.67 x 0.35 x 0.30</td>
<td>0.30 x 0.20 x 0.20</td>
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\[ R = \frac{\sum |F_{\text{obs}}| - |F_{\text{calc}}|}{\sum |F_{\text{obs}}|} \]
\[ R_w = \sqrt{\frac{\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum w|F_{\text{obs}}|^2}} \]
\[ \text{GOF} = \frac{\sum (|F_{\text{obs}}| - |F_{\text{calc}}|)}{\sigma_i / (n - m)} \approx 1 \]
A solution of $\alpha$-C$_6$H$_4$(P(0)Ph$_2$)$_2$ (0.9 g, 2 mmol) in CHCl$_3$ (15 cm$^3$) was treated with a solution of diiodine (1.05 g, 4 mmol) in CHCl$_3$ (5 cm$^3$). The brownish solution was transferred to a separating funnel and shaken with aqueous 2 M NaOH (20 cm$^3$). The colourless organic phase was separated and the CHCl$_3$ removed under reduced pressure. The oil produced was recrystallised from CHCl$_3$/EtOH to give white crystals. Yield 0.80 g, 83 %. $^3$P$^4$[H] NMR (CH$_2$Cl$_2$) + 33.6, IR (Nujol mull) ν(P=O) = 1200 cm$^{-1}$. Found: C, 75.1; H, 5.3. Calculated for C$_{30}$H$_{24}$O$_2$P$_2$: C, 75.3; H, 5.0 %. EI mass spectrum $m/z$ = 477, 401. Calculated $P^+$ = 477, [P-Ph]$^+$ = 401.

**Complex Synthesis**

[$\text{SnX}_4(\text{PMe}_3)_2$]

A solution of tin(IV) halide (1 mmol) in dichloromethane (20 cm$^3$) was added to a solution of trimethylphosphine (0.15 g, 2 mmol) in dichloromethane (20 cm$^3$). With tin(IV) chloride (0.26 g) the complex, [$\text{SnCl}_4(\text{PMe}_3)_2$], precipitated as a white powder which was filtered off and dried in vacuo. For the same method with tin(IV) bromide (0.44 g, 0.1 mmol) and iodide (0.63 g, 1 mmol), the complexes [$\text{SnBr}_4(\text{PMe}_3)_2$] and [$\text{SnI}_4(\text{PMe}_3)_2$] were produced as yellow precipitates.

[$\text{SnX}_4(\text{dmpe})$]

A solution of tin(IV) chloride (0.26 g, 1 mmol) in dichloromethane (20 cm$^3$) was added to a solution of dmpe (0.15 g, 1 mmol) in dichloromethane (20 cm$^3$). The complex, [$\text{SnCl}_4(\text{dmpe})$], precipitated as a white powder which was filtered off and dried in vacuo. The same method with tin(IV) bromide (0.44 g, 1 mmol) formed the complex, [$\text{SnBr}_4(\text{dmpe})$], as a yellow precipitate. The complex [$\text{SnI}_4(\text{dmpe})$] as obtained on removal of solvent from the reaction of tin(IV) iodide (0.63 g, 1 mmol) and dmpe (0.15 g, 1 mmol) in dichloromethane (40 cm$^3$).

[$\text{SnX}_4(\text{dppe})$]

Using the same method tin(IV) chloride (0.13 g, 1 mmol) reacted with dppe (0.2 g, 0.5 mmol) to give the complex, [$\text{SnCl}_4(\text{dppe})$], as a white precipitate which was filtered and dried in vacuo. The same method with tin(IV) bromide (0.22 g, 0.5 mmol) yielded the complex, [$\text{SnBr}_4(\text{dppe})$], as a yellow precipitate. Removal of solvent from
the reaction of tin(IV) iodide (0.32 g, 0.5 mmol) with dppe (0.2 g, 0.5 mmol) in dichloromethane (40 cm$^3$) produced the complex [SnI$_4$(dppe)] as a dark red solid.

$[\text{SnX}_4(\sigma$-$\text{C}_6\text{H}_4(\text{PPh}_2)_2)$]

The same method for the reaction of tin(IV) chloride (0.13 g, 0.5 mmol) and (σ-$\text{C}_6\text{H}_4(\text{PPh}_2)_2$) (0.23 g, 0.5 mmol) formed the complex, [SnCl$_4$(σ-$\text{C}_6\text{H}_4(\text{PPh}_2)_2$)], as a white precipitate. Tin(IV) bromide (0.22 g, 0.5 mmol) reacted with (σ-$\text{C}_6\text{H}_4(\text{PPh}_2)_2$) (0.23 g, 0.5 mmol) to form a yellow precipitate. Tin(IV) iodide (0.32 g, 0.5 mmol) reacted with (σ-$\text{C}_6\text{H}_4(\text{PPh}_2)_2$) (0.23 g, 0.5 mmol) in dichloromethane (40 cm$^3$) to give a red solution. The complex, [SnI$_4$(σ-$\text{C}_6\text{H}_4(\text{PPh}_2)_2$)], was isolated by removal of solvent in vacuo.

$[\text{SnX}_4(\text{dpae})]$

Reaction of tin(IV) chloride (0.13 g, 0.5 mmol) with dpae (0.245 g, 0.5 mmol) in dichloromethane (40 cm$^3$) produced the complex, [SnCl$_4$(dpae)], as a white precipitate which was filtered and dried in vacuo. The same reaction with tin(IV) bromide (0.22 g, 0.5 mmol) produced a yellow solution which yielded the complex [SnBr$_4$(dpae)] as a yellow solid on removal of solvent in vacuo.

$[\text{SnX}_4(\text{diars})]$

The same method for the reaction of tin(IV) chloride (0.13 g, 0.5 mmol) with diars (0.145 g, 0.5 mmol) yielded the complex, [SnCl$_4$(diars)], as a white precipitate which was filtered off and dried in vacuo. With tin(IV) bromide (0.22 g, 0.5 mmol) a yellow solution was produced which yielded a yellow solid, [SnBr$_4$(diars)], on removal of solvent in vacuo. The same reaction with tin(IV) iodide (0.33 g, 0.5 mmol) formed a red solution, with a dark red solid, [SnI$_4$(diars)], isolated by removal of solvent in vacuo.

$[\text{SnX}_4(\sigma$-$\text{C}_6\text{H}_4(\text{P(O)Ph}_2)_2)$])

Following the same method reaction of tin(IV) chloride (0.13 g, 0.5 mmol) with (σ-$\text{C}_6\text{H}_4(\text{P(O)Ph}_2)_2$) (0.24 g, 0.5 mmol) produced a white precipitate which was filtered and dried in vacuo. Tin(IV) bromide (0.22 g, 0.5 mmol) with (σ-$\text{C}_6\text{H}_4(\text{P(O)Ph}_2)_2$) (0.13 g, 0.5 mmol) produced a yellow solution by the same method, from which a yellow solid was isolated by removal of solvent in vacuo. Similarly tin(IV) iodide (0.33 g, 0.5 mmol) formed a red solution with (σ-$\text{C}_6\text{H}_4(\text{P(O)Ph}_2)_2$) (0.13 g, 0.5 mmol)
in dichloromethane (40 cm$^3$) which yielded a dark red solid on removal of solid in vacuo.
References

Chapter 5  Tin(IV) Halide Complexes With Mono- and Bidentate Ligands of Group 15

41 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.
Chapter 6

Bismuth(III) Halide Complexes of Bidentate Group 15 and 16 Ligands
6.1. Introduction

The complexes of tin(IV) halides with a variety of group 15 and group 16 ligands were studied in chapters 2-5 of this work. They formed octahedral complexes with either mono- or bi-dentate ligands, even forming highly strained four-membered chelate-rings in some cases. This chapter examines the complexes formed between the bismuth(III) halides and a variety of bidentate ligands of differing architecture from groups 15 and 16.

In the +3 oxidation state the elements of group 15 have a lone pair of electrons. It is not clear whether this lone pair of electrons will be stereochemically active in a particular compound but a number of trends have been observed. The stereochemical activity of this lone pair appears to decrease with increasing coordination number, increasing atomic number of the halogen (Cl > Br > I) and with increasing atomic number in group 15 (i.e., As > Sb > Bi).

