Halide Transfer Reactions of
Arsenic, Antimony and Bismuth

Helen Collins

Thesis Submitted for the Degree of Doctor of Philosophy

University of Warwick,
Department of Chemistry.

June 1991
To Mum and Dad

-for making this possible
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Declaration - All of the work described in this thesis is original and was, except where otherwise indicated, carried out by the author.

Helen Collins
(June 1991)

Some of the work described in this thesis has been published in the following references.

Halide Abstraction Reactions of Sb(V) Chloride: Synthesis and Characterisation of Hexachloroantimonate Salts of M(II) M = Zn, Mg; M(III) M = Cr, M(IV) M = Ti, Sn and Related Cp2M(IV) M = Ti, Zr and Hf.


Halide Transfer Reactions Involving Bismuth(III) Chloride: Synthesis and Identification of the Ternary Complexes BiCl₃.SbCl₅.4MeCN (I), 2MgCl₂.4BiCl₃.12MeCN (II) and 3MgCl₂.4BiCl₃.18MeCN (III). X-ray Structural Characterisation of (II) as the Tetranuclear Bismuth(III) Complex [Mg(MeCN)₆]₂[Bi₄Cl₁₆] and Comments on its Structural Relationships with Other Complex Chloro-Bismuth(III) Anions.

### Abbreviations

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<tr>
<td>Bipy</td>
<td>Bipyridyl</td>
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<tr>
<td>DMO</td>
<td>N, N’-Dimethyloxamide</td>
</tr>
<tr>
<td>DEDTO</td>
<td>N, N’-Diethylthiooxamide</td>
</tr>
<tr>
<td>en</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>TMEDA</td>
<td>N, N’, N’, N’-Tetramethylethylenediamine</td>
</tr>
<tr>
<td>TPP</td>
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</tr>
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<td>Acetonitrile</td>
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<td>nitrogen</td>
</tr>
<tr>
<td>Cl₂</td>
<td>chlorine</td>
</tr>
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<td>mol</td>
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<tr>
<td>p.p.m.</td>
<td>parts per million</td>
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<tr>
<td>R.T.</td>
<td>room temperature</td>
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<tr>
<td>h</td>
<td>hour</td>
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<tr>
<td>m.p.</td>
<td>melting point</td>
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<tr>
<td>I.R.</td>
<td>infra-red</td>
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<tr>
<td>vs</td>
<td>very strong</td>
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<td>strong</td>
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<tr>
<td>br</td>
<td>broad</td>
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<tr>
<td>U.V.</td>
<td>ultra-violet</td>
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<td>(sh)</td>
<td>shoulder</td>
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<tr>
<td>N.M.R.</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>m</td>
<td>multiplet</td>
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<td>S.C.E.</td>
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<tr>
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<td>standard electrode potential</td>
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<td>$\Lambda_e$</td>
<td>equivalent conductivity</td>
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<tr>
<td>$\Lambda_e$</td>
<td>molar conductivity at infinite dilution</td>
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Summary

The study of Group 15 (As, Sb, Bi) halide exchange reactions.

The Lewis acidity of SbCl₅ was displayed using various metal halides. Treatment of the metal halides MCl₄ (n=2, M=Mg, Sn; n=3, M=Sb, Y, La, Ti, In; n=4, M=Ti, Sn) with SbCl₅ in MeCN provided antimonate(V) salts of the type [MCl₄L₃][SbCl₆] characterised by ¹²¹Sb nmr, electronic and infra-red spectroscopy and accompanying microanalytical data. Depending upon the stoichiometry of the reactants used the antimonate salts have been formulated as [MCl₄-xL₆-(n-x)]x⁺[SbCl₆]x⁻ (where n=2, 3, 4; x=1, 2, 3). The formation of mono-, di- and tricationic metal species has been effected by single and multiple halide abstraction, the resultant formation of 1:1, 1:2 and 1:3 electrolytes in MeCN has been confirmed by conductivity studies.

The Lewis acidity and basicity of BiCl₃ was illustrated by treatment of MCl₄ (n=2, M=Mg; n=5, M=Sb respectively) with BiCl₃ in MeCN. Reaction with MCl₄ gave bismuthate(III) salts of the type [Mg(MeCN)₆][Bi₄Cl₉]Cl₂Cl₂ where n=3 gave a tetranuclear anion [Bi₄Cl₉]Cl₂Cl₂ which contains three different types of chlorine atoms: ten terminal, four μ₂ and two μ₃. Further variation of the stoichiometry of the MgCl₂/BiCl₃ system did not give any other products. Conductivity measurements confirm the products as 2:1 and 3:1 electrolytes in DMF. However reaction of BiCl₃ with MgCl₂ and TiCl₃ with SbCl₅ gave the neutral [MCl₃L₃] adducts.

The Lewis acidity of SbCl₅ towards MCl₄ was displayed by reaction of MCl₄ (n=3, M=Mg, Ti, In, Bi; n=4, M=Ti, Sn) with SbCl₅ in MeCN which gave the neutral MCl₄L₃ (L=MeCN, x=2, 3) adducts. Reaction with MCl₄ gave SbCl₅-SbCl₅.₄MeCN.

The oxidation of As(III) to As(V) using chlorine and reaction with MCl₄ (n=4, M=Ti, Sn, n=2, M=Zn) gave the MCl₄Lₓ adducts. Reaction with MCl₄ gave the ternary complex MgCl₂.TiCl₄.6MeCN.
CHAPTER 1
1.1 Some Group Trends

Amongst the elements of the Periodic Table, those of Group 15, the Pnictides, namely nitrogen, phosphorus, arsenic, antimony and bismuth, show an extremely diverse range of physical and chemical properties.

There is a distinct trend from non-metallic to metallic properties with increasing atomic number. Arsenic and antimony behave as metalloids, while bismuth is a typical B metal, like tin or lead. 1

Phosphorus and nitrogen form covalent compounds; arsenic, antimony and bismuth exhibit increasing tendencies towards cationic behaviour. 2 There is a steady decrease in the strength of covalent bonds in the order $P > As > Sb > Bi$, which is well illustrated by the instability of $\text{BiH}_3$. 3

Except in its valence shell electronic configuration, nitrogen bears very little resemblance to the other elements of the group. The ground state electronic configuration, $s^2p^3$ dictates the two main valence states of the group, three and five. These result from the loss or use of the three outer shell $p$ electrons and the five outer shell $s$ and $p$ electrons respectively.

Group 15 compounds display a wide variety of donor/acceptor properties. Trivalent $\text{ER}_3$ compounds (where $E=P, \text{As, Sb}, \text{Bi}$ and $R=\text{alkyl, aryl, alkoxy, aryloxy, halide, hydrogen}$) vary enormously in their donor/acceptor abilities, depending, on $R$. Pentavalent $\text{EX}_5$ compounds; where $X=\text{halogen}$ invariably behave as acceptor molecules.
1.2. Trivalent Group 15 Compounds as Ligands

NR₃ compounds can function as simple donors by virtue of the lone pair on the central atom. Nitrogen has no other available orbitals, but other ER₃ compounds (E=P, As, Sb, Bi; R=alkyl, aryl, alkoxy, aryloxy, halide, hydrogen) have empty d orbitals of fairly low energy. When the acceptor atom has partially or fully filled orbitals of similar symmetry and energy to these empty d orbitals, back donation of electron density may occur. This results in overall multiple bond character; in particular, dx•-dx bonding crucially affects the stability of transition metal complexes with EX₃ compounds. Mono-, bi- and multidentate ligands and macrocyclic phosphines, arsines, stibines and bismuthines have been reported in the literature. Rather more unusual Group 15 ligands such as arsenobenzene have been recently reported. Transition metals do not bond directly to the arsenic atom of arsenobenzene, but to a delocalized π bonded system analogous to metallocenes and η-allyl complexes. In addition ligands containing pnictide-element and pnictide-pnictide multiple bonds, can form cluster compounds.

1.2.1. Bonding of Tertiary Group 15 Ligands

Pnictide-transition metal bonds are essentially covalent. The simplest model comprises donation of the lone pair of the pnictide atom (which behaves as a Lewis base), to a suitably available empty orbital on the metal, thus generating a donor covalent bond.

This simple picture involves only σ type bonding, but π bonding and steric effects, modify the ligand's contribution to
the M-E bond. In an octahedral transition metal complex the eg orbitals participate in σ bonding with the six ligands, leaving the t_{2g} orbitals as non-bonding orbitals directed between the six M-E bonds. When ligand coordination occurs the pyramidal (approximately \( p^3 \)) bonding of the ligand changes towards tetrahedral \( sp^3 \). (This increase in s character has important steric implications). The σ bond can thus be viewed as forming between a \( d^2sp^3 \) hybrid metal orbital and an \( sp^3 \) hybrid phosphorus orbital.

The Lewis basicities (σ donor ability) of ER\(_3\) ligands vary dramatically with R. \(^{13}\) (R=alkyl, aryl, alkoxy, aryloxy, halide, hydrogen). This is reflected in pK\(_a\) values (Table 5.2, pK\(_a\)(H\(_2\)O) is a measure of Bronsted basicity (proton affinity), which differs from Lewis basicity, but there is a close correlation). The basicity of some common phosphine ligands decrease in the order PBu\(_3\) > P(OR)\(_3\) > PR\(_3\) > PPh\(_3\) > PF\(_3\) > P(OPh)\(_3\). Electron-releasing substituents increase the electron availability on phosphorus thus increasing basicity. Bulky substituents expand the R-P-R angle, which increases the \( p \) character of the lone pair and subsequently the basicity. The basicity of the pnictides decreases in the order P > As > Sb > Bi, according to enthalpy \(^{14}\) and photoelectron spectroscopy data. \(^{15}\)

Pnictide ligands can also accept \( \pi \) electron density, resulting in transition metal backbonding. The extents of σ donation and back-bonding depend upon the substituents attached to phosphorus, and the synergistic relationship between them is the cause of some dispute. \(^{16}\) Pi backbonding was originally thought to involve a transfer of charge to empty
$d$ orbitals on the pnictide atom. The symmetry of the $d_{x}-d_{x}$ orbitals involved in such bonding is illustrated in Figure 1.1.

**Figure 1.1: M-P Back-bonding Using Phosphorus d-orbitals**

Recent quantum mechanical calculations imply that the EX$_3$ acceptor orbitals are $p$ orbitals on E$^{17}$ and E-X $\sigma^*$ orbitals$^{18}$ with a rebuttal of the $dx$ orbitals. Such ideas find support in the electron transmission spectroscopy measurements of Giordan et al.$^{19}$ On the basis of bond length calculations Orpen and Connelly$^{20}$ have suggested that the LUMO's of PX$_3$, PR$_3$ etc have $\sigma^*$ nature which incorporate some 3$d$ character from phosphorus. There is now a general consensus that M-P $\pi$ "backbonding" involves the P-X antibonding $\sigma^*$ orbitals rather than the 3$d$ orbitals of phosphorus.