A large amount of work has been done involving anionic complexes of the bismuth(III) halides. These have been discussed in detail in previous reviews and since this study involves neutral complexes they will not be discussed here. Alonzo et al. examined the products formed from the reactions of bismuth(III) halides with a variety of nitrogen and phosphorus chelating ligands such as 1,10-phenanthroline and 1,2-bis(diphenylphosphino)ethane (dppe). Using a combination of analytical, mass and IR spectroscopic techniques they studied a number of solids which were assigned as chelates. They also found that in some cases the reaction did not occur in a 1:1 stoichiometry. The only structurally characterised examples of multidentate amine complexes of Bi(III) involve the macrocyclic ligands Me₂[9]aneN₃ (1,4,7-trimethyl-1,4,7-triazacyclononane) and [12]aneN₄ (1,4,7,10-tetraazacyclododecane) with bismuth (III) chloride and perchlorate respectively. In both cases the structures feature the pyramidal bismuth(III) species with the tri- or tetra-dentate macrocycle capping the Bi(III) ion.
Clegg et al.\textsuperscript{7} have studied various phosphine complexes of the group 15 halides including [Bi\textsubscript{2}Cl\textsubscript{6}(dmpe)\textsubscript{2}] (Figure 6.1), [Bi\textsubscript{4}Br\textsubscript{12}(PET\textsubscript{3})\textsubscript{4}], [Bi\textsubscript{2}Br\textsubscript{6}(PMe\textsubscript{3})\textsubscript{4}] and [Bi\textsubscript{2}Br\textsubscript{6}(PMe\textsubscript{2}Ph)\textsubscript{2}(OPMe\textsubscript{2}Ph)\textsubscript{2}]. [Bi\textsubscript{4}Br\textsubscript{12}(PET\textsubscript{3})\textsubscript{4}] is a tetramer with four octahedral Bi centres bound to one phosphine and five Br atoms. The other complexes all consist of an edge-shared, bioctahedral structure.
Chapter 6  
Bismuth(III) Halide Complexes of Bidentate Group 15 and 16 Ligands

Willey et al.\textsuperscript{8} have also examined the structures of crystals obtained from the reactions of BiCl\textsubscript{3} with dppe and also dpdm. For the reaction of BiCl\textsubscript{3} with dpdm the complex was characterised as [Bi\textsubscript{2}Cl\textsubscript{6}(dpdm)\textsubscript{2}] (Figure 6.2) consisting of a Bi\textsubscript{2}Cl\textsubscript{6} dimer with two bridging chlorides and with the two dpdm molecules bridging the Bi centres. The crystal structure of the complex formed between BiCl\textsubscript{3} and dppe features two independent molecules of formula [Bi\textsubscript{2}Cl\textsubscript{6}(dppe)\textsubscript{2}] (Figure 6.3a) and [Bi\textsubscript{2}Cl\textsubscript{6}(dppe)\textsubscript{3}] (Figure 6.3b). The first is the same as that identified by Clegg et al.\textsuperscript{7} for [Bi\textsubscript{2}Cl\textsubscript{6}(dmpe)\textsubscript{2}], while the second consists of two BiCl\textsubscript{3}(dppe) moieties bridged by a single dppe molecule, thus involving both chelating and bridging dppe ligands.

Figure 6.3 View of the centrosymmetric dimeric structures of a) [Bi\textsubscript{2}Cl\textsubscript{6}(dppe)\textsubscript{2}] and b) [Bi\textsubscript{2}Cl\textsubscript{6}(dppe)\textsubscript{3}] (taken from ref. 8)

The reason for the complexes adopting these edge-shared, bioctahedral dimers in the majority of cases is unclear. Norman and Pickett\textsuperscript{2} observe that the Bi-X trans to a phosphine ligand is typically ca. 0.2 Å greater than similar Bi-X bonds trans to X. This observation is attributed to the large trans influence of the phosphine vs. halide. They also note that of the four possible isomers (Figure 6.4) for structures of this type (A-D), isomer A is formed. On steric grounds isomer C would be the favoured isomer and Norman and Pickett suggest that the preference for isomer A can be assigned to an electronic effect arising from the trans influence of the phosphine ligands.
If a phosphine were placed trans to a bridging halide (as in isomer B), this would weaken the Bi-X bond, effectively creating a pair of $[\text{BiX}_2\text{L}_2]^+$ cations in close proximity, not energetically favoured. The products formed from the reactions of BiCl$_3$ and BiBr$_3$ with o-C$_6$H$_4$AsMe$_2$ (diars) have also been studied by Sutton, though their characterisation was restricted to analyses.

For group 16 donor systems the preference is again for the harder oxygen-donor ligands. The crown ethers in particular have been studied in great detail and all show a monomeric BiX$_3$ unit capped by the multidentate ligand. A number of monodentate ligand systems [e.g. $\text{fac-}[\text{BiX}_3(\text{thf})_3]$ (where $X = \text{Cl}^{15}$ or Br$^{16}$) $\text{fac-}[\text{BiX}_3(\text{dmso})_3]$ (where $X = \text{Cl}^{17}$ or Br$^{18}$)] have also been characterised structurally, and these do not adopt the edge-shared, biotahedral unit observed for the chelates. Instead they form mononuclear octahedral 1:3 Bi:ligand systems. A series of acyclic ethylene glycols of varying denticities have also been studied by Rogers et al. The interdonor linkages in these species are no larger than dimethylene, and all form monomeric units with Bi centres which are 7-coordinate with O$_4$X$_3$ donor sets (e.g. Figure 6.5 –
Figure 6.5 View of the monomeric structure of [BiCl₃(pentaethylglycol)] (taken from ref. 11)

[BiCl₃(pentaethylglycol)]. The ether donor is preferred to the hydroxyl donor in the cases where five oxygen donors are present within the ligand. Eveland et al.¹⁵ have also characterised the products formed from the reaction of BiCl₃ with MeO(CH₂)₂O(CH₂)₂OEt and EtO(CH₂)₂O(CH₂)₂OEt. In both cases the product formed adopts the edge-shared, bioctahedral dimers commonly observed in Bi(III) complexes. Similarly, the edge-shared, bioctahedral structure was also found by Willey et al.¹⁹ for the five-membered chelate system of [BiCl₃{Pr₃P(S)P(S)Pr₃}]²⁻. Willey et al.²⁰ have also characterised [BiCl₃{Ph₂P(O)CH₂P(O)Ph₂}]₂ (formed as a result of oxidation of [BiCl₃(dppe)]⁻) (Figure 6.6) and [BiCl₃{As(O)MePh₂}{Ph₂As(O)CH₂CH₂As(O)Ph₂}]ₙ (similarly formed by the oxidation of [BiCl₃(dpae)] – Figure 6.7). Interestingly, where dppe had formed a bridge between the two Bi centres of an edge-shared, bioctahedral unit, the oxide forms the more usual edge-shared, bioctahedral unit with one ligand chelated to each Bi. For the arsine-oxide, the ligand does not chelate to give a seven-membered ring, but rather bridges between Bi monomers forming an extended infinite chain.
Figure 6.6 View of the centrosymmetric dimeric structure of $[\text{BiCl}_3\{\text{Ph}_2\text{P(O)CH}_2\text{P(O)Ph}_2\}]_2$ (taken from ref. 19)

Figure 6.7 View of the polymeric structure of $[\text{BiCl}_3\{\text{As(O)MePh}_2\}\{\text{Ph}_2\text{As(O)CH}_2\text{CH}_2\text{As(O)Ph}_2\}]_n$. O(2*) is related by the symmetry operator $(x - \frac{1}{2}, \frac{1}{2} - y, z)$ and Bi(1') by $(\frac{1}{2} + x, \frac{1}{2} - y, z)$. (taken from ref. 19)
A number of thioether ligand complexes of Bi(III) halides are also known. The ionic species \([\text{Me}_3\text{S}]_2[\text{Bi}_2\text{I}_8(\text{Me}_2\text{S})_2]\) produced from the reaction of BiI₃ in neat Me₂S has been characterised structurally by Clegg et al.\(^{21}\) The structure features the same edge-shared bioctahedral dimer with each Bi coordinated to three terminal I atoms, two bridging I atoms and one Me₂S ligand. The bridging Bi-I distances (3.229(3) and 3.234(3) Å) for this structure are considerably longer than those of the terminal I atoms (2.934(3) – 2.955(3) Å). A number of the macrocyclic thioether systems with different denticities have also been studied and characterised structurally.\(^{22}-^{24}\) In all cases the macrocycle is found to cap the pyramidal BiCl₃ unit. All of these structurally characterised bismuth(III) halide complexes involving polyethylene glycols, ethers, crown ethers and crown thioethers reflect the dominance of the pyramidal BiX₃ unit on the structures adopted. The five weaker secondary halide interactions which are evident within the structure of the parent Bi(III) halide\(^{25}\) (Figure 6.8) are replaced with weak Bi-O or Bi-S interactions, generating 7-, 8- or 9-coordinate compounds.

Figure 6.8 Projection of the structure of BiCl₃ on the \(ab\) plane, showing the chlorine bridging that is present between a single BiCl₃ molecule and its neighbours. Two units cells in the \(z\) direction are involved. (taken from ref. 25)
A stereochemically active lone pair on the Bi, directed towards the weakly interacting S- or O-donors can be invoked for these species. This is clearly seen in the structure of \([\text{BiCl}_3\text{([24]aneS}_8)]^{24}\) (Figure 6.9) which contains two such BiCl₃ pyramidal units, each with weak interactions to five S-donors. Further evidence for the dominance of the pyramidal BiX₃ unit in these species comes from the observation that the Bi-Cl bond distances do not change significantly upon complexation. The same model can be applied to the isomers formed with dppe,⁷ dmpe⁸ and all other structures adopting isomer \(A\) detailed above.² In those cases two pyramidal bismuth(III) halide units can be identified with weaker secondary interactions linking them, and other ligand donor atoms replacing the other weak secondary interactions. This behaviour is apparently independent of the ether or thioether ligand denticity, and similar results have also been observed for SbX₃ derivatives.²⁶

Figure 6.9 View of \([\text{BiCl}_3\text{([24]aneS}_8)]\) (taken from ref. 23)