CO stretching frequencies and $^{13}$C chemical shifts of LN$_3$(CO)$_3$ and LCr(CO)$_5$ (L=pnictide ligand)$^{21}$ indicate that $\pi$ acceptor ability decreases in the following order: NO > RCN = PF$_3$ > PCl$_3$ > PCl$_2$(OR) > PCl$_2$R > PBr$_2$R > PCl(OR)$_2$ > PClR$_2$ > P(OR)$_3$ > PR$_3$
(π acid series). 22 The π acidity of As and Sb ligands follows that of the corresponding P ligands. It was previously thought that the greater π acidity of PF₃ and PCl₃ was due to the electronegativity of the substituents lowering the energy of the phosphorus d-orbitals, thus increasing their availability for π bonding. According to Marynick et al. 18 the highly polar P-F bonds give rise to low lying σ* orbitals of similar symmetry to the metal d orbitals. In addition the σ bond is highly polarised towards F, so the σ* orbital necessarily polarises towards P, increasing σ*-metal dπ orbital overlap. By contrast the most basic phosphines, PBU₃ and PCy₃ are best described as σ and π donors. 16 with very limited π acceptor ability.

Steric factors play a subtle role in the chemistry of transition metal-pnictide ligand complexes. Steric requirements of phosphine ligands are expressed by Tolman's Cone Angle, θ. The cone just encloses the Van der Waals surface of all ligand atoms over all rotational orientations about an M-P bond of length 2.28Å. The cone angles of ER₃ ligands have been measured or calculated using X-ray data and molecular models. The bulkiness of phosphine ligands modifies the solubility 24 and rates of reaction of complexes 25 and, most importantly, the coordination numbers and geometries that complexes can adopt.

To summarize the bonding of ER₃ ligands 26
- σ donor ability decreases in the order P > As > Sb > Bi.
- π acceptor ability increases in the order P < As < Sb < Bi.
- Steric effects due to the donor atom increase in the order P < As < Sb < Bi.
Steric effects of the substituents on the donor atom decrease in the order P > As > Sb.

1.3. GROUP 15 HALIDES

1.3.1. Trihalides

All twelve trihalides are known, they exhibit considerable diversity in their chemical and physical properties, and in their structures (Table 1.1).[^2][^3][^5]

**Table 1.1: Physical Properties of Group 15 Trihalides**

<table>
<thead>
<tr>
<th>Halide</th>
<th>Physical state at 25°C</th>
<th>M.p(°C)</th>
<th>B.p(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsF₃</td>
<td>Liquid</td>
<td>-6.0</td>
<td>62.8</td>
</tr>
<tr>
<td>AsCl₃</td>
<td>Liquid</td>
<td>-16.2</td>
<td>130.2</td>
</tr>
<tr>
<td>AsBr₃</td>
<td>Solid</td>
<td>+13.2</td>
<td>221</td>
</tr>
<tr>
<td>AsI₃</td>
<td>Solid</td>
<td>140.4</td>
<td>400</td>
</tr>
<tr>
<td>SbF₃</td>
<td>Solid</td>
<td>290</td>
<td>345</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>Deliquescent solid</td>
<td>73.4</td>
<td>223</td>
</tr>
<tr>
<td>SbBr₃</td>
<td>Deliquescent solid</td>
<td>96.0</td>
<td>288</td>
</tr>
<tr>
<td>SbI₃</td>
<td>Solid</td>
<td>170.5</td>
<td>401</td>
</tr>
<tr>
<td>BiF₃</td>
<td>Solid</td>
<td>649</td>
<td>900</td>
</tr>
<tr>
<td>BiCl₃</td>
<td>Deliquescent solid</td>
<td>233.5</td>
<td>441</td>
</tr>
<tr>
<td>BiBr₃</td>
<td>Deliquescent solid</td>
<td>219.0</td>
<td>462</td>
</tr>
<tr>
<td>BiI₃</td>
<td>Solid</td>
<td>408.6</td>
<td>542 (extrap)</td>
</tr>
</tbody>
</table>
Melting points and boiling points reflect the different structures and bonding modes adopted by the trihalides, hence AsF₃, AsCl₃, AsBr₃, SbCl₃ and SbBr₃ are volatile molecular species, while the other trihalides interact significantly in the solid state.

The trihalides have low conductivities (Table 1.2), hence the degree of auto-ionization is negligible:\(^3\)

\[ 2EX_3 \rightleftharpoons EX_2^+ + EX_4^- \]

<table>
<thead>
<tr>
<th>Table 1.2: Conductivities of Trihalides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halide</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>AsCl₃/20°C</td>
</tr>
<tr>
<td>SbCl₃/75°C</td>
</tr>
</tbody>
</table>

Above its melting point SbCl₃ is a molecular liquid similar to water in its physical properties. Liquid SbCl₃ has low conductivity and viscosity, but a high dielectric constant, (33.2 at 75°C.).\(^{27}\) Both it and AsCl₃ are therefore suitable for use as nonaqueous solvents for inorganic solutes.\(^{28, 29}\) They have liquid ranges of 150°C and are good media for chloride ion transfer reactions. Both have such low electrical conductivities that they have been suggested as solvents for nmr spectroscopy.\(^{30}\)
1.3.2 Structural Properties

The principle valence orbitals of EX$_3$ undergo approximate sp$^3$ hybridization; the XEX angles fall short of the tetrahedral angle (109°) due to lone pair-bond pair repulsions (Table 1.3). $^{31}$

Table 1.3 shows that weak secondary contacts are a common feature of the crystal structures of the Group 15 halides. $^{49}$ Thus while the lone pair and the primary E-X bonds describe a polyhedron whose shape can be predicted from VSEPR theories, $^{50}$ the secondary contacts cap the faces or bridge the edges of this polyhedron. More detailed discussion of the stereochemistry of the Group 15 trihalide complexes appears later in this chapter.

In the vapour phase AsF$_3$ $^{51}$, AsCl$_3$ $^{52}$, AsBr$_3$ $^{53}$, AsI$_3$ $^{54}$, SbCl$_3$ $^{55}$, SbBr$_3$ $^{56}$ and BiCl$_3$ $^{57}$ are essentially pyramidal monomers (Figure 1.2). The XAsX angles increase from 96.2° (X=F) $^{51}$ to 100.2° (X=I). $^{54}$

**Figure 1.2: Pyramidal Shape of Group 15 Trihalides EX$_3$**
### Table 1.3
Bond Lengths, Contact Lengths, and Bond Angles of Group 15 Trihalides

<table>
<thead>
<tr>
<th>Halide</th>
<th>E-X Length(A)</th>
<th>E-X Length(A)</th>
<th>Angle XEX°</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCl₃(s)</td>
<td>1.71(2)-1.78(1)</td>
<td>&lt;3.19(2)</td>
<td>103.1(9)-109.6(13)</td>
<td>32</td>
</tr>
<tr>
<td>PCl₃(s)</td>
<td>2.019, 2.034(2)</td>
<td>3.892(2)(x2), 3.657(2), 3.874(1)(x2)</td>
<td>100.04, 100.19(7)</td>
<td>33, 34, 35</td>
</tr>
<tr>
<td>AsF₃(s)</td>
<td>1.699(12), 1.700(11), 1.721(10)</td>
<td>2.886(12), 2.990(10), 3.052(11), 3.184(12), 1.099(12)</td>
<td>92.9, 93.3, 95.5(5)</td>
<td>36</td>
</tr>
<tr>
<td>AsCl₃(s)</td>
<td>2.162, 2.169, 2.171(2)</td>
<td>3.692, 3.727, 3.773(3), 3.865, 3.968(2)</td>
<td>97.3, 97.5, 98.3(1)</td>
<td>31, 37</td>
</tr>
<tr>
<td>αAsBr₃(s)</td>
<td>2.345(15)</td>
<td>3.738, 3.717, 3.863</td>
<td>97.3, 97.5, 98.2(5)</td>
<td>38</td>
</tr>
<tr>
<td>AsI₃(s)</td>
<td>2.591(1)</td>
<td>3.467(2)</td>
<td>99.67(5)</td>
<td>39</td>
</tr>
<tr>
<td>SbF₃(s)</td>
<td>1.90, 1.94(2)</td>
<td>2.60(2), 2.60(2), 2.63(3)</td>
<td>95.7(8), 89.0(8)</td>
<td>40</td>
</tr>
<tr>
<td>SbCl₃(s)</td>
<td>2.340(2), 2.368(2), 3.738(1)(x2), 3.609(2), 3.457(1)(x2)</td>
<td>90.98, 95.7(5)(x2)</td>
<td>41, 42</td>
<td></td>
</tr>
<tr>
<td>SbBr₃(s)</td>
<td>2.50(5)</td>
<td>3.79</td>
<td>95</td>
<td>36</td>
</tr>
<tr>
<td>SbI₃(s)</td>
<td>2.586</td>
<td>3.32(1)</td>
<td>95.8(3)</td>
<td>43</td>
</tr>
<tr>
<td>BiF₃(s)</td>
<td>2.23, 2.31, 2.34(1)(x2)</td>
<td>2.40(1)(x2), 2.50(1)(x2)</td>
<td>135.1(3), 100.5(1), 72.9-88.8</td>
<td>44, 45</td>
</tr>
<tr>
<td>BiCl₃(s)</td>
<td>2.468(4), 2.513, 2.517</td>
<td>3.224(3), 3.398(8), 3.450(9), 3.216(9), 3.256(9)</td>
<td>84.45, 93.2, 94.9(3)</td>
<td>46</td>
</tr>
<tr>
<td>αBiBr₃(s)</td>
<td>2.660, 2.642, 2.636(4)</td>
<td>3.246, 3.306, 3.699</td>
<td>88.2, 90.1, 96.3(1)</td>
<td>47</td>
</tr>
<tr>
<td>βBiBr₃(s)</td>
<td>2.82(6)(6), 3.39(7), 4.106</td>
<td>90</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>BiI₃</td>
<td>3.07</td>
<td></td>
<td>90.0</td>
<td>43</td>
</tr>
</tbody>
</table>

Contact lengths describe the intermolecular and interionic contacts shorter than Van der Waals distances, but significantly longer than conventional single bonds. They can be defined as secondary bonds. 48
In most of the crystal structures of the Group 15 trichlorides and tribromides discrete $\text{EX}_3$ molecules are the primary structural units.