Sawyer and Gillespie²⁷ have reviewed the stereochemistry of Sb¹¹ halides and showed that the weak interactions form around the direction of maximum electron density of the lone pair, but not directly over it. In the complexes involving edge-shared, biotahedral dimers, this is consistent with the lone pairs of Bi lying within the plane of the bridging halides.²³,⁷,⁸,²⁰,²¹
The aim of this work is to conduct an investigation into the reaction of the bismuth(III) halides (Cl, Br or I) with a range of bidentate group 16 ligands, MeE(CH₂)ₙEMe (where n = 2 or 3; E = S or Se), PhE(CH₂)ₙEPh (where n = 2 or 3; E = S or Se) and α-C₆H₄(SMe)₂, and the group 15 ligands Ph₂As(CH₂)₂AsPh₂ (dpae), α-C₆H₄(AsMe₂)₂ (diars) and MeC(CH₂AsMe₂)₃ (triars). The affects of changing halide, the ligand interdonor linkage and terminal substituents are studied. Microanalysis and IR spectroscopy have been used to characterise these complexes in the solid state. The first structurally characterised example of a bismuth(III)-arsine complex, [Bi₂I₆(diars)]₂, is reported. The X-ray structures of the group 16 bismuth(III) halide complexes, [BiBr₃{MeS(CH₂)₂SMe}₂], [Bi₃I₆{MeS(CH₂)₂SMe}₂], [Bi₂Br₆{PhS(CH₂)₂SPh}ₙ], [Bi₄Cl₁₂{MeS(CH₂)₂SMe}₄]ₙ.nH₂O, [BiBr₃{MeSe(CH₂)₂SeMe}]ₙ, [BiCl₃{MeSe(CH₂)₂SeMe}]ₙ, and [BiBr₃{MeSe(CH₂)₂SeMe}]ₙ are reported.
6.2. Results & Discussion

6.2.1. Synthesis and Properties of Bidentate Group 16 Complexes of BiX₃

A range of complexes of stoichiometry BiX₃(L-L)₂ (where X = Cl, Br or I; L-L = MeE(CH₂)₂EMe, E = S or Se), Bi₂X₆(L-L) (where X = Cl, Br or I; L-L = PhE(CH₂)₂EMe, E = S or Se) and BiX₃(L-L) (where X = Cl, Br or I; L-L = MeE(CH₃)₃EMe or o-C₆H₄(SMe)₂) have been isolated from reaction of BiX₅ and L-L in MeCN. Concentration of the resultant coloured solutions produced solids which were filtered, washed with anhydrous CH₂Cl₂ and dried in vacuo. Due to the moisture sensitivity of the bismuth(III) halides, all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. All complexes were stored in a dinitrogen purged dry-box. The thioether complexes were found to be relatively stable in moist air, but the selenoether complexes were found to change to viscous black materials over a period of a few weeks in the dry-box. Satisfactory microanalyses were recorded for all freshly prepared solids and IR spectra of the BiCl₃ species show several features in the range 230-280 cm⁻¹ assigned to v(Bi-Cl) (c.f. 242 and 288 cm⁻¹ in the parent halide, BiCl₃). The poor solubility of the complexes in non-coordinating solvents such as CH₂Cl₂ and CHCl₃ meant that ¹H and ⁷⁷Se-{¹H} NMR spectra did not provide any useful information. The reaction of BiCl₃ with MeSCH₂SMe was attempted but, while a yellow solution was formed, no solid was isolable. The analogous ditelluroethers were also studied but the highly coloured products formed from reaction with BiX₃ proved too unstable to isolate.

6.2.2. Single Crystal X-ray Diffraction Studies

Prior to this study the only bidentate group 16 complexes of the bismuth(III) halides characterised structurally were restricted to phosphine or arsine oxides²⁰ (Figures 6.6 and 6.7), sulfides¹⁹ (e.g. [BiCl₃{Pr₃P(S)P(S)Pr₃}]) or the polyethylene glycols (e.g. Figure 6.5), ethers, crown ether and crown thioether complexes²²⁻²⁴ which feature pyramidal BiX₃ units capped by the macrocycle. The structures obtained for [BiBr₃{MeS(CH₂)₂SMe}₂], [BiI₃{MeS(CH₂)₂SMe}₂], [BiBr₃{MeS(CH₂)₃SMe}]ₙ, [Bi₂Br₆{PhS(CH₂)₂SPh}]ₙ, [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₙ.nH₂O,
Bismuth(III) Halide Complexes of Bidentate Group 15 and 16 Ligands

[BiCl₃{MeSe(CH₂)₃SeMe}]₄ and [BiBr₃{MeSe(CH₂)₃SeMe}]₄ exhibit a wide variety of different structural motifs for relatively small alterations in ligand architecture.

Crystals obtained from the reaction of BiBr₃ with MeS(CH₂)₂SMe show that the 7-coordinate species [BiBr₃{MeS(CH₂)₂SMe}₂] is formed as a monomer with two chelating ligands lying equatorially within a distorted pentagonal bipyramid (Figure 6.10). The coordination sphere created about the bismuth centre has three terminal Br atoms and four S-donors from the two chelated ligands.

**Figure 6.10** View of [BiBr₃{MeS(CH₂)₂SMe}₂] with numbering scheme adopted. Ellipsoids are drawn at 40% probability, hydrogen atoms have been omitted for clarity.

Bond lengths (Å) and angles (°) for [BiBr₃{MeS(CH₂)₂SMe}₂] are presented in Tables 6.1 and 6.2 respectively. The pyramidal unit found in the parent halide is severely disrupted here, with the BiBr₃ unit becoming almost planar to accommodate the two chelating ligands. One thioether ligand (S(1) and S(2)) adopts the *meso* and the other (S(3) and S(4)) the *dl* configuration. It is extremely unusual for a ligand to adopt both forms within a molecule. The only structurally characterised example where this occurs was [Ru{MeTe(CH₂)₃TeMe}₂(PPh₃)Cl]PF₆. In that case it is most likely the
influence of the triphenylphosphine that determines the isomer adopted. Here it likely
to be the strained nature of the 5-membered chelate ring. The S-Bi-S bond angles
observed for the two ligands, 70.3(2) and 72.6(1) Å, are much less than the angle
observed in chapter 2 for the octahedral species [SnCl₄{MeS(CH₂)₂SMe}] (84(1)°)
involving the same ligand.

Table 6.1 Selected bond lengths with e.s.d.s for [BiBr₃{MeS(CH₂)₂SMe}₂]

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Table 6.2 Selected bond angles (°) with e.s.d.s for [BiBr₃{MeS(CH₂)₂SMe}₂]

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The Bi-S distances for this structure (2.918(5), 2.963(5), 3.004(5), 3.090(5) Å) are typically shorter than those observed in [Me3S]2[Bi2I6(Me2S)2]21 (3.054(8) Å) and the macrocyclic thioether complexes (cf. 2.987(3) – 3.206(3) Å for [BiCl3([12]aneS4])22; 3.058(7) – 3.251(7) Å for [BiCl3([15]aneS4)]22; 3.146(4) and 3.225(4) Å for [BiCl3([18]aneS6)]23; 3.134(2) – 3.313(2) Å for [(BiCl3)2([24]aneS8)]24). The Bi-Br bond distances observed (2.787(2), 2.813(2) and 2.826(2) Å) are at the upper end of those observed in previous BiBr₃ complexes (cf. 2.66(1) – 2.76(1) for [BiBr₃(12-crown-4)]11; 2.672(4) – 2.714(4) Å for [BiBr₃(15-crown-5)]11; 2.656(2) – 2.694(2) Å for [BiBr₃(benzo-15-crown-5)]11; 2.669(2) – 2.739(2) Å for [BiBr₃(tetraethyleneglycol)]11). Within each of the thioether ligands chelated to the BiBr₃ there is one shorter and one longer Bi-S bond distance, possibly due to the presence of the stereochemically active lone pair on Bi pointing in the direction of S(2) and S(3), consistent the observations of Sawyer and Gillespie.27

A number of diamond-shaped crystals of the analogous iodo-complex, [BiI₃{MeS(CH₂)₂SMe}₂] were obtained upon concentration of the reaction mix of BiI₃ and MeS(CH₂)₂SMe in MeCN. Two datasets were collected from two different samples both of which turned out to be weakly diffracting. The structure was found to be enantiomorphic, with the choice of enantiomorph unclear. Depending on the direction of the screw-axis within the structure, 4₁ or 4₃, a different space group, P4₁2₁₂ or P4₃2₁, is necessary for each enantiomorph. There was also evidence of disorder within the C atoms of the thioether. These factors prevented satisfactory solution and refinement however, refinement of the heavy atoms was sufficient to show that the structure adopted was the same as was found for the mononuclear bromide analogue, [BiBr₃{MeS(CH₂)₂SMe}₂], discussed above.

The effects of altering the terminal ligand substituent from methyl to phenyl prove quite dramatic. Rather than discrete monomeric units, the X-ray structure of crystals obtained from a 1:1 mix of BiBr₃ with PhS(CH₂)₂SPh shows the product has a 2:1 Bi:dithioether ligand stoichiometry, with the structure forming an extended array, incorporating a form of the edge-shared, biocahedral dimers. The asymmetric unit and nearest symmetry related atoms as shown in Figure 6.11, the extended structure for [Bi₂Br₆{PhS(CH₂)₂SPh}ₙ is shown in Figure 6.12. Bond lengths (Å) and angles (°) have been presented in Tables 6.3 and 6.4. Each BiIII atom is coordinated to a slightly distorted octahedral arrangement (Br(1)-Bi-Br(2) 94.93(8)°, Br(1)-Bi-Br(3) 94.19(8)°, Br(1)-Bi-S(1) 90.3(1)°) of four μ₂-Br atoms, one terminal Br atom and one S-donor. The terminal Br atom and the S-donor are mutually cis. This gives infinite chains of
edge-shared octahedra formed via linking Bi$_2$Br$_2$ rectangles. The dihedral angle between adjacent Bi$_2$Br$_2$ units is 82.65(7)°.