An early crystal structure determination of antimony trichloride $^{58}$ illustrates its pyramidal shape. Discrete $\text{SbCl}_3$ molecules are located on mirror planes, with three pyramidal directed single $\text{Sb-Cl}$ bonds of average length $2.36(3)\text{Å}$ (two at $2.37\text{Å}$ and one at $2.35\text{Å}$). The average $\text{XEX}$ angle is $95.2^\circ$. The lone pair occupies the fourth distorted tetrahedral position, exerting a substantial steric control over the shape of the molecule. A redetermination by Lipka $^{41}$ reveals the same triangular pyramidal shape (with mirror symmetry), but the coordination polyhedra differ in their intermolecular contacts. There are three covalent $\text{Sb-Cl}$ bonds, two of $2.368(1)\text{Å}$, the third of length $2.340(2)\text{Å}$, and five intermolecular $\text{Sb-Cl}$ contacts, all significantly shorter than the Van der Waals radii of $4.0\text{Å}$ (Table 1.3). These secondary bonds increase the coordination number of the antimony atom to eight, yielding a bicapped trigonal prism (Figure 1.3). Presumably the lone pair occupies an orbital below the pyramidal $\text{SbCl}_3$ unit within the trigonal prism, which causes the observed lengthening of the contacts to the trigonal base.
The coordination of the Sb atom is best described as [3+2+3]. One trigonal base of the bicapped trigonal prism is formed by three covalently bonded Cl atoms, the other by the three most distant Cl atoms. The remaining two secondary Sb-Cl bonds are trans to the two shortest intermolecular contacts. All interactions, including the two longest Sb-Cl contacts involve the same crystallographically independent Cl atom. In the resulting three-dimensional network the Cl atoms adopt distorted hexagonal close-packing. The [3+2+3] coordination of the Sb atom is unique to the SbCl$_3$ structure. In SbCl$_3$ complexes the intermolecular contacts usually complete octahedral, ψ-octahedral or pentagonal bipyramidal coordination of the Sb atom. SbCl$_3$ is similar in structure to BiC$_3$ which has five nearest neighbours in addition to the three pyramidally directed Bi-Cl bonds. The eightfold coordination of a bicapped trigonal prism around the metal seems to be a common feature of Group 15 trihalides and can also be seen in the structures of SbBr$_3$ and PBr$_3$. 
The closely related coordination polyhedron of a tricapped trigonal prism is found in AsCl$_3$, AsBr$_3$, and PCl$_3$. All edges and faces of the EX$_3$A tetrahedron (A=lone pair) are involved in secondary bonding interactions, the overall geometry being EX$_3$Y$_3$Y'A (X=primary bonds, Y=face-capping and Y'=edge-bridging secondary bonds). This tricapped trigonal prism of ligands is distorted by the lone pair, which caps a triangular face of the trigonal prism (Figure 1.4).

Figure 1.4: Tricapped Trigonal Prism in PCl$_3$.

The structure of NCl$_3$ differs from the above trigonal prismatic structures; the chlorine atoms build up distorted octahedra, tetrahedra and trigonal prisms around the nitrogen atom.

In some Group 15 trihalides the stereochemical activity of the lone pair A influences the geometry of both the primary and secondary bonds while in others it has no effect on the formation of the secondary bonds. Such a "non stereochemically active" lone-pair is apparent in the anion SbCl$_5^2^-$. This square pyramidal ion displays weak secondary interactions in
the remaining octahedral position, close to the presumed direction of the lone pair. Stereochemical inactivity of the lone pair usually occurs when there is an excess of primary bonds over secondary interactions. In SbCl$_3$, which has only three primary bonds, the five secondary interactions avoid the presumed direction of the lone pair.

Where the lone pair exerts little or no steric control over the geometry of the secondary bonds it occupies a spherical s-type orbital. When as many as five primary bonds form to relatively large ligands, as in SbCl$_5^-$, there is insufficient room for the lone pair to remain in the valence shell, and it moves inside the bonding pairs to occupy an s-type orbital. An extreme case arises in the SbCl$_6^{3-}$ anion, which has a regular octahedral structure but rather long Sb-Cl bonds of average length 2.643(6)Å. The lone pair occupies a spherical 5s orbital, which has no effect upon the orientation of the primary bonds. The Sb-Cl bonds approximate as three-centre four electron bonds formed from 5p (of Sb) orbitals only, in agreement with the Mossbauer work of Birchall et al. The increased length of the Sb-Cl bonds, 2.643Å compared with those of SbCl$_3$ itself (2.340(2)Å and 2.368Å) is in accordance with the greater coordination number of Sb in SbCl$_6^{3-}$.

There is a trend towards decreasing stereoactivity of the lone pair in the order As > Sb >> Bi, due to a greater tendency of the lone pair to occupy an s-type orbital, thus losing its steric influence. The unshared pair is stabilized by being able to distribute its electron density over the large surface of the heavy atom. In AsCl$_3$, SbCl$_3$ and BiCl$_3$, the difference in length between the primary bonds and the
secondary contacts decreases with increasing size of the central atom (Table 1.3), which implies a reduction in the stereochemical activity of the lone pair.

1.3.3 Pentafluorides

All four Group 15 pentafluorides exist. They are powerful fluoride ion acceptors, forming $\text{EF}_6^-$ anions or more complex species e.g. $\text{E}_2\text{F}_{11}$.

The chlorides of the group vary enormously in their stabilities. Only $\text{PCl}_5$ and $\text{SbCl}_5$ are stable at room temperature, although the stability of the latter extends only to 140°C. $\text{AsCl}_5$ was eventually synthesized in 1976 by the ultra-violet irradiation of $\text{AsCl}_3$ in liquid $\text{Cl}_2$ at -105°C. It was shown, by means of Raman spectroscopy to have a trigonal bipyramidal structure.

$\text{BiCl}_5$ and $\text{EX}_5$ ($\text{E}=\text{As, Sb, Bi}$ and $\text{X}=\text{Br, I}$) do not exist. This can be formally attributed to the inability of the halide ions to coexist with the +5 oxidation state of the Group 15 elements (compare the non-existence of $\text{Fel}_3$, $\text{CuI}_2$ and $\text{TI}_3$).

The curious instability of $\text{AsCl}_5$ compared to that of $\text{PCl}_5$ and $\text{SbCl}_5$ can be attributed to the "d- block contraction": The highest valence state of p-block elements following completion of the first (3d) transition series are, in general, unstable in comparison to the other members of the group. 3 Incomplete shielding of the nucleus by the d electrons leads to a lowering of the energy of the 4s orbital in $\text{AsCl}_3$. Hence it is more difficult to involve 4s$^2$ electrons in bonding for the formation of $\text{AsCl}_5$, than it is for phosphorus or antimony. Similarly the energy of the 6s$^2$ electrons in bismuth is low. This is probably
due to the "lanthanoid contraction," analogous to the effects experienced by arsenic. Table 1.4 shows that the sum of the fourth and fifth ionization energies of arsenic and bismuth are greater than for antimony.

**Table 1.4 Ionization Energies of Arsenic, Antimony and Bismuth**

<table>
<thead>
<tr>
<th>Ionization energies (MJmol⁻¹, sum of IV and V)</th>
<th>As</th>
<th>Sb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10.880</td>
<td>9.636</td>
<td>9.776</td>
</tr>
</tbody>
</table>

The pentavalent compounds of Group 15 generally adopt trigonal-bipyramidal (tbp) and square-pyramidal (sp) geometries. The tbp and sp configurations differ very little in energy and their interconversion is facile. The trigonal bipyramid is usually more stable for EX₅ molecules when X are separate groups; the square-pyramidal geometry is favoured when the X groups are connected to give two unsaturated five membered chelate rings, or in the presence of a more strained four-membered ring. ²⁷,²⁸

Phosphorus pentafluoride is a trigonal bipyramidal molecule with axial P-F bonds of length 1.571 Å and equatorial fluorine atoms at a distance of 1.542 Å. However all five fluorine atoms appear to be equivalent in the ¹⁹F nmr spectrum of PF₅, ⁸⁰ even at low temperatures: on the slower nmr time scale, rapid rotation of the axial-equatorial bonds via a square pyramidal intermediate results in the observed equivalence of the fluorine atoms. This rapid interchange of F-
AsF₅ also has a \textit{tbp} structure, exhibiting stereochemical nonrigidity, whereas SbF₅, a viscous liquid at room temperature, is quite different. Even in the gas phase it associates by F bridges to form a cyclic trimer (SbF₅)₃. In the liquid phase the SbF₅ moieties are linked by \textit{cis} Sb-F-Sb bridges, resulting in polymeric chains of SbF₆ octahedra, while in the solid state a tetramer forms (Figure 1.5). BiF₅ is a crystalline solid, comprising infinite \textit{trans} chains of BiF₆ octahedra.

\textbf{Figure 1.5: The (SbF₅)₄ Tetramer}

In the vapour and liquid phases PCl₅ has a molecular \textit{tbp} structure; in the crystalline state it exists in the ionic form [PCl₄][PCl₆], comprising tetrahedral PCl₄ cations and octahedral PCl₆ anions. A well documented metastable solid form [PCl₄]₂⁺[PCl₆]Cl⁻ also exists. The solution structure of PCl₅ depends upon the nature of the solvent. Disproportionation, according to equation 1, occurs in moderately polar solvents.
such as MeCN and PhNO₂. In highly polar solvents such as HCl, the ionization process (equation 2) competes with disproportionation.

\[
\begin{align*}
2\text{PCl}_5 & \rightarrow [\text{PCl}_4]^+ + [\text{PCl}_6]^-
\text{(1)} \\
\text{PCl}_5 & \rightarrow [\text{PCl}_4]^+ + \text{Cl}^-
\text{(2)}
\end{align*}
\]

In non-polar solvents (such as benzene) PCl₅ is monomeric with a trigonal bipyramidal structure.

In vapour and liquid phases SbCl₅ exists in the monomeric form. This geometry is retained in the crystal structure at -30°C. At even lower temperatures there is spectroscopic evidence for dimerization, according to equation 3.

\[
2\text{SbCl}_5(\text{monomer}) \rightarrow \text{Cl}_4\text{Sb} \mu(\text{Cl})_2\text{SbCl}_4
\text{(3)}
\]

PBr₅ is the only known pentabromide of the heavier Group 15 elements, in the gas phase it dissociates fully to PBr₃ and Br₂. This dissociation occurs in non-polar solvents of low dielectric constant, while in more polar solvents such as MeCN, disproportionation is thought to occur, according to equation 4.

\[
2\text{PBr}_5 \rightarrow (\text{PBr}_4)^+ [\text{PBr}_6]^-
\text{(4)}
\]

Solid PBr₅ consists of [PBr₄]⁺ and Br⁻ ions; each Br⁻ ion is surrounded by four bromine atoms, each belonging to a different PBr₄⁺ unit. Unlike PCl₆⁺ the [PBr₆]⁻ anion seems to be unknown in the solid state. The octahedral PBr₆⁻ anion is, however, stabilized by solvent molecules. This behaviour is analogous to that of phosphorus pentachloride in solvents of varying polarity.
Antimony pentabromide has been isolated only as an adduct with ether, i.e. (C$_2$H$_5$)$_2$O.SbBr$_5$. The neutral ether ligand increases the electron density on Sb(V), and reduces its oxidising strength.