Figure 6.11 View of the [Bi$_2$Br$_6${PhS(CH$_2$)$_2$SPh}]$_n$ asymmetric unit with numbering scheme adopted. Ellipsoids are drawn at 40% probability. Neighbouring atoms are included marked with an asterisk (*) (related by a crystallographic inversion center).

The chain retains some of the characteristics of the parent halide with a pyramidal core (Bi-Br ca. 2.7 Å), three weaker secondary halide interactions (Bi-Br ca. 3 Å) and the S-donor displacing one of the other secondary interactions. The Bi-S distance, 3.082(6) Å, is consistent with previously observed values. Of interest are the Bi-Br distances (2.596(2), 2.692(3), 2.751(3), 3.148(3) and 3.274(3) Å), which are consistent with [BiBr$_3${MeS(CH$_2$)$_2$SMe}$_2$] and previous examples, but vary greatly within the molecule. The shortest distance (2.696(2) Å) is for the terminal Br atom, as expected, then one of the bridging Br atoms (2.692(3) Å), then the Br trans to the sulfur donor (2.751(3) Å). The remaining two Bi-Br distances are considerably longer and probably indicate the position of the stereochemically active lone pair on...
bismuth, according to the findings of Sawyer and Gillespie. Dithioether ligands of this type and other group 16 ligands have previously been shown to bind to Cu and Ag centres and in a small number of cases also yield polymeric arrays, although quite different in detail to this complex.

Table 6.3 Selected bond lengths (Å) with e.s.d.s for [Bi₂Br₆{PhS(CH₂)₂SPh}]₆; atoms marked with an asterisk (*) are related by a crystallographic inversion centre

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Table 6.4 Selected bond angles (°) with e.s.d.s for [Bi₂Br₆{PhS(CH₂)₂SPh}]₆; atoms marked with an asterisk (*) are related by a crystallographic inversion centre

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Figure 6.12  View of a portion of [BiBr₆(PhS(CH₃)₂SPh)]₄, structure (phenyl) rings at C(2) and C(2') are omitted for clarity. Ellipsoids are drawn at 40% probability. Atoms marked with an asterisk (*) are related by a crystallographic inversion centre.
In chapter 2 it was seen that PhS(CH₂)₂SPh was a poorer σ-donor than MeS(CH₂)₂SMe, and hence the structure adopted by [Bi₂Br₆{PhS(CH₂)₂SPh}]ₙ is dominated by the influence of the parent BiBr₃ precursor, as is seen for the crown ethers¹⁰⁻¹⁴ and macrocyclic thioethers.²²⁻²⁴ However, further examples are necessary to prove this.

Altering the interdonor-linkage from dimethylene to trimethylene has an equally dramatic effect. The product obtained from a 1:1 mix of BiCl₃ with MeS(CH₂)₃SMe is found to have 1:1 stoichiometry by analysis. However, rather than a simple 5- or 7-coordinate monomer featuring chelating ligands, the X-ray crystal analysis of this species shows a very different and highly unusual structure. The structure reveals a three-dimensional polymeric network with the structural formula [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₙ.nH₂O. The asymmetric unit is shown in Figure 6.13, and a portion of the three-dimensional polymeric network is shown in Figures 6.14 and 6.15. Bond lengths (Å) and angles (°) are presented in Tables 6.5 and 6.6. Traces of moisture in the CH₂Cl₂ most likely account for the H₂O solvent molecules identified in the structure. The water molecules themselves are not involved in binding to any other centre so it is assumed they have little influence on the structure adopted.

Figure 6.13 View of the [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄] asymmetric unit with numbering scheme adopted. Ellipsoids are drawn at 40 % probability. Neighbouring atoms are included marked with an asterisk (*) (related by a crystallographic 4 symmetry).

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![Figure 6.13](image-url)
Figure 6.14  View of a portion of the [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₜ structure with numbering scheme adopted showing the tetramer unit (H atoms are omitted for clarity and atoms marked with an asterisk are related by a crystallographic 4 operation. Ellipsoids are drawn at 40 % probability.
Figure 6.15 View of a portion of the [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₙ structure viewed down the c-axis of the three-dimensional polymer, illustrating the channels running through the structure (H atoms are omitted for clarity). Ellipsoids are drawn at 40% probability.
The structure involves $\text{Bi}_4\text{Cl}_{12}\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}_4$ tetramer units (related by crystallographic 4 symmetry) which are linked by bridging dithioether ligands to give a three-dimensional polymeric network. Each Bi$^{III}$ ion is therefore coordinated to two terminal Cl atoms, two $\mu_2$-bridging Cl atoms and two S-donors from different bridging dithioether ligands. The geometry at each Bi atom therefore approximates to a severely distorted octahedron, with an open triangular face within which it is assumed the Bi lone pair lies. The $\mu_2$-bridging Bi-Cl distances (2.913(7) and 2.969(6) Å) are much longer than the terminal Bi-Cl distances (2.538(7) and 2.533(7) Å), which are themselves only slightly different. Hence an alternative description of this structure is that it comprises of $[\text{BiCl}_2\{\eta^1\text{-MeS}(\text{CH}_2)_3\text{SMe}\}_2]^+$ cations loosely associated into tetramers through interactions with chloride ions, Cl(1) and Cl(1*). There are additional long range, weak interactions which link the $\mu_2$-bridging Cl atoms to Bi centres across the Bi$_4$Cl$_4$ ring, $\text{Bi} \cdots \text{Cl}(1*) = 3.268(7)$ Å. This distance is significantly longer than would be expected for a genuine $\mu_2$-bridging Cl.$^{31}$ The Bi$_4$Cl$_4$ core forms an 8-membered heterocyclic ring which, as a result of the weak Bi$\cdots$Cl interactions adopts an open-cradle conformation (Figure 6.16). The secondary $\text{Bi} \cdots \text{Cl}(1*)$ interaction is in the general direction of the void assumed to be occupied by the lone pair, but not in the direction of the maximum electron density, again consistent with behaviour previously observed for Sb$^{III}$ and Bi$^{III}$ chemistry.$^{27}$ Bismuth halides often form compounds incorporating condensed Bi$_4$X$_4$ polyhedra,$^{31}$ however, the open cradle arrangement adopted by $[\text{Bi}_4\text{Cl}_{12}\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}_4]_n \cdot n\text{H}_2\text{O}$ is very unusual. The Bi-S (2.857(7) and 2.977(7) Å) and Bi-Cl$_{\text{terminal}}$ (2.538(7) and 2.533(7) Å) bond lengths are similar to those observed in the reported thioether complexes$^{21-24}$
Table 6.5 Selected bond lengths (Å) with e.s.d.s for [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₙ; atoms marked with an asterisk (*) are symmetry related by a crystallographic 4 operation

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Table 6.6 Selected bond angles (°) with e.s.d.s for [Bi₄Cl₁₂{MeS(CH₂)₃SMe}₄]ₙ; atoms marked with an asterisk (*) are symmetry related by a crystallographic 4 operation

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</table>

Figure 6.16 View of the Bi₄Cl₄ core, illustrating the open cradle conformation. The dashed lines indicate secondary Bi···Cl interactions
When the analogous reaction is undertaken using BiBr$_3$ in place of BiCl$_3$, a totally different structure is found. A weakly diffracting crystal was obtained from a sample which analysed as [BiBr$_3${MeS(CH$_2$)$_3$SMe}]$_n$. The X-ray crystal structure shows that the stoichiometry remains 1:1 Bi:thioether ligand, but this time the structure incorporates the edge-shared bioctahedral dimeric unit which is commonly observed for bismuth halide complexes.$^{2,3,7,8,20}$ However, for this structure, these are not discrete dimers, but rather are linked by bridging dithioether ligands to give a two-dimensional sheet. The asymmetric unit is shown in Figure 6.17, and a portion of the extended sheet system is included in Figure 6.18. Bond lengths (Å) and angles (°) are presented in Tables 6.7 and 6.7. Each Bi$^{III}$ atom is coordinated to distorted octahedral arrangement (two terminal Br atoms, two μ$_2$-bridging Br atoms and two mutually trans S-donors from different bridging dithioethers. The Bi$_2$Br$_6$ units are planar and, although the bond distances are somewhat asymmetric within the Bi$_2$(μ$_2$-Br$_2$) ring, there is a crystallographic inversion centre at the centre of this unit. One methyl substituent (C(5) on S(1)) of the ligand is disordered and has been satisfactorily modelled across the two possible sites such that 60% of the ligand is in the meso configuration and the remaining 40% in the dl form.

There is evidence, once again, for the stereochemically active Bi based lone pair. The bond distances for the terminal Br atoms (2.697(2) and 2.719(2) Å) are considerably shorter than those for the bridging Br atoms (2.980(2) and 3.004(2) Å). This suggests that the stereochemically active lone pair on the Bi atoms lie within the plane of the Bi$_2$Br$_6$ dimer, between the two bridging BiBr bonds.

This structure starkly contrasts with that of the chloride example, [Bi$_4$Cl$_{12}${MeS(CH$_2$)$_3$SMe}]$_n$.nH$_2$O, discussed earlier and, although that structure incorporates H$_2$O solvent molecules, it seems unlikely that they account for the difference as they are not involved in binding and are not sterically demanding.
Figure 6.17 View of the asymmetric unit for \([\text{BiBr}_3\{\text{MeS(CH}_2)_3\text{SMe}\}]_n\) with numbering scheme adopted. Ellipsoids are drawn at 40\% probability. Neighbouring atoms are included marked with an asterisk (related by a crystallographic inversion centre). C(5) is disordered across two sites, C(5) and C(5b), in a 6:4 ratio.

Table 6.7 Selected bond lengths (Å) with e.s.d.'s for \([\text{BiBr}_3\{\text{MeS(CH}_2)_3\text{SMe}\}]_n\); atoms marked with an asterisk (*) are symmetry related by a crystallographic inversion centre.

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Table 6.8  Selected bond angles (°) with e.s.d.s for \([\text{BiBr}_3\{\text{MeS(CH}_2)_3\text{SMe}\}\}_n\); atoms marked with an asterisk (*) are symmetry related by a crystallographic inversion centre

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Figure 6.18 View of a portion of the meso form of $[\text{BiBr}_3\{\text{MeS(CH}_2)_3\text{SMe}\}]_n$ structure with the numbering scheme adopted (ellipsoids are drawn at 40% probability; H atoms are omitted for clarity and atoms marked with an asterisk (*) are related by a crystallographic inversion centre.)
Crystals were also obtained from a 1:1 mix of BiCl₃ and the selenoether analogue, MeSe(CH₂)₃SeMe. Analysis showed that the 1:1 Bi:diselenoether ligand stoichiometry was maintained. The X-ray structure obtained for this compound, shows the same two-dimensional array as seen for [BiBr₃{MeS(CH₂)₃SMe}]ₙ (Figure 6.18). The edge-shared, bioctahedral Bi₂Cl₆ dimers are linked by the diselenoether ligand which bridges between staggered Bi₂Cl₆ dimer units. The asymmetric unit for this structure is shown in Figure 6.19, with bond lengths (Å) and angles (°) presented in Tables 6.9 and 6.10. Each Bi³⁺ is bound to two terminal Cl atoms, two μ₂-bridging Cl atoms and two mutually trans Se-donor atoms. The octahedral geometry is slightly distorted from the ideal (Se(1)-Bi-Se(2) 173.19(4)°, Se(1)-Bi-Cl(1) 89.9(1)°, Se(1)-Bi-Cl(2) 97.3(1)°, Se(1)-Bi-Cl(3) 83.6(1)°). As with [BiBr₃{MeS(CH₂)₃SMe}]ₙ, there is an inversion centre at the centre of the Bi₂Cl₆ dimer.

**Figure 6.19** View of the asymmetric unit for [BiCl₃{MeSe(CH₂)₃SeMe}]ₙ with numbering scheme adopted. Ellipsoids are drawn at 40 % probability. Neighbouring atoms are included marked with an asterisk (related by a crystallographic inversion centre)
### Table 6.9
Selected bond lengths (Å) with e.s.d.s for [BiCl$_3$\{MeSe(CH$_2$)$_3$SeMe\}]$_n$; atoms marked with an asterisk are related by a crystallographic inversion centre

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<td>Cl(3*)</td>
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### Table 6.10
Selected bond angles (°) with e.s.d.s for [BiCl$_3$\{MeSe(CH$_2$)$_3$SeMe\}]$_n$; atoms marked with an asterisk are related by a crystallographic inversion centre

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<td>Se(1)</td>
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<td>Cl(2)</td>
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<td>Cl(3)</td>
<td>Bi(1)</td>
<td>Se(2*)</td>
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<td>Cl(3*)</td>
<td>Bi(1)</td>
<td>Se(2*)</td>
<td>87.0(1)</td>
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<td>Se(2)</td>
<td>Bi(1)</td>
<td>Se(1)</td>
<td>173.19(4)</td>
<td></td>
</tr>
</tbody>
</table>
The only other structurally characterised example of a bismuth complex, \([\text{Me}_2\text{N}]_3\text{PSeSeP(Me}_2\text{N})_3][\text{Bi}_2\text{Cl}_6]\), is ionic and the Se-donors are not coordinated. Subsequent work within the Southampton research group on multidentate selenoether complexes of the bismuth(III) halides has produced further structures for comparison. The structures of \([\text{BiCl}_3[[8]\text{aneSe}_2]]_n\) (where \([8]\text{aneSe}_2 = 1,5\text{-diselenyclooctane} \)), \([\text{BiBr}_3[[16]\text{aneSe}_4]]_n\) (Figure 6.20; where \([16]\text{aneSe}_4 = 1,5,9,13\text{-tetrascelenycyclohexadecane} \)), \([\text{Bi}_2\text{Cl}_6\{\text{MeC(Ch}_2\text{SeMe)}_3\}]_n\) and \([\text{Bi}_2\text{I}_6\{\text{MeC(Ch}_2\text{SeMe)}_3\}]_n\) have been determined and all feature the edge-shared,
bioctahedral dimer subunits. The two structures involving macrocyclic ligands, [BiCl₃([8]aneSe₂)]₄ and [BiBr₃([16]aneSe₄)]₄, form one-dimensional 'ladder' structures (Figure 6.20) with the Bi₂X₆ dimers forming the 'steps' and the selenoether ligands forming the 'uprights'. The tripod selenoether, MeC(CH₂SeMe)₃, which might have been expected to cap the BiX₃ units in a *fac* conformation, form two very different structures. [Bi₂I₆{MeC(CH₂SeMe)₃}] incorporates dimeric units analogous to the literature examples of dimethylene backboned diphosphine complexes,²³,²⁷,³⁸,²⁰ with one arm of the tripod remaining uncoordinated. In contrast to this, the BiCl₃ adduct forms an extended two-dimensional sheet incorporating Bi₂Cl₆ dimers with bidentate selenoether coordination at each Bi centre. The third Se-donor from each tripodal ligand crosslinks these to give the sheet, and gives an Se₃Cl₄ donor set at each Bi centre. The Bi-Se bond distances (2.989(3) and 3.035(3) Å) seen in [BiCl₃{MeSe(CH₂)₃SeMe}]₄ are in good agreement with these other selenoether complexes (2.952(2) – 3.19(1) Å). Significantly, the Bi-Se bond distances for this species are similar to the Bi-S bond distances in the macrocyclic thioether complexes²²,²⁴ (2.987(3) – 3.313(2) Å), despite the larger radius of Se over S, suggesting a stronger interaction between the Bi(III) centre and the donor atoms for this species. The Bi-Cl bond distances (2.555(7), 2.570(7), 2.829(7) and 2.883(7) Å) are also consistent with previous literature examples²²-²⁴ and also with [BiCl₃{MeC(CH₂SeMe)₃}]₄ (2.55(1), 2.622(9) and 2.776(8) Å). The Bi-Cl bond distances for the terminal Cl atoms in [BiCl₃{MeSe(CH₂)₃SeMe}]₄ are also considerably shorter, 2.555(7) and 2.570(7) Å, than those of the μ₂-bridging Cl atoms, 2.829(7) and 2.883(7) Å, as has been observed for the previous examples of this study and consistent with the observations of Sawyer and Gillespie²⁷ that the stereochemically active lone pair of electrons of Bi lying within the Bi₂Cl₆ plane. The same pattern is seen for [BiCl₃{MeC(CH₂SeMe)₃}]₄.³²

When the analogous reaction was undertaken using BiBr₃ and MeSe(CH₂)₃SeMe, a solid analysing as [BiBr₃{MeSe(CH₂)₃SeMe}]₄ was obtained. Crystals obtained for this compound show the same structure as [BiBr₃{MeS(CH₂)₃SMe}]₄ (Figure 6.18) with an extended two-dimensional sheet of Bi₂Br₆ edge-shared, bioctahedral dimers crosslinked by the diselenoether ligands. The asymmetric unit for this structure is shown in Figure 6.21, with bond lengths (Å) and angles (°) presented in Tables 6.11 and 6.12.
Figure 6.21 View of the asymmetric unit for \([\text{BiBr}_3\{\text{MeSe(CH}_2)_3\text{SeMe}\}]_\infty\) with numbering scheme adopted. Ellipsoids are drawn to 40% probability. Neighbouring atoms are included marked with an asterisk (*) (related by a crystallographic inversion centre).

Table 6.11 Selected bond lengths (Å) with e.s.d.s for \([\text{BiBr}_3\{\text{MeSe(CH}_2)_3\text{SeMe}\}]_\infty\); atoms marked with an asterisk (*) are related by a crystallographic inversion centre.