The synthesis of PI$_5$, formulated as [Pl$_4$]+I$, was reported in 1978, but it is probable that a mixture of PI$_3$ and I$_2$ was analysed. Pl$_4$+AsF$_6$ has been isolated and characterised by Raman spectroscopy as the first example of a salt containing the discrete tetrahedral cation Pl$_4^+$, a derivative of the unknown PI$_5$. It is thermodynamically unstable with respect to PF$_3$(g), AsF$_3$(l) and I$_2$(s). Although Pl$_4$+All$_4^-$ has been reported, the Pl$_4$ and All$_4$ units are connected into a three dimensional structure by weak secondary iodine-iodine bonds. In the solid state the structure can be regarded as intermediate between molecular PI$_3$/I$_2$/All$_3$ and the ionic formulation given above. IF, SbF$_5$ and Pl$_3$ together yield Pl$_4$+SbF$_6^-$, which is less stable than its arsenic congener.

Stereochemical nonrigidity in pentavalent molecules increases in the order P < As < Sb (i.e. as the electronegativity of the central atom decreases). This is in accordance with a simple repulsion model which favours a trigonal bipyramidal geometry. As repulsion effects are reduced in the order P > As > Sb, the energy difference favouring the $tbp$ geometry decreases (hence so does the energy barrier between them).

Both AsF$_5$, SbF$_5$ and to a lesser extent PF$_5$ are very powerful fluoride ion acceptors, yielding EF$_6^-$ ions or more complex species. The hexafluorophosphate(V) anion is frequently used as a non-complexe$ing$_anion which has even less
coordinating ability than the ClO₄⁻ and BF₄⁻ anions. SbF₅ is used to generate SbF₆⁻, another non-complexing anion. In Fe(TPP)(F₅SbF)PhF however, it is found to be a ligand covalently bound to iron, not the expected anion. Hexafluoroantimonate(V) likewise binds to some coordinatively unsaturated cations.

BiF₅ has markedly weaker Lewis acidic properties than those of SbF₅, as illustrated by the structures of the adducts formed with xenon tetrafluoride. The antimony pentafluoride adduct is essentially ionic, [XeF₃]⁺[SbF₆]⁻ with a bridging fluorine ligand 2.49Å from the XeF₃⁺ unit. In the bismuth analogue the (F-XeF) distance of 2.25Å is shorter and has a much greater covalent character. The structure is intermediate between the molecular XeF₄.BiF₅ and the ionic [XeF₃]⁺[BiF₆]⁻ formulations.

SbF₅ is the strongest Lewis acid of the Group 15 pentafluorides, and forms the strongest superacid with HSO₃F ("magic acid"). The strong halide acceptor properties of the pentahalides are also exploited in their use as Friedel Crafts catalysts. The elimination of HF by SbF₅ finds utility in the synthesis of fluoro-alkene derivatives in a novel approach to conjugated polymers. The Lewis acidity of the pentafluorides will be discussed more fully later in this chapter.

The pentafluorides are extremely powerful fluorinating and oxidising agents, some typical reactions including:
SbF₅ + ClICH₂PCl₂ → ClCH₂PF₄
BiF₅ + UF₄ → UF₆
BiF₅ + Br₂ → BrF₃ + BrF₅
BiF₅ + Cl₂ → ClF

SbF₅ (known as the Swarts reagent) and AsF₅ are also used as fluorinating agents:

RCl → RF
R₃PS → R₃PF₂

Antimony pentachloride behaves as a chlorinating and oxidising agent, e.g.

Me₃As + SbCl₅ → Me₃AsCl₂ + SbCl₃
R₃P + SbCl₅ → [R₃PCl][SbCl₆]⁻ (R=Ph, Et₂N, Cl)

The addition of small amounts of SbCl₅ to SbF₅ greatly reduces its viscosity by cleavage of the Sb-F-Sb bridges. This is of importance in industrial applications of the Swarts reactions.

1.3.4. Mixed Pentahalides

Several covalent mixed pentahalides are known (e.g. PCl₄F, SbCl₃F₂, SbCl₂F₃). Others have ionic structures: the conductivity of AsCl₅F in excess AsF₃ suggests the ionic formulation [AsCl₄⁺][AsF₆⁻]. In the vapour phase (below 55°C) AsCl₅F₃ monomers adopt a trigonal bipyramidal shape in which the two chlorines occupy equatorial positions. The entire series of mixed chlorofluoroarsanes, AsClₙFₙ₋₁(n=1-5), have been synthesized from AsCl₂F₃. The ionic mixed halides [AsCl₄⁺][PCl₆]⁻ and [AsCl₄⁺][SbCl₆]⁻ stabilize the +5 oxidation state of arsenic.
1.4. Group 15 Halides as Acceptors:

1.4.1. Trihalides

EX₃ (X=halogen; E=P, As, Sb, Bi) compounds can behave both as ligands and acceptors: this duality leads to some interesting chemistry. PX₃ molecules are important σ acid ligands, due to the polarity of the P-X bond (especially when X=F). The ligand PCl₃ is a good donor and forms purely σ bonded complexes with the boron halides. Phosphorus trihalides also exhibit some Lewis acceptor behaviour, as shown by their formation of weak complexes with trimethylamine.

The trihalides of arsenic also show significant Lewis acidity, but it is with the Sb(III) and Bi(III) halides that extensive complex formation occurs. They form a great variety of adducts with neutral and anionic ligands. The compatibility of donors for complexation can be rationalised by the Hard-Soft-Acid-Base (HSAB) rule. SbX₃ and BiX₃ are hard acids, they form very stable complexes with chloride ion ligands. SbCl₃ forms very weak complexes with "soft" S-donor ligands. The HSAB principle is a very useful rule of thumb for coordination chemistry, yet more and more complexes are being synthesized when the acid-base interactions are thought to be unfavourable (Chapter 5).

1.4.1.1. Group 15 Trihalide Adducts with Neutral Ligands

The trihalides of arsenic, antimony and bismuth form a great number of adducts with neutral ligands, yielding coordination numbers from 4 to 8.
Four Coordinate Structures

The majority of four coordinate mono-adducts, EX₃L (E=As,Sb,Bi; X=halogen; L=neutral ligand) retain stereochemical activity of the lone pair. The mono-adduct with aniline, SbCl₃·PhNH₂,¹¹¹ has a distorted trigonal bipyramidal geometry, the lone pair occupies one of the equatorial positions, as predicted by VSEPR. This is an example of a "hard" Lewis base (nitrogen donor) interacting with the hard Sb(III) (Lewis acid) centre. AsCl₃·NMe₃¹¹² displays a similar interaction, although the As-N bond is very long (Figure 1.6). In both these structures the donor ligand occupies an axial position.

Figure 1.6: Structures of SbCl₃·PhNH₂ and AsCl₃·NMe₃

![Figure 1.6]

This contrasts SbCl₃·dmit¹¹³ (dmit=1, 3-dimethyl-2-(3H)-imidazothione), in which both the ligand and the lone pair occupy equatorial positions (Figure 1.7).
Oxygen donor adducts \( \text{EX}_3\text{L} \) (\( \text{L} = \text{POCl}_3 \) and \( \text{POMe}_3 \)) have also been isolated. 114

**Five Coordinate Structures**

Five coordinate structures fall into two classes; 1:1 complexes with bidentate ligands and 1:2 complexes with monodentate ligands. The distorted square-pyramidal species \( \text{SbCl}_3.2\text{PhNH}_2 \) illustrates the latter possibility. The Sb atom lies below the basal plane of the square pyramid while the lone pair occupies the sixth coordination site. In \( \text{SbCl}_3.\text{DEDTM} \) (Figure 1.8) the N, N'-diethylthiomalonamide molecule bonds to \( \text{SbCl}_3 \) as a \( \text{cis} \) chelate ligand through the sulphur atoms. The Sb atom lies below the Cl(2), Cl(3), S, S plane, the sixth octahedral position is taken up by the lone pair.
These structures contrast $\text{[SbCl}_3\text{]}^2^-$ where the lone pair seems to be stereochemically inactive. 59,62

**Six Coordinate Structures**

The six coordinate arrangement of ligands is highly favoured in the structures of the Group 15 trihalides. A good example is found in the polymeric SbCl$_3$.DMO adduct. 117 Each Sb atom binds strongly to three chlorine atoms (Sb-Cl; 2.35-2.40Å) and weakly to three oxygen atoms, resulting in a *regular octahedral* Sb geometry. In SbCl$_3$.($\text{DEDTO})_1,5$ each Sb atom is bound by three Cl atoms and three loosely bound sulphur atoms 118 to give a more *distorted octahedral* geometry. In both cases the lone pair seems to have very little stereochemical activity.

However, the lone pair is stereochemically active when the ligand contains "hard" donor atoms or "narrow bite" ligands. For example, Bi(S$_2$CNEt$_2$)$_3$. 119 features an octahedral coordination sphere. The lone pair acts through the centre of one of the faces, resulting in a *pseudo* seven-coordinate structure.
Seven Coordinate Structures

Seven coordination is seen in the monomeric BiCl₃.(DEDTO)₂ molecule. The geometry approaches ideal pentagonal-bipyramidal, with two chlorine ligands in axial positions, and the remaining ligands in the equatorial plane. There is no vacancy in the Bi(III) coordination sphere for a stereochemically active lone pair. Such pentagonal bipyramidal geometry is usual in complexes of Group 15 trihalides with two bidentate ligands of large bite.

Eight Coordinate Structures

The compound BiCl₃.18-crown-6 has the ionic formulation 2[BiCl₂.18-crown-6]+[Bi₂Cl₈]²⁻. The bismuth cation is eight coordinate, involving the six oxygens of the crown ether and the two chlorine atoms in a bicapped trigonal prismatic geometry. The lone pair on bismuth(III) is thought to be active, pointing in the direction of the third potential capping position of the trigonal prism. Eightfold coordination of Sb(III) is also observed in the adduct SbF₃.15-crown-5. The Sb atom is surrounded by three F atoms and the five oxygen atoms of the crown ether molecule. The analogous SbCl₃.15-crown-5 features a stereochemically active lone pair, which points towards the centre of the crown ring. The three Sb-Cl bonds are pyramidally directed, the SbCl₃ molecule suffering very little structural change upon complexation to the crown molecule. The Sb-O distances vary from 2.787(5) to 2.997(4)Å, averaging 2.902Å (c.f. sum of covalent radii 2.2Å). These observations indicate weak SbCl₃-crown ether interactions. Even weaker interactions are found in SbCl₃.18-crown-6.
where the mean Sb-O distance is 3.183Å, the lone pair is again stereochemically active.

**Menshutkin Complexes**

Aromatic donor ligands form a great number of complexes with Group 15 trihalides which vary enormously in their structures. These adducts involve weak interactions between the EX₃ molecule and the π cloud, and are known as "Menshutkin" complexes.

Smith and Davies 125 described adducts of antimony tribromide and trichloride with benzene and napthalene more than 100 years ago, and in 1912 Menshutkin 126 prepared and characterised several complexes between substituted aromatics and SbCl₃. Crystallographic investigations have more recently extended to complexes of both arsenic 127,128 and bismuth 129, 130,131 trichlorides and tribromides.

The 2:1 complex between SbCl₃ and napthalene 132 illustrates the bonding between the metal centre and the arene (Figure 1.9).
The two SbCl$_3$ moieties lie on opposite sides of the ring plane. The Sb atoms adopt distorted trigonal bipyramidal coordination: Cl(1), Cl(2) and the Sb lone pair lie in the equatorial plane, while the axial positions are occupied by Cl(3) and the electrons donated from the $\pi$-system of napthalene. The axial Sb-Cl(3) distance (2.367Å), is longer than the equatorial Sb-Cl(1), Sb-Cl(2) distances of 2.347 and 2.348Å respectively. The lone pair on antimony points over the aromatic ring, and is well positioned for interaction with the $\pi$-$\pi$-orbitals. The complex exhibits $\eta^3, p\text{seudo } \pi$-allyl coordination. This contrasts the 1:1 hexaethylbenzene: trichloroantimony complex, which shows centroid or hexahapto ($\eta^6$) coordination of the arene molecule (i.e. the lone pair on Sb(III) is oriented towards the centre of the ring).

Bismuth-arene complexes are more stable than those of arsenic and antimony. Metal-arene distances in Menshutkin complexes decrease in the order As > Sb > Bi. This is
surprising in the light of the standard covalent radii of As, Sb and Bi (1.21, 1.41 and 1.52 Å), reflecting an increasing metal-arene interaction in the order As < Sb < Bi. (This parallels the increased $s$ character of the lone pair on the heavier atom, as suggested by the "inert pair" effect based on relativistic phenomena).

$[\text{Ph}_4\text{P}]_2[\text{Sb}_2\text{I}_8].2\text{MeCN}$ displays weak interactions between the phenyl groups of the cation and the antimony atoms of the anion, similar to those found in the Menshutkin complexes. The antimony atoms in the dimeric $[\text{Sb}_2\text{I}_8]^{2-}$ anion are square pyramidaly coordinated by the iodine ligands, octahedral coordination being completed by $\eta^2$-bonded phenyl rings of the cation.

1.4.1.2. Complexes with Halide Ion Ligands

The trihalides of arsenic, antimony and bismuth combine with halide ions to form an extensive series of complex anions. Examples include: $[\text{SbCl}_4]^{-}$, $[\text{SbCl}_5]^{2-}$, $[\text{BiCl}_6]^{3-}$, $[\text{As}_2\text{Br}_8]^{2-}$, $[\text{Sb}_2\text{Cl}_9]^{3-}$, $[\text{As}_4\text{Cl}_{16}]^{4-}$, and $[\text{Bi}_4\text{Cl}_{18}]^{6-}$. In the majority of these reactions the source of the halide ion is an organic molecule, RX, or an alkali metal halide, MX.

The conductivities of the trihalides are increased by addition of substances such as KF, Me$_4$NCl, SbF$_5$ and FeCl$_3$ which can donate or accept halide ions to give ionic species.

Arsenic and antimony trifluorides accept fluoride ions from MF, (M=Na, K, Rb, Cs) resulting in the formation of a variety of fluoroanions. Lithium fluoride fails to donate $F^-$ ions doubtless due to the small size and polarizing power of the lithium cation.
The stoichiometry of the resulting species is not particularly informative about their structures. This is due to oligomerisation of the resultant $[\text{MF}_4]^-$ ions which depends upon the nature of M. (No monomeric $C_2 \sigma$ SbF$_4^-$ anion (isoelectronic with SeF$_4$) exists).

The anion in NaSbF$_4$\textsuperscript{145} is based on a trigonal bipyramid of four primary Sb-F bonds and a lone pair. There are two secondary Sb-F contacts of 2.66 and 2.87Å which bridge the edges of the equatorial plane. This results in dimerisation of $\{\text{SbF}_4\}$ units. There is a third weaker contact of 3.33Å which caps one face of the bipyramid. In K$_2$SbF$_4$\textsuperscript{146} association of $\{\text{SbF}_4\}$ units occurs to give the tetrameric, cyclic anion $[\text{Sb}_4\text{F}_{16}]^4-$ (Figure 1.10). The geometry of the Sb(III) atom is slightly distorted from the EX$_5$A octahedral geometry of the SbF$_5^2-$ anion and is intermediate between EX$_3$Y$_3$A and EX$_5$YA. Two of the equatorial Sb-F bonds are longer than the other two, and there is one long Sb-F contact of 2.94(2)Å, which caps an octahedral face.
The SbF$_5^-$ anion in (NH$_4$)$_2$SbF$_5$ has a short apical Sb-F bond (1.92Å) (compare 1.90 and 1.94(2)Å in SbF$_3$ itself), which is trans to the lone pair, while the longer Sb-F bonds of average length 2.08Å form the base of the square pyramid. The Sb atom is slightly below the basal plane. This ion has a discrete structure, there are no secondary Sb···F contacts shorter than the Van der Waals radii (Figure 1.11). The K, Rb, Cs and Tl salts are isostructural with the ammonium salt.

Figure 1.10: The Tetrameric Cyclic Anion [Sb$_4$F$_{16}^-$]

The SbF$_5^-$ anion in (NH$_4$)$_2$SbF$_5$ has a short apical Sb-F bond (1.92Å) (compare 1.90 and 1.94(2)Å in SbF$_3$ itself), which is trans to the lone pair, while the longer Sb-F bonds of average length 2.08Å form the base of the square pyramid. The Sb atom is slightly below the basal plane. This ion has a discrete structure, there are no secondary Sb···F contacts shorter than the Van der Waals radii (Figure 1.11). The K, Rb, Cs and Tl salts are isostructural with the ammonium salt.

Figure 1.11: The [SbF$_5$]$^2^-$ Anion
The mononuclear SbF$_6^{3-}$ anion appears to be absent in the series of Sb(III) fluoroanions.

The structures of several salts of the Sb$_2$F$_7^{-}$ anion have been determined. The ion consists of two SbF$_3$ groups bridged by a fluoride ion. In K$_2$SbF$_7$ and Rb$_2$SbF$_7$ the Sb-F-Sb bridges are asymmetric (Sb-F lengths are 2.082 and 2.409(3)Å and 2.12 and 2.33Å respectively). In Cs$_2$SbF$_7$, however, the bridge is symmetrical with Sb-F distances of 2.240Å. In the three salts the environment of the Sb(III) atoms can be considered in two ways. A basic trigonal bipyramidal EX$_4$A geometry results if the bridging Sb-F bond is considered to be a primary bond. In this case the three (or four) secondary contacts cap two of the faces and bridge one (or two) of the edges. If the bridge is thought of as a secondary interaction the basic geometry is EX$_3$A tetrahedral. Four (or five) secondary contacts yield a partial EX$_3$Y$_3$V$_3$A tricapped trigonal prismatic arrangement of atoms in which one or two of the Y' contacts are absent (Figure 1.12).

Figure 1.12: The Sb$_2$F$_7^{-}$ Anion in Cs$_2$SbF$_7$

The anions (SbF$_3$)$_x$F$^-$, (x =3, 4) occur in (NH$_4$)$_2$Sb$_3$F$_{10}$, Na$_2$Sb$_3$F$_{10}$ and K$_2$Sb$_4$F$_{13}$. The primary geometry of the Sb(III) atoms in the potassium salt is best described as
tetrahedral EX₃A, with three relatively short face-capping contacts of lengths 2.51 to 2.75 Å, and three longer contacts of length 3.03 to 3.19 Å. These bridge the edges of the tetrahedron, giving an overall EX₃Y₃'3Å geometry. If the shortest of the secondary contacts (2.51 Å) is considered as a primary bond, a basic EX₄A geometry results with two face-capping and three edge-bridging contacts. An overall EX₄Y₃'4Å geometry describes the Sb(III) atoms in NaSb₃F₁₀.

The structure of the ammonium salt seems to be quite different; the anion can be viewed either as an SbF₃ group interacting with an Sb₂F₇⁻ moiety or as two SbF₃ groups interacting with an SbF₄⁻ anion. Sb(I) has an overall EX₄Y₄'3Å geometry, while Sb(2) and Sb(3) have EX₃Y₃'2Å and EX₄Y₃A geometries respectively.

The Sb₂F₉⁻ anion is found in [Co(NH₃)₆]₃⁺[Sb₂F₉]³⁻; it comprises two SbF₅ square pyramids which share a common F⁻ atom. The Sb(III) geometry is based on pentagonal bipyramidal (EX₆Y₃A) coordination, with the lone pair in an axial position surrounded by three longer contacts. The mixed Sb(III)/Sb(V) species Sb₃F₁₄⁻ occurs in, for example, [S₄N₄][Sb₃F₁₄][SbF₆]. [S₈][Sb₃F₁₄][SbF₆] and [I₄][Sb₃F₁₄][SbF₆]. The trimeric anion in the former salt consists of an angular Sb³⁺[F₂] cation linked by trans asymmetric bridges to two Sb⁴⁻ anions (Figure 1.13). The central Sb(III) atom has a trigonal bipyramidal geometry with the lone pair in an equatorial position. It forms four additional contacts to fluorine atoms in other SbF₆⁻ and Sb₃F₁₄⁻ anions; these surround the lone pair to give overall distorted square-capped antiprismatic (EX₄Y₄A) coordination. Other salts of the
Sb$_3$F$_{14}^{-}$ anion have up to six secondary contacts to Sb(III), which bridge the edges or cap the faces of the trigonal bipyramid containing the lone pair as a vertex. Differences in secondary bond formation arise from the packing requirements of the cations in the lattice. Weak Sb(III)...F interactions can cause Sb$_3$F$_{14}^{-}$ anions to form oligomeric chains or layers as in [Te$_2$Se$_4$][Sb$_3$F$_{14}$][SbF$_6$].