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<td>3.027(2)</td>
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Table 6.12  Selected bond angles (°) with e.s.d.s for [BiBr$_3$\{MeSe(CH$_2$)$_3$SeMe\}]$_n$; atoms marked with an asterisk (*) are related by a crystallographic inversion centre

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<td>96.62(7)</td>
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The Bi-Se bond distances in this species, 2.976(3) and 3.027(2) Å, are consistent with those of the chloride analogue, 2.989(3) and 3.035(3) Å, and are similar to the Bi-S bond distances in reported macrocyclic thioether complexes$^{22-24}$ (2.987(3) – 3.313(2) Å), which again suggests that the interaction between the Bi(III) centre and the donor atoms in this system are stronger than those observed in the macrocyclic thioether systems. The bond distances within the Bi$_2$Br$_6$ dimer show the same pattern as seen in the Bi$_2$Cl$_6$ analogue. The bond distances for terminal Br atoms, 2.711(3) and 2.725(3) Å, are significantly shorter than those of the $\mu_2$-bridging Br atoms, 2.980(2) and 2.995(3) Å, again pointing to the presence of the bismuth based lone pair within the plane of the Bi$_2$Br$_6$ dimer.
6.2.3. Synthesis and Properties of Bidentate Group 15 Complexes of BiX₃

A number of bidentate amine⁴-⁶ and phosphine⁷,⁸ complexes of Bi(III) have been characterised previously, but to-date very little work has been reported on arsine complexes of the bismuth(III) halides.⁹ A range of complexes of type BiX₃(L-L) (where X = Cl, Br or I; L-L = Ph₂As(CH₂)₂AsPh₂ (dpae) or Ω-C₆H₄(AsMe₂)₂) and BiX₃(L-L-L) (where X = Cl, Br or I; L-L-L = MeC(CH₂AsMe₂)₃ (triars)) have been produced by reaction of BiX₅ with the appropriate ligand in MeCN. Concentration of the resultant coloured solutions produced solids which were filtered, washed with anhydrous CH₂Cl₂ and dried in vacuo. The solids were treated as air-sensitive and stored in a dinitrogen purged dry-box. However, the complexes were found to decompose only slowly in moist air, although they appear to be more easily hydrolysed in solution. Satisfactory microanalyses were recorded for all solids isolated and IR spectra of the BiCl₃ species show several features in the range 230-280 cm⁻¹ assigned to ν(Bi-Cl). The IR spectra of all complexes formed were also checked for the formation of arsine-oxide (ν(As=O) = 800 - 860 cm⁻¹ for [BiCl₃(dpae)]²⁻). As has been seen from the complexes of group 16 ligands, however, it is difficult to formulate any structural information from the limited range of spectroscopic and analytical techniques available. Therefore it was necessary to resort to X-ray crystallography.
Figure 6.22 View of the dimeric structure of [Bi$_2$I$_6$(diars)$_2$] with numbering scheme adopted. Ellipsoids are drawn at 40% probability. Atoms marked with an asterisk (*) are related by a crystallographic inversion centre. H atoms omitted for clarity.

6.2.4. Single Crystal X-ray Diffraction Studies

Crystals were obtained for the solid isolated from the 1:1 mix of BiI$_3$ with diars. The analytical data obtained for this product indicate a 1:1 stoichiometry. The X-ray structure shows that the complex adopts the same form as the phosphine complexes previously characterised,$^{7,8}$ with formula [Bi$_2$I$_6$(diars)$_2$]. The structure for this complex is shown in Figure 6.22, with bond lengths (Å) and angles (°) are presented in Tables 6.13 and 6.14. The structure features the edge-shared, biocahedral dimer with each Bi atoms bound to two terminal I atoms, two $\mu_2$-bridging I atoms and two mutually cis As atoms from the chelating diars ligands. The fact that this ligand chelates, whereas PhS(CH$_2$)$_2$SPh bridges, is not surprising, since o-phenylene backboned ligands of this type have been shown to form very stable complexes.$^{33}$ The pyramidal unit of the parent halide is retained, with one weaker, secondary Bi···I interaction and with two As atoms replacing the remaining secondary iodide interactions. This again means that the
octahedral geometry is quite severely distorted (I(1)-Bi-I(2) 164.24(4)°, I(1)-Bi-I(3) 101.97(4)°, I(1)-Bi-As(1) 84.60(4)°, I(1)-Bi-As(2) 82.95(4)°). This is the first structurally characterised example of a Bi(III) - arsine complex. The Bi-As bond distances observed for this complex, 2.801(2) and 2.974(2) Å, are ca. 0.2 Å longer than the Bi-P bond distances observed for [Bi₂Br₆(dmpe)₂]⁷ (2.678(8) and 2.791(7) Å) or [Bi₂Cl₆(dppe)₂]⁸ (2.699(8), 2.945(9) and 2.956(10) Å) consistent with the increased radius of As over P, combined with the poorer σ-donor nature of the arsine. The Bi-I bond distances for [Bi₂I₆(diars)] (2.992(2), 3.032(1), 3.117(2) and 3.328(1) Å) are consistent with the observed values for [Me₃S]₂[Bi₂I₆(Me₂S)₂]²¹ (2.934(3), 2.954(3), 2.955(3), 3.229(3) and 3.234(3) Å) and both have considerably longer bond lengths for the μ₂-bridging I atoms than the terminal I atoms.

Table 6.13 Selected bond lengths (Å) with e.s.d.s for [Bi₂I₆(diars)]₂. Atoms marked with an asterisk (*) are related by a crystallographic inversion centre

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Chapter 6  Bismuth(III) Halide Complexes of Bidentate Group 15 and 16 Ligands

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Table 6.14  Selected bond angles (°) with e.s.d.s for [Bi\textsubscript{2}I\textsubscript{6}(diars)\textsubscript{2}]. Atoms marked with an asterisk (*) are related by a crystallographic inversion centre.
6.3. Conclusions

This work represents the first investigation of bismuth(III) halide complexes of acyclic group 16 donor ligands and the selenoether complexes are the first examples of their type.

By the very nature of these Bi(III) species, their characterisation is restricted to analytical data, IR spectroscopy and single crystal X-ray diffraction studies. While the stoichiometry of the products is not in question, the structural motifs described here represent those species which yielded suitable quality crystals. Other motifs may be obtainable under different conditions. At present we can only discuss those structures which we have identified, but there is clearly the caveat that the discussion may need modification in light of further results. The large variety of different structural motifs for these group 16 ligand complexes means that it is not possible to formulate any structures on the basis of the analytical data or IR spectroscopy. The X-ray crystal structures obtained for these species have shown some very unexpected structural motifs in stark contrast to previous examples involving acyclic or macrocyclic ligand complexes. For the methyl substituted ligands, MeS(CH₂)ₙSMe (n = 2 or 3), when n = 2 discrete monomers are obtained of the form [BiX₃{MeS(CH₂)₂SMe}]₂ with the two ligands chelated, but for n = 3 the group 16 ligands bridge between edge-shared, biocathedral Bi₂X₆ dimers. These Bi₂X₆ units have been identified in other bismuth(III) halide complexes but only as discrete dimeric units. The fact that [Bi₂Br₆{PhS(CH₂)₂SPh}] does not form the same in the same stoichiometry as the methyl substituted systems may be due to the added steric hindrance of the larger phenyl groups and the weaker σ-donor capability of the ligand over the methyl substituted analogues. Clearly more examples are required to deduce exactly why these complexes adopt such different structures.

The complex formed between diaryl and bismuth(III) iodide has been found to form the same dimeric structural type as previously studied group 15 ligands. The presence of the Ω-phenylene backbone will promote the formation of a chelate structure. However, in light of the large number of structural motifs that have been characterised for Bi(III) complexes, a large structural diversity may also be expected for these species depending on the arsine ligand employed.
6.4. Experimental

The bismuth(III) chloride, bromide and iodide and anhydrous CH2Cl2 were purchased from Aldrich Chemicals. The ligands RS(CH2)nSR where n = 2 or 3; R = Me or Ph, RSe(CH2)2SeR where n = 2 or 3; R = Me or Ph, C6H4(EMe)2 (where E = S or Se), Ph2As(CH2)2AsPh and were all produced by literature methods. MeC(CH2AsMe2)3 was kindly produced by Professor W. Levason.

MeCN was dried over P2O5 prior to use.

Tin(IV) halides are extremely moisture sensitive and phosphines easily oxidised in solution, therefore all of the reactions were carried out under an atmosphere of dry nitrogen in dry solvents purchased from Aldrich Chemicals, using standard Schlenk, vacuum-line and dry box techniques.

Single Crystal X-ray Diffraction

Single crystals of [Bi4Cl12{MeS(CH2)3SMe}4]n.nH2O were obtained by slow evaporation of a solution of the compound in CH2Cl2. Crystals of [BiBr3{MeS(CH2)2SMe}2], [BiI3{MeS(CH2)2SMe}2], [Bi2Br6{PhS(CH2)2SPh}], [BiBr3{MeSe(CH2)3SeMe}], [BiCl3{MeSe(CH2)3SeMe}] and [BiBr3{MeSe(CH2)3SeMe}] and [Bi2I6(diars)2] were all obtained by slow evaporation of a solution of the relevant compound in MeCN. It was assumed that the crystals were moisture sensitive and therefore in each case the selected crystal was coated with mineral oil, mounted on a glass fibre using silicone grease as adhesive, and immediately placed in a stream of cold nitrogen gas. Data collection for [BiBr3{MeS(CH2)3SMe}] used an Enraf-Nonius Kappa-CCD diffractometer. Data collection for the remaining structures used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low temperature attachment operating at 150 K, using graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å), T = 150 K, θ-2θ scans. The intensities of three standard reflections were monitored every 150 reflections. No significant crystal decay or movement was observed. As there were no identifiable faces for [BiBr3{MeS(CH2)2SMe}2] and [BiCl3{MeSe(CH2)3SeMe}] the raw data were corrected for absorption using psi-scans. The weighting scheme \( w^{-1} = σ^2(F) \) gave satisfactory agreement analyses in each case. The structures were solved by direct methods, and then developed by iterative cycles of full-matrix least-
squares refinement (based on $F$) and difference Fourier syntheses which located all non-H atoms in the asymmetric unit. For $[\text{Bi}_4\text{Cl}_{12}\{\text{MeS(CH}_2)_3\text{SMe}\}_4]_n\cdot n\text{H}_2\text{O}$, $[\text{Bi}_2\text{Br}_6\{\text{PhS(CH}_2)_2\text{SPh}\}]$, $[\text{BiBr}_3\{\text{MeSe(CH}_2)_2\text{SeMe}\}]$ and $[\text{Bi}_2\text{I}_6(\text{diars})_2]$ an empirical absorption correction using DIFABS was applied to the raw data at isotropic convergence, as psi scans did not provide a satisfactory absorption correction. For $[\text{BiBr}_3(\text{MeS(CH}_2)_3\text{SMe})]$ the raw data were corrected for absorption using SORTAV. All non-H atoms in the structures were refined anisotropically (with the exception of $[\text{Bi}_4\text{Cl}_{12}\{\text{MeS(CH}_2)_3\text{SMe}\}_4]_n\cdot n\text{H}_2\text{O}$ and $[\text{BiBr}_3\{\text{MeSe(CH}_2)_2\text{SeMe}\}]$ for which the C atoms were refined isotropically as they turn non-positive definite when refined anisotropically, probably a result of an imperfect absorption correction, and one methyl carbon (C(6)) which is disordered across two sites) and H atoms were placed in fixed, calculated positions with $d$(C-H) = 0.96 Å for $[\text{Bi}_4\text{Cl}_{12}\{\text{MeS(CH}_2)_3\text{SMe}\}_4]_n\cdot n\text{H}_2\text{O}$, $[\text{BiBr}_3\{\text{MeS(CH}_2)_3\text{SMe}\}_2]$, $[\text{BiBr}_3\{\text{MeS(CH}_2)_2\text{SMe}\}]$, $[\text{BiCl}_3\{\text{MeSe(CH}_2)_2\text{SeMe}\}]$ and $[\text{Bi}_2\text{I}_6(\text{diars})_2]$. For $[\text{Bi}_4\text{Cl}_{12}\{\text{MeS(CH}_2)_3\text{SMe}\}_4]_n\cdot n\text{H}_2\text{O}$ and $[\text{BiBr}_3\{\text{MeS(CH}_2)_2\text{SMe}\}]_2$ the Flack parameter was refined and indicated the correct enantiomorph in each case.

Crystallographic data for these structures are presented in Table 6.15.
Table 6.15. Crystallographic data

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<th>Compound</th>
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<th>[Bi₂Br₆(PhS(CH₂)₂Ph)]</th>
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\[ R = \frac{\Sigma (|F_{obs}| - |F_{calc}|)}{\Sigma |F_{calc}|} \]
\[ R_w = \sqrt{\Sigma w(|F_{obs}| - |F_{calc}|)^2} / \Sigma w|F_{obs}|^2 \]
\[ \text{GOF} = \frac{\Sigma (|F_{obs}| - |F_{calc}|)^2}{|F_{calc}|^2(n - m)} = 1 \]
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R = Σ (|F_{obs}| - |F_{calc}|) / Σ |F_{obs}|
R_m = \sqrt{\sum w_i (|F_{obs,i} - |F_{calc,i}|)^2} / \sum w_i |F_{obs,i}^2|
GOF = Σ (|F_{obs,i} - |F_{calc,i}|)/\sigma_i (m - n) ≈ 1
Complex Synthesis

\[ \text{[BiCl}_3\text{MeS(CH}_2\text{)}_2\text{SMe}]_2 \]

A solution of \( \text{BiCl}_3 \) (0.160 g, 0.52 mmol) in dry, degassed MeCN (4 cm\(^3\)) was added to a stirring solution of \( \text{MeS(CH}_2\text{)}_2\text{SMe} \) (0.060 g, 0.52 mmol) in \( \text{CH}_2\text{Cl}_2 \) (2 cm\(^3\)) at room temperature. A yellow solution is formed almost immediately. Concentrating the solution \textit{in vacuo} gave a yellow solid which was filtered, washed with \( \text{CH}_2\text{Cl}_2 \) and dried \textit{in vacuo}. Yield 0.147 g, 67 %. IR (CsI disc): \( \nu_{\text{Bi-Cl}} \) 227, 250, 281 cm\(^{-1}\). Found: C, 17.2; H, 3.3. Calculated for \( \text{C}_8\text{H}_2\text{O}_4\text{Cl}_3\text{Bi} \): C, 11.0; H, 3.6 %.

\[ \text{[BiBr}_3\text{MeS(CH}_2\text{)}_2\text{SMe}]_2 \]

The same general method with \( \text{BiBr}_3 \) (0.16 g, 0.35 mmol) in MeCN (6 cm\(^3\)) and \( \text{MeS(CH}_2\text{)}_2\text{SMe} \) (0.040 g, 0.35 mmol) in \( \text{CH}_2\text{Cl}_2 \) (2 cm\(^3\)) yielded a dark yellow solid. Yield 0.122 g, 61 %. Found: C, 13.5; H, 2.6. Calculated for \( \text{C}_8\text{H}_2\text{O}_4\text{Br}_3\text{Bi} \): C, 13.9; H, 2.9 %.

\[ \text{[BiI}_3\text{MeS(CH}_2\text{)}_2\text{SMe}]_2 \]

\( \text{BiI}_3 \) (0.206 g, 0.035 mmol) in MeCN (15 cm\(^3\)) reacted with \( \text{MeS(CH}_2\text{)}_2\text{SMe} \) (0.04 g, 0.035 mmol) in \( \text{CH}_2\text{Cl}_2 \) (2 cm\(^3\)) to yield dark red diamond shaped crystals on concentration. Yield 0.91, 37 %. Found: C, 11.7; H, 2.5. Calculated for \( \text{C}_8\text{H}_2\text{O}_4\text{I}_3\text{Bi} \): C, 11.5; H, 2.4 %.

\[ \text{[BiCl}_3\text{MeS(CH}_2\text{)}_3\text{SMe}] \]

The same general method with \( \text{BiCl}_3 \) (0.16 g, 0.52 mmol) and \( \text{MeS(CH}_2\text{)}_3\text{SMe} \) (0.071 g, 0.52 mmol) in MeCN (10 cm\(^3\)) gave a yellow solid. Yield 0.18 g, 78 %. IR (CsI disc): \( \nu_{\text{Bi-Cl}} \) 245, 263, 274 cm\(^{-1}\). Found: C, 13.1; H, 2.7. Calculated for \( \text{C}_5\text{H}_12\text{S}_2\text{Cl}_3\text{Bi} \): C, 13.3; H, 2.7 %.

\[ \text{[BiCl}_3\text{MeS(CH}_2\text{)}_3\text{SMe}]_{n\cdot\text{nH}_2\text{O}} \]

When \( \text{BiCl}_3 \) (0.16 g, 0.52 mmol) was stirred with \( \text{MeS(CH}_2\text{)}_3\text{SMe} \) (0.071 g, 0.52 mmol) in \( \text{CH}_2\text{Cl}_2 \) (20 cm\(^3\)) the white \( \text{BiCl}_3 \) solid was seen to turn yellow and a yellow solution formed. Concentration of the solution yielded yellow crystals which were filtered, washed with Na-dried petroleum ether and dried \textit{in vacuo}. Yield 0.046 g, 20 %. IR (CsI disc): \( \nu_{\text{Bi-Cl}} \) 239, 258, 279 cm\(^{-1}\). Found: C, 13.0; H, 2.8. Calculated for \( \text{C}_5\text{H}_14\text{O}_1\text{S}_2\text{Cl}_3\text{Bi} \): C, 12.8; H, 3.0 %.
[BiBr₃{MeS(CH₂)₃SMe}]  
BiBr₃ (0.16 g, 0.35 mmol) was treated with MeS(CH₂)₃SMe (0.05 g, 0.35 mmol) in MeCN (10 cm³) forming a yellow solution which yielded a yellow solid on concentration in vacuo. This was filtered, washed with CH₂Cl₂ and dried in vacuo. Yield 0.16 g, 76%. Found: C, 10.4; H, 2.0. Calculated for C₅H₁₂S₂Br₃Bi: C, 10.3; H, 2.1%.

[BiI₃{MeS(CH₂)₃SMe}]  
The same reaction method with BiI₃ (0.206 g, 0.35 mmol) yielded a dark red powder. Yield 0.15 g, 59%. Found: C, 8.5; H, 1.9. Calculated for C₅H₁₂S₂I₃Bi: C, 8.3; H, 1.7%.

[Bi₂Cl₆{PhS(CH₂)₂SPh}]  
The same method with BiCl₃ (0.16 g, 0.52 mmol) and PhS(CH₂)₂SPh (0.128 g, 0.52 mmol) in MeCN/CH₂Cl₂ (10 cm³) gave an orange solid which was filtered, washed with CH₂Cl₂ and dried in vacuo. Yield 0.187 g, 67%. IR (CsI disc): v₇Bi-Cl 219, 234, 271 cm⁻¹. Found: C, 19.6; H, 1.7. Calculated for C₁₄H₁₄S₂Cl₆Bi₂: C, 19.2; H, 1.6%.

[Bi₂Br₆{PhS(CH₂)₂SPh}]  
The same method with BiBr₃ (0.16 g, 0.35 mmol) and PhS(CH₂)₂SPh (0.086 g, 0.35 mmol) yielded a dark orange powder. Yield 0.133 g, 54%. Found: C, 13.4; H, 1.2. Calculated for C₁₄H₁₄S₂Br₆Bi₂: C, 13.6; H, 1.1%.

[BiCl₃{o-C₆H₄(SMe)₂}]  
BiCl₃ (0.16 g, 0.52 mmol) and o-C₆H₄(SMe)₂ (0.09 g, 0.52 mmol) in MeCN (10 cm³) gave an orange solid on concentration in vacuo. Yield 0.133 g, 53%. IR (CsI disc): v₇Bi-Cl 227, 246, 282 cm⁻¹. Found: C, 19.4; H, 2.0. Calculated for C₈H₁₀S₂Cl₃Bi: C, 19.8; H, 2.1%.