Figure 1.13: The [Sb$_3$F$_{14}$]$^-$ ion in (S$_2$N$_4$)[Sb$_3$F$_{14}$][SbF$_6$]

Other mixed Sb(III)/Sb(V) species are known. The Sb$_4$F$_{17}^{-}$ anion in [SeS]$_2$[Sb$_4$F$_{17}$][SbF$_6$]$_3$ can be formulated as [SbF$_6$.SbF$_2$.F.SbF$_2$.SbF$_6$.] or as [SbF$_6$.Sb$_2$F$_5$.SbF$_6$.]. The central fluorine atom forms the crystallographic centre of symmetry; the Sb$_2$F$_5$. cation has a linear Sb-F-Sb bridge with Sb-F distances of 2.11Å. (Compare the analogous Sb$_2$F$_5$. cation in [Se$_4$]$_2$[Sb$_2$F$_4$]$_2$.Sb$_2$F$_5$.SbF$_6$.] which has an asymmetric fluorine bridge, with Sb-F distances, 2.09(1) and 2.15(1)Å, and an Sb-F-Sb angle of 149.8(6)°). In "Sb$_2$F$_4$Cl$_5$", formulated
The cation contains a central Sb(III) atom bonded via F bridges to an Sb(V) atom, and which is weakly bound to terminal F atoms of the anion to give overall 8 coordination of the Sb(III).

SbF$_3$.SbF$_5$ mixtures yield several other mixed oxidation state species: crystal structures of the 1:1, 2:1, 3:1, 6:5, 5:3 and 3:4 adducts have been determined. The 1:1 adduct consists of Sb$_2$F$_4^{2+}$ cations and SbF$_6^{-}$ anions. The cation, which has an asymmetric bridge (Sb-F lengths of 2.01Å and 2.15Å; F-Sb-F angle of 148°), may be considered as an SbF$_3$ molecule interacting with an SbF$_2^{2+}$ cation (Figure 1.14).

**Figure 1.14:** The [Sb$_2$F$_4$]$^{2+}$ cation in SbF$_3$.SbF$_5$ (showing contacts shorter than 2.15Å)

Sb(1) has an EX$_3$Y$_3$Y'$_2$A geometry based upon a pyramidal EX$_3$A coordination, while Sb(2) is based upon an EX$_5$A pentagonal bipyramid. Three long contacts avoid the axial lone pair and cap three faces of the bipyramid (these are not shown.
in Figure 1.14). The axial Sb(2)-F(4) bond (1.86\AA) is shorter than the equatorial contacts, which range from 2.14 to 2.41\AA. Bond angles in the equatorial pentagonal plane are close to the ideal 72°. The Sb\textsuperscript{III} atoms of the cation interact with fluorine atoms of the SbF\textsubscript{6}\textsuperscript{-} anion to form a three dimensional polymeric structure. This \([\text{Sb}_2\text{F}_4]^2+\) unit contrasts the similar ion in \([\text{Se}_4]^2+[\text{Sb}_2\text{F}_4]^2+[\text{Sb}_2\text{F}_5]^+\text{SbF}_6\textsubscript{5}^−\), \textsuperscript{160} which is situated around a centre of symmetry. Here the Sb(III) atoms form primary bonds to two fluorine atoms related by the centre of symmetry to give planar Sb\textsubscript{2}F\textsubscript{2} rings. There are additional bonds; a primary axial Sb-F bond and five further secondary fluorine contacts.

The unit cell of S\textsubscript{11}F\textsubscript{43}, (i.e. 6SbF\textsubscript{3}.5SbF\textsubscript{5}) contains five SbF\textsubscript{6}\textsuperscript{-} anions and a section of the polymeric Sb(III) chain cation [Sb\textsubscript{6}F\textsubscript{13}]\textsubscript{n}\textsuperscript{5+}. \textsuperscript{162} There are a large number of contacts between the Sb(III) atoms and the fluorine atoms of the SbF\textsubscript{6}\textsuperscript{-} octahedra. If only the shorter Sb\textsuperscript{III}-F bonds are considered, the cation can be considered as separate SbF\textsubscript{2}\textsuperscript{+} and Sb\textsubscript{2}F\textsubscript{5}\textsuperscript{+} units. The Sb\textsubscript{2}F\textsubscript{5}\textsuperscript{+} unit has a linear symmetric fluorine bridge. By comparison, the Sb\textsubscript{2}F\textsubscript{5}\textsuperscript{+} unit in the 3:1 adduct 3Sb\textsubscript{3}F\textsubscript{3}.SbF\textsubscript{5} \textsuperscript{164} has a bent symmetric bridge (Sb-F-Sb angle, 147.4°). It joins SbF\textsubscript{3} units by Sb-F bridges to form parallel strands of [Sb\textsubscript{3}F\textsubscript{8}]\textsuperscript{+\textsubscript{\textbullet}}, associated by weak contacts of 2.716-3.056\AA with the fluorine atoms of SbF\textsubscript{6}\textsuperscript{-}. The component SbF\textsubscript{3} and Sb\textsubscript{2}F\textsubscript{5}\textsuperscript{+} units are distinguished when only bonds shorter than 2.15\AA are considered (Figure 1.15). The Sb\textsubscript{2}F\textsubscript{5}\textsuperscript{+} unit has mirror symmetry.
Bond angles around the Sb(III) atoms Sb(2) and Sb(3) are consistent with the presence of stereochemically active lone pairs. Sb(3) is square-pyramidal, the shortest Sb-F bond being trans to the lone pair. Four equatorial fluorine atoms form a plane 0.395(1)Å below Sb(3) (F<sub>eq</sub>-Sb-F<sub>ax</sub> < 90°). An additional contact of 2.833(7)Å with an F atom of SbF<sub>6</sub>· completes the monocapped octahedral (EX<sub>3</sub>Y<sub>3</sub>A) geometry. The coordination around Sb(2), including all contacts less than 3.00Å, is based upon a pentagonal bipyramid (EXY<sub>5</sub>A).

By comparison 5SbF<sub>3</sub>·3SbF<sub>5</sub> consists of three dimensional cross-linked [Sb<sub>5</sub>F<sub>12</sub>]<sup>n</sup>·<sup>3n+</sup> cations and SbF<sub>6</sub>· anions. The cation consists of F-linked Sb<sub>2</sub>F<sub>5</sub>·, Sb<sub>2</sub>F<sub>3</sub><sup>3+</sup> and SbF<sub>3</sub> units. The Sb<sub>2</sub>F<sub>5</sub>· component has a linear symmetric F bridge, similar to that found in 6SbF<sub>3</sub>·5SbF<sub>5</sub>. The Sb<sub>2</sub>F<sub>3</sub><sup>3+</sup> component (Figure 1.16), has a cis planar configuration. This ion strongly interacts with two SbF<sub>3</sub> units to form the Sb<sub>4</sub>F<sub>9</sub><sup>3+</sup> cation, if bonds ≤ 2.25Å are taken into consideration.
In all these fluoroanions the lone pair on Sb(III) exerts stereochemical influence over the geometry of the primary and secondary bond formation. The lone pair has less effect upon the stereochemistry of the complex halides of trivalent As, Sb, and Bi as

1) the coordination number on the central atom increases,
2) the atomic mass of the central atom increases and
3) the atomic mass of the halide increases.
1.4.2. Pentahalides

As previously mentioned, the pentafluorides of arsenic, antimony, and bismuth all exhibit Lewis acidic properties, and are powerful fluoride ion acceptors. Antimony pentachloride, the only stable pentachloride of As, Sb, and Bi, is also a powerful chloride ion acceptor. Acceptance of a halide ion increases the coordination number of the pentahalide to six, resulting in the formation of the octahedral, hexahalo anions \( [E \times X_6]^- \) (\( E = P, As, Sb, Bi; X = \text{halide} \)).

Early crystal structure determinations of \( M E F_6 \) salts (\( M = Li, Na, K, Rb, Ca, Ag, Tl; E = As, Sb \)) show almost symmetrical octahedral anions. \(^{168}\) (Preparation of these salts involved fluorination of the appropriate Group 15 trioxide \( E_2O_3 \) and metal halide using bromine trifluoride). Cation size influences the structure type; smaller cations such as lithium coordinate fluorines from six \( SbF_6^- \) groups, while larger cations such as caesium are coordinated by twelve fluorine atoms. Divalent metal fluorides react with \( AsF_5 \) in liquid HF \(^{169}\) to give hexafluoroarsenates: \( MF_2.2AsF_5 (M=Mg, Ca, Co, Pb) \), \( 2MF_2.3AsF_5 (M=Fe, Cu, Zn) \) and \( MF_2.AsF_5 (M=Ag \text{ and } Sn) \).

The hexafluoro anions \( EF_6^- \) occur with a variety of quite elaborate cations. For example, \([Te_4Se_6][Te_2Se_8][AsF_6]_4(SO_2)_2\) \(^{170}\) forms in \( SO_2 \) solution by condensing \( AsF_5 \) onto a mixture of Te, Se, and S.

\( AsF_5 \) is used as a means of breaking the S-F bond in \( RSF_3 \), yielding the fluorosulfonium hexafluoroarsenates \( RSF_2+.AsF_6^- \), \( R = Me_2N, CF_3 \). \(^{171}\) Tribromosulfonium(IV) hexafluoroantimonate(V) \( SBr_3+.SbF_6^- \) has short contacts between the S atom of the cation and F atoms of surrounding...
SbF$_6^-$ anions, providing a distorted octahedral coordination around sulphur. In addition, S-Br and Sb-F bonds and short Br-F contacts in the crystal yield nine and ten membered heterocycles.

The non-coordinating hexafluoroarsenate anion also stabilises the (iodocyano)iodonium, [ICNI]$^+$ cation, providing the first example of an N$^+$-I bond stable at room temperature.

The pentahalides also form octahedral adducts with neutral ligands. In arsenic pentafluoride: N-methyl-S, S-difluorosulfoximine the As-N bond length, 1.985Å is longer than the normal As-N bond length of 1.87Å, but is shorter than in AsCl$_3$.NMe$_3$ (2.286Å). This is consistent with the more acidic arsenic(V) atom, whose acceptor ability is further enhanced by the F atoms.

Antimony and arsenic pentafluorides also form adducts with uranyl fluoride, UF$_2$O$_2$, illustrating their powerful Lewis acidity. UF$_2$O$_2$.3SbF$_5$ comprises chains of UO$_2$ groups bridged to SbF$_6^-$ units, with Sb$_2$F$_{11}^-$ side chains. Adducts of SbF$_5$ and BiF$_5$ with uranium tetrafluoride oxide, UF$_4$O are fluorine bridged with some ionic character, once again illustrating the great Lewis acidity of the pentafluorides, in the order Sb ≥ Bi.

More complex anions such as Sb$_2$F$_{11}^-$ and Sb$_3$F$_{16}^-$ are formed by fluoride bridging. The former have been observed in many structures, and consist of an SbF$_6^-$ ion and an SbF$_5$ molecule joined by a fluorine bridge. Higher polymeric anions [Sb$_n$F$_{5n+1}$]$^-$, n=3,4, consisting of cis-bridged SbF$_5$ units can also be formed. The [Bi$_2$F$_{11}$]$^-$ anion exists in adducts of noble gas...
fluorides, and has been characterised, using Raman spectroscopy, as a linear species. 179

Force constant calculations by Bougon et al. 180 suggest that the fluoride ion acceptor strengths increase in the order BiF₅ < AsF₅ < SbF₅. SbF₅ removes a fluoride ion from AsF₅ to yield AsF₂⁺ and SbF₆⁻ ions. 181 There is some degree of cation-anion interaction resulting from fluorine bridging.

Cp₂Ti[PF₆]₂ is unstable with respect to Cp₂TiF₂ and PF₅, whereas the increased fluoride ion affinities of AsF₅, SbF₅ and BiF₅ stabilise the titanocene group in Cp₂Ti[AsF₆]₂. 182 Cp₂Ti[SbF₆]₂ 183 and Cp₂Ti[BiF₆]₂. 184 These represent the first well characterised F-coordinated metalloocene hexafluoropnictate species. All these compounds are prepared by the reaction of Cp₂TiF₂ with the corresponding pentafluoride, which behaves as a fluoride ion acceptor i.e.

\[ \text{Cp}_2\text{TiF}_2 + 2\text{EF}_5 \rightarrow \text{Cp}_2\text{Ti}[\text{EF}_6]_2 \quad \text{E} = \text{As}, \text{Sb}, \text{Bi}. \]

The AsF₆⁻ and SbF₆⁻ ions adopt regular octahedral geometry, while the hexafluorobismuthate unit has a distorted structure due to smaller differences between bridging (Ti—F—E) and non-bridging (E-F) lengths in the bismuth species.

Reaction of NiF₂ with the corresponding pentafluoride in anhydrous HF 185 yields Ni[BiF₆]₂ and Ni[SbF₆]₂. Addition of acetonitrile affords the ternary adducts [Ni(MeCN)₆][BiF₆]₂ 186 and [Ni(MeCN)₆][SbF₆]₂. 187 In the unsolvated hexafluoropnictates the SbF₆⁻ anion has an octahedral structure of C₃ symmetry, while BiF₆⁻ 186 has a distorted structure. Introduction of six acetonitrile ligands reduces the polarising effect of Ni(II), relieving these distortions.
The adducts BiF₅(SbF₅)n (n=1.5, 2, 3) have been prepared; they consist of SbF₅ and BiF₅ units joined by cis-bridged fluorine atoms to form tetramers (like solid (SbF₅)₄). (BiF₅)nSbF₅ (n≥1) on the other hand have trans-bridged polymeric BiF₅ structures. No ionic species are present in these compounds although SbF₅ has been shown to be a better Lewis acid than BiF₅.

In vapour, liquid and crystalline phases, SbCl₅ has a trigonal-bipyramidal structure (Figure 1.17). Upon interaction with a donor group the coordination number increases to six, which results in the formation of an octahedral complex.

*Figure 1.17: Trigonal Bipyramidal Shape of SbCl₅*

In particular SbCl₅ readily accepts a chloride ion to give the octahedral hexachloroantimonate(V) anion SbCl₆⁻. Whereas ionic species occur with halide ion donors, molecular adduct formation occurs with nitrogen, oxygen and sulphur donors.

For example S₄N₄·SbCl₅ has an octahedral Sb(V) atom which bonds five chlorine atoms and one nitrogen atom of the S₄N₄.
ring (Figure 1.18). However with excess SbCl₅ in liquid SO₂ a redox reaction occurs to yield \([S₄N₄]^{2+}[SbCl₆]₂\), consisting of discrete \(S₄N₄^{2+}\) cations and SbCl₆⁻ anions.

Figure 1.18: \(S₄N₄,SbCl₅\). ¹⁹¹

The adduct SbCl₅·SeOCl₂ was prepared in 1865, ¹⁹² but its structure was only elucidated 100 years later: ¹⁹³ the central Sb(V) atom has a distorted octahedral geometry, adjacent chlorines bending towards the donor-acceptor bond.

The 1:1 adduct S₈O·SbCl₅ stabilises the cyclo-octa sulphur monoxide molecule; ¹⁹⁴ upon coordination to SbCl₅ the exocyclic oxygen occupies the sixth coordination site on Sb(V) to give a distorted octahedron; Sb-Cl distances average 2.33Å, and Cl-Sb-Cl angles lie between 86 and 94°.

Antimony pentachloride reacts with a wide range of chlorine donors RCl, with the formation of a cationic species \([R^+]\) and the \([SbCl₆]⁻\) anion. This chloride abstracting ability has been exploited in the formation of many hexachloroantimonate(V) salts and has been further investigated during the course of this work.

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CHAPTER 2
Halide Abstracting Properties of Antimony Pentachloride

2.1. Introduction

One of the characteristic properties of Sb(V) is its ability to accept halide ions with consequent salt formation.

\[ RX + SbX_5 \rightarrow [R][SbX_6] \quad (R=\text{organic group}) \]

Antimony pentachloride finds use as a non-aqueous solvent because many covalent chlorides readily dissolve to give conducting solutions. Auto-ionization is negligible, hence the formation of charged species results from halide transfer, which gives rise to the \( \text{SbCl}_6^- \) anion:

\[ \text{acceptor} \]

\[ \text{MCln} + \text{SbCl}_5 \rightarrow \{\text{MCln}_{1.1}\}^+\text{[SbCl}_6^- \}

\text{SbCl}_5 \text{ is used in organic synthesis as a chloride abstractor. } \text{PFCl}_2 \text{ and PR}_2\text{Cl react with excess SbCl}_5 \text{ to give phosphonium and chlorophosphonium salts.}

\[ \text{PFCl}_2 + \text{SbCl}_5 + \text{Cl}_2 \rightarrow \text{[PFCl}_3][\text{SbCl}_6] \]

\[ \text{Ph}_3\text{PCl}_2 + \text{SbCl}_5 \rightarrow \text{[Ph}_3\text{PCl}][\text{SbCl}_6] \]

Infra-red data supports the existence of the \([\text{PFCl}_3]^+\) cation.

Antimony pentachloride forms adducts with ICl\(_3\) and ECl\(_4\) (E = Se, Se, Te). The former consists of strongly interacting distorted \( \text{SbCl}_6^+ \) octahedra and angular ICl\(_2\) groups; it is actually intermediate between \([\text{ICl}_2][\text{SbCl}_6]\) and \([\text{SbCl}_4][\text{ICl}_4]\). This is a rare example where Sb(V) is described as being cationic.

Our interest in this property of Sb(V) lies in the development of non-redox halide abstraction as a direct route to reactive cationic metal species that may otherwise be inaccessible. Previous work has resulted in the formation...
of the ionic species \([\text{TiCl}_3(\text{MeCN})_3]^+\text{[SbCl}_6]^-. \text{CH}_2\text{Cl}_2\). The structure consists of discrete \textit{fac} - \([\text{TiCl}_3(\text{MeCN})_3]^+\) cations and almost regular octahedral \([\text{SbCl}_6]^-\) anions. The dichloromethane molecule results from recrystallisation. The salts \([\text{MCl}_2(\text{MeCN})_4][\text{SbCl}_6]\) are formed from \(\text{MCl}_3\) (\(M=\text{V}, \text{Cr}, \text{Fe}\)).

We have developed mono-, di- and tricationic metal species from anhydrous metal chlorides by use of increased stoichiometric ratios of \(\text{SbCl}_5\). This programme has yielded the following hexachloroantimonate(V) salts (by the treatment of the anhydrous metal chloride with antimony pentachloride):

\[
\begin{align*}
\text{[Mg(MeCN)}_6\text{][SbCl}_6]}& \text{I} \\
\text{[Sn(MeCN)}_6\text{][SbCl}_6]}& \text{II} \\
\text{[SnCl}_3\text{(MeCN)}_3]\text{[SbCl}_6]}& \text{III} \\
\text{[SnCl}_2\text{(MeCN)}_4]\text{[SbCl}_6]}& \text{MeCN (IV)} \\
\text{[InCl}_2\text{(MeCN)}_4]\text{[SbCl}_6]}& \text{V} \\
\text{[In(MeCN)}_6\text{][SbCl}_6]}& \text{VI} \\
\text{[ScCl}_2\text{(MeCN)}_4]\text{[SbCl}_6]}& \text{VII} \\
\text{[YCl}_2\text{(MeCN)}_4]\text{[SbCl}_6]}& \text{VIII} \\
\text{[LaCl}_2\text{(MeCN)}_4]\text{[SbCl}_6]}& \text{IX} \\
\text{[Ti}^{\text{III}}\text{Cl}_2\text{(MeCN)}_4]\text{[SbCl}_6]}& \text{X} \\
\text{[Ti}^{\text{IV}}\text{Cl}_2\text{(MeCN)}_4]\text{[SbCl}_6]}& \text{2 XI} \\ 
\end{align*}
\]
2.2 Discussion of Results

2.2.1 General Comments

Formulation of these adducts as monocationic, dicationic, and tricationic antimonate(V) salts is based upon $^{121}\text{Sb}$ NMR and UV spectroscopic identification of the $\text{SbCl}_6^-$ anion and accompanying microanalytical, electronic and infra-red spectroscopic data. In addition, conductivity measurements define the salts as 1:1, 1:2, or 1:3 electrolytes. The majority of the compounds give well defined melting points.

The $^{121}\text{Sb}$ NMR spectra ($I=5/2$) show a clearly resolved singlet in all complexes containing the $\text{SbCl}_6^-$ anion. These lie within the range $\delta=\pm0.14$ to $-0.55$ ppm, with linewidths essentially the same as in the reference $[\text{Et}_4\text{N}][\text{SbCl}_6]$ $\delta=0$, $W_{1/2}$, 190Hz. These contrast neat $\text{SbCl}_3$, $\delta=428.68$ ppm; $W_{1/2}$ 7000 Hz. (Kidd and Matthews 201 report values of 8509 ± 20 ppm, $W_{1/2}$, 8000 Hz at 14.4 MHz). The $^{121}\text{Sb}$ nucleus has an electric quadrupole moment, hence its linewidth is dominated by the rate of quadrupolar relaxation. The relatively narrow linewidths observed reflect the reduced rate of quadrupole relaxation of the $^{121}\text{Sb}$ nucleus in the highly symmetrical environment of the octahedral $\text{SbCl}_6^-$ anion.

Further identification of $\text{SbCl}_6^-$ comes from the presence of a diagnostic UV charge transfer band at $\lambda_{\text{max}}$ ca. 36 765 cm$^{-1}$ in acetonitrile solution.

All the salts studied exhibit a sharp doublet in the 2350-2250 cm$^{-1}$ region of the infra-red spectra, characteristic of coordinated acetonitrile. $\nu(\text{CN})$ bands at ca. 2320 and 2290 cm$^{-1}$ compare with those at 2287 and 2251 cm$^{-1}$ for the free ligand, implying strong binding to these cationic metal species.
Similarly $v$(CN) stretching frequencies of aliphatic and aromatic nitriles increase by $80 \pm 9$ cm$^{-1}$ in complexes with boron trichloride. 203

The increase in $v$(CN) on complex formation by nitriles (compare the decrease in $v$(CO) in CO complexes) arises through coupling of the M-N and C=\(\text{N}\) stretching vibrations: 204 $\sigma$-Donation to the metal raises $v$(CN) as electrons are removed from the weakly antibonding $5\sigma$, while $\pi$-backbonding tends to decrease the $v$(CN) because the electrons enter the $2\text{px}^\ast$ orbital. The peak at ca. 2290 cm$^{-1}$ in the doublet profile comprises the C=\(\text{N}\) stretch coupled to the M-N stretch. The other peak at ca. 2320 cm$^{-1}$ has been assigned to either a combination band of the symmetric CH$_3$ deformation and the symmetric C-C stretch, 205 or to an overtone. 206 The increase in $v$(CN) of the complexes do not correlate with the polarising power of the metal ion (i.e. a highly polarising M$^{n+}$ does not give rise to a higher $v$(CN)).

In the far IR region (450-200 cm$^{-1}$) the complexes commonly feature a broad intense band at ca. 345 cm$^{-1}$. This compares the exceptionally strong $v$(SbCl) ($F_{1u}$ bending mode ($v_3$)) observed at 346 cm$^{-1}$ in [K][SbCl$_6$] 207 and at 348 cm$^{-1}$ in [PyH]$^+$/[SbCl$_6$]$^-$. 208 In the complexes which retain a metal-chlorine bond (III-V and VII-XI) $v$(SbCl) is likely to include a pertinent $v$(M-Cl) stretching component. 209 Absorptions in the far IR region are not only due to M-Cl vibrations. 210 For example the adduct SnCl$_4$.2MeCN 211 has a weak band at approximately 420 cm$^{-1}$ due to coordinated acetonitrile, (which itself has a medium band at 377 cm$^{-1}$, assigned to the $\delta$(CCN) bending mode $v_\delta$). 206 A similar weak band occurs at 400 cm$^{-1}$
in SbCl₅·MeCN. Internal ligand vibrations absorb more weakly than ν(MX) stretching vibrations, but can be observed in complex metal ions fully solvated with acetonitrile.

2.2.2. Magnesium system \([\text{Mg(MeCN)}_6]^{2+}[\text{SbCl}_6]^{2-}(I)\)

Due to the negligible self-ionization of SbCl₅ itself, generation of hexachloroantimonate has occurred by halide transfer from electropositive magnesium. Double halide transfer occurs to form the fully solvated magnesium dication \([\text{Mg(MeCN)}_6]^{2+}\), which is counter-balanced by two \([\text{SbCl}_6]^{-}\) anions. Evidence for the formation of a 1:2 electrolyte in solution is verified by conductivity studies.

The only previous structural report of the \([\text{Mg(MeCN)}_6]^{2+}\) cation occurs in \([\text{Mg(MeCN)}_6][\text{SbCl}_4]\), although it has been postulated in solution studies. The structure of \([\text{Mg(MeCN)}_6]^{2+} 2[\text{AlCl}_4]^{-}\) was not possible to solve due to crystal twinning and disorder, although the corresponding Fe²⁺/Fe³⁺ structure was solved.

Similar halide transfer reactions occur in THF; removal of both chlorine atoms from \([\text{MgCl}_2(\text{THF})_2]\) by \([\text{MoOCl}_3(\text{THF})_2]\) leads to the formation of \([\text{Mg(THF)}_6][\text{MoOCl}_4(\text{THF})]\). MgCl₂ behaves similarly in the formation of a series of halogen-bridged magnesium species: \([\text{Mg(THF)}_6][\text{TiCl}_5(\text{THF})]\), \([\text{THF}_4\text{Mg}(\mu\text{-Cl})_2\text{TiCl}_4]\) and \([\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6][\text{TiCl}_5(\text{THF})]\). The coupling of MgCl₂ and MgCl⁺ from \([\text{THF}_4\text{Mg}(\mu\text{-Cl})_2\text{TiCl}_4]\) leads to production of the bimetallic magnesium cation \([\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]\).
2.2.3. Tin(II) System [Sn(MeCN)₆][SbCl₆]²⁻ (II)

Reaction of SnCl₂ and SbCl₃ in MeCN also leads to double chloride abstraction yielding [Sn(MeCN)₆][SbCl₆]²⁻ (II). The formation of these species in solution is verified by spectroscopic identification of the hexachloroantimonate(V) anion and conductivity studies lending support to formulation of the salt as a 1:2 electrolyte. Reaction of SnCl₂ with an equimolar quantity of SbCl₅ results in an identical salt; formation of [SnCl(MeCN)₅][SbCl₆] does not occur.

SnCl₂ has great tendency to behave as a Lewis acid to form the [SnCl₃]²⁻ ion (isoelectronic with SbCl₃); it dissolves in solutions containing excess halide ions. Discrete [SnCl₃]²⁻ anions are found in [Co(en)₃][SnCl₃]Cl₂. The pseudo trigonal bipyramidal [SnCl₄]²⁻ ion is also found in [Co(NH₃)₆][SnCl₄]Cl₂ and [NH₄]₂[SnCl₃]Cl.H₂O which appears to be intermediate between SnCl₅²⁻ and SnCl₄⁻. The solid phases, for example Cs₄SnCl₆ have been characterized. It can function simultaneously as both a Lewis acid and Lewis base in the complexes BSnX₂BF₃ (X=Cl, Br, I; B=NMMe₃, bipy, TMEDA and DMSO).

The tin(II) ion [Sn]²⁺ is found in acid perchlorate solutions, obtained by the reaction:
Cu(ClO₄)₂ + Sn/Hg → Cu + Sn²⁺ + 2ClO₄⁻

The "bare" Sn²⁺ cation occurs in Sn(SbF₆)₂.2AsF₃ formed from reaction of SnF₂ and SbF₅ in AsF₃. This illustrates the fluoride donor ability of SnF₂ in combination with the powerful fluoride abstracting properties of antimony pentafluoride. The cation coordinates six F atoms from SbF₆⁻ and three F atoms from AsF₃, and distorts due to lone pair effects on Sn. 

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abstraction by antimony pentachloride at room temperature provides a novel route to the solvated \([\text{Sn(MeCN)}_6]^{2+}\) cation. Rigorous oxygen free conditions are required in order to prevent oxidation to Sn(IV) species.

2.2.4. Tin (IV) Systems \([\text{SnCl}_3(\text{MeCN})_3]^+|\text{SbCl}_5|=(\text{III})\) and \([\text{SnCl}_2(\text{MeCN})_4]^{2+}|\text{SbCl}_6|_2=(\text{IV})\)

Addition of 1 equivalent of antimony pentachloride to \(\text{SnCl}_4\) results in the formation of the monocationic species; \([\text{SnCl}_3(\text{MeCN})_3]^+(\text{III})\). Removal of a second halide ion is effected by a further equivalent of \(\text{SbCl}_5\) to generate the highly reactive dication \([\text{SnCl}_2(\text{MeCN})_4]^{2+}\) (IV). The conductivity data suggest that the species generated in solution are strong 1:1 and 1:2 electrolytes. Use of a great excess of \(\text{SbCl}_5\) also gives the dication (IV), therefore it does not appear possible to remove more than two chlorides from \(\text{SnCl}_4\).

Attempts to mount crystals of both III and IV in Lindemann tubes under argon for structural determination were unsuccessful. Hydrolysis occurred during manipulation under sodium-dried nujol, indicating that both products are highly air sensitive.

By analogy with its Ti(IV) counterpart the monocationic \([\text{SnCl}_3(\text{MeCN})_3]^+\) species most likely comprises the \textit{fac} isomer. \((\text{Fac } \text{MX}_3L_3(C_3v)\) should yield two IR active (M-Cl); \textit{mer} \text{MX}_3L_3 (C_2v ) three). The presence of the exceptionally strong \(v(\text{Sb-Cl})\) at \(ca 345 \text{ cm}^{-1}\) prevents full interpretation of the low IR bands.

\(\text{SnCl}_4\) behaves as a Lewis acid, commonly forming anionic complexes \(eg\) the chloro anions \([\text{SnCl}_6]^{2-}\) and organotin halides...
Neutral species are also numerous; six-coordinate adducts of SnCl₄ and SnBr₄ with neutral ligands generally exhibit cis geometry, although the trans geometry is observed with bulky donor molecules.

Cationic complexes of Sn(IV) are much less known. Terdentate ligands like 2, 2', 2"-terpyridine promote the displacement of halide from tin resulting in the formation of ionic complexes such as [Me₂Sn(terpy)Cl]⁺[Me₂SnCl₃]⁻. Ionization takes place more readily with bromine and iodine which bind Sn(IV) more weakly. Organotin chlorides can achieve high coordination number by intramolecular coordination of a donor atom remote in the organic ligand. When two nitrogen atoms are present on the organic group, ionization of halide from tin can occur in 2,6-bis[(dimethylamino)methyl] phenyldiorganotin bromide \( \text{Am} = 84.8 \text{ Scm}^2\text{mol}^{-1} \). Halide abstraction by SbCl₅ provides a direct route for the generation of solvated tin (IV) chloride mono- and dicationic species.

2.2.5. Indium (III) Systems \([\text{InCl}_2(\text{MeCN})_4]^{2±}[\text{SbCl}_6]^{-}(\text{V})\) and \([\text{In(MeCN)}_6]^{3±}[\text{SbCl}_6]_{3±}(\text{VI})\)

Removal of two chlorides from MgCl₂, SnCl₂ and SnCl₄ raises the possibility of further halide abstraction. Is it possible to remove 3Cl⁻ from InCl₃? Spectroscopic, analytical and conductivity measurements verify formation of the monocationic, \([\text{InCl}_2(\text{MeCN})_4]^{+}[\text{SbCl}_6]^{-}(\text{V})\) and tricationic \([\text{In(MeCN)}_6]^{3+}[\text{SbCl}_6]_{3}^{-}(\text{VI})\) species, depending upon the stoichiometry of the reactants.
InCl₃ + xSbCl₅ → [InCl₃₋ₓL