[BiCl₃{MeSe(CH₂)₂SeMe}]  
The same general method with BiCl₃ (0.16 g, 0.52 mmol) and MeSe(CH₂)₂SeMe (0.112 g, 0.52 mmol) in MeCN (10 cm³) gave a yellow solid. Yield 0.155 g, 57%. IR (CsI disc): v₇Bi-Cl 234, 256, 279 cm⁻¹. Found: C, 9.7; H, 2.0%.
Chapter 6  Bismuth(III) Halide Complexes of Bidentate Group 15 and 16 Ligands

[BiBr₃{MeSe(CH₂)₂SeMe}]

The same general method with BiBr₃ (0.16 g, 0.35 mmol) and MeSe(CH₂)₂SeMe (0.075 g, 0.35 mmol) in MeCN (10 cm³) yielded a dark yellow solid. Yield 0.108 g, 46 %. Found: C, 7.0; H, 1.5. Calculated for C₄H₁₀Se₂Br₃Bi: C, 7.2; H, 1.5 %.

[BiI₃{MeSe(CH₂)₂SeMe}]

The same general method with BiI₃ (0.206 g, 0.35 mmol) and MeSe(CH₂)₂SeMe (0.075 g, 0.35 mmol) in MeCN (10 cm³) produced a blood red solid. Yield 0.045 g, 16 %. Found: C, 6.4; H, 1.4. Calculated for C₄H₁₀Se₂I₃Bi: C, 6.0; H, 1.2 %.

[BiCl₃{MeSe(CH₂)₃SeMe}]

BiCl₃ (0.16 g, 0.52 mmol) and MeSe(CH₂)₃SeMe (0.240 g, 1.04 mmol) in MeCN (10 cm³) formed a yellow solid. Yield 0.21 g, 75 %. IR (CsI disc): ν₁Bi-Cl 238, 252, 263 cm⁻¹. Found: C, 10.8; H, 2.3. Calculated for C₅H₁₂Se₂Cl₃Bi: C, 11.0; H, 2.2 %.

[BiBr₃{MeSe(CH₂)₃SeMe}]

BiBr₃ (0.16 g, 0.35 mmol) and MeSe(CH₂)₃SeMe (0.16 g, 0.36 mmol) in MeCN (10 cm³) gave a dark yellow solid. Yield 0.16 g, 64 %. Found: C, 9.1; H, 2.1. Calculated for C₅H₁₂Se₂Br₃Bi: C, 8.9; H, 1.8 %.

[BiCl₃(dpae)]

A solution of BiCl₃ (0.16 g, 0.52 mmol) in MeCN (5 cm³) was added to dpae (0.253 g, 0.52 mmol) in CH₂Cl₂ (5 cm³). A pale yellow solution formed immediately. On concentration in vacuo this gave a pale yellow solid which was filtered, washed with CH₂Cl₂ and dried in vacuo. Yield 0.292 g, 71 %. IR (CsI disc): ν₁Bi-Cl 229, 247, 273 cm⁻¹. Found: C, 39.0; H, 3.1. Calculated for C₂₆H₂₄As₂Cl₃Bi: C, 39.0; H, 3.0 %.

[BiBr₃(dpae)]

The same method with BiBr₃ (0.16 g, 0.035 mmol) and dpae (0.170 g, 0.35 mmol) in MeCN (10 cm³) produced a yellow solid. Yield 0.195 g, 59 %. Found: C, 32.9; H, 2.4. Calculated for C₂₆H₂₄As₂Br₃Bi: C, 33.4; H, 2.6 %.
[BiI₃(dpae)]

The same method with BiI₃ (0.206 g, 0.035 mmol) and dpae (0.170 g, 0.35 mmol) in MeCN (10 cm³) gave a yellow solid. Yield 0.135 g, 36 %. Found: C, 29.3; H, 2.6. Calculated for C₂₆H₂₄As₂I₃Bi: C, 29.0; H, 2.3 %.

[BiCl₃(diars)]

BiCl₃ (0.16 g, 0.52 mmol) in MeCN (4 cm³) gave a pale yellow solution when added to diars (0.150, 0.52 mmol) in CH₂Cl₂ (5 cm³). Concentrating in vacuo produced a yellow solid. Yield 0.227 g, 73 %. IR (CsI disc): νBi-Cl 232, 254, 268 cm⁻¹. Found: C, 19.6; H, 2.6. Calculated for C₁₀H₁₆As₂Cl₃Bi: C, 20.0; H, 2.7 %.

[BiBr₃(diars)]

BiBr₃ (0.16 g, 0.52 mmol) in MeCN (4 cm³) gave a pale yellow solution when added to diars (0.101, 0.52 mmol) formed a dark orange solid. Yield 0.167 g, 64 %. Found: C, 16.4; H, 2.2. Calculated for C₁₀H₁₆As₂Br₃Bi: C, 16.40; H, 2.20 %.

[BiI₃(diars)]

BiI₃ (0.206 g, 0.35 mmol) and diars (0.101, 0.35 mmol) in MeCN gave a red solid. Yield 0.175 g, 57 %. Found: C, 13.8; H, 2.0. Calculated for C₁₀H₁₆As₂I₃Bi: C, 13.7; H, 1.8 %.

[BiCl₃(triars)]

BiCl₃ (0.16 g, 0.52 mmol) in MeCN (5 cm³) gave a pale yellow solution when added to a solution of triars (0.2 g, 0.52 mmol) in CH₂Cl₂ (5 cm³). Concentration in vacuo gave a pale yellow solid. Yield 0.043 g, 12 %. IR (CsI disc): νBi-Cl 236, 255, 282 cm⁻¹. Found: C, 18.5; H, 4.0. Calculated for C₁₁H₂₇As₃Cl₃Bi: C, 18.9; H, 3.9 %.

[BiBr₃(triars)]

BiBr₃ (0.16 g, 0.4 mmol) with triars (0.155 g, 0.4 mmol) in MeCN (5 cm³) gave a yellow solid which was filtered and dried in vacuo. Yield 0.200 g, 64 %. Found: C, 15.5; H, 3.0. Calculated for C₁₁H₂₇As₃Br₃Bi: C, 15.9; H, 3.3 %.

[BiI₃(triars)]

BiI₃ (0.206 g, 0.4 mmol) with triars (0.155 g, 0.4 mmol) in MeCN (10 cm³) gave an orange solution. Removal of solvent in vacuo produced an orange oil. Stirring
this oil in anhydrous dichloromethane (10 cm$^3$) produced an orange precipitate which was filtered and dried *in vacuo*. Yield 0.170 g, 47 %. Found: C, 13.7; H, 2.8. Calculated for C$_{11}$H$_{27}$As$_3$I$_3$Bi: C, 13.6; H, 2.8 %.
References

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Chapter 6  Bismuth(III) Halide Complexes of Bidentate Group 15 and 16 Ligands


41 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.


APPENDIX

Infrared spectra were recorded on either a Perkin-Elmer 983G spectrometer or a Perkin-Elmer FTIR 1710 spectrometer in the range 4000-1800 cm\(^{-1}\). Samples were prepared as nujol mulls and mounted between caesium iodide plates.

C and H analyses were performed by the microanalytical laboratory of Imperial College, London and by Dr. W. Levason on an F&M Model 185 Analyser at the University of Southampton. Br and I analyses were performed by the microanalytical laboratory of the University of Strathclyde.

Variable temperature \(^1\)H NMR spectra were recorded over the range 180 - 300 K using a Bruker AM360 spectrometer operating at 360 MHz and are referenced to TMS.

Multinuclear NMR \(^{31}\)P-\(^1\)H, \(^{77}\)Se-\(^1\)H, and \(^{119}\)Sn-\(^1\)H NMR spectra were recorded on a Bruker AM360 spectrometer. The samples were prepared in 10 mm NMR tubes containing 10 - 15 % deuteriated solvent. Cr(acac)\(_3\) was also added to the samples to as a relaxation agent prior to recording the spectra, to avoid signal diminuation via the Nuclear Overhauser Effect (NOE) resulting from the negative magnetogyric moment of the tin nucleus. \(^{31}\)P-\(^1\)H spectra were recorded at 145.5 MHz and referenced to neat external 85 % H\(_3\)PO\(_4\); \(^{77}\)Se-\(^1\)H spectra were recorded at 68.7 MHz and are referenced to neat external Me\(_2\)Se; \(^{119}\)Sn-\(^1\)H spectra were recorded at 134.2 MHz and are referenced to neat external Me\(_4\)Sn.

Solid state \(^{119}\)Sn NMR spectra were obtained by Dr. Sandra Dann using a Bruker AM300 spectrometer fitted with multinuclear solid state probe at 111.9 MHz and 300 K. 400 - 500 mg of material were packed into ZrO\(_2\) or SiN rotors and data collected using a spinning speed of 4.5 - 6.5 kHz for best spectra. In cases where insufficient material was available the rotors were topped up with spectroscopic grade KBr. Typical spectral parameters were; contact time 6 ms, recycle time 2 seconds and number of transients typically 20,000. Spectra were rerun at lower speeds (2.5 kHz) to establish central band position where spinning side bands were present. Spectra were referenced to Me\(_4\)Sn (\(\delta = 0\)) and a secondary reference of SnCl\(_4\) (\(\delta = -150 \text{ ppm}\)) was also employed. The magic angle was initially set using the \(^79\)Br resonance of KBr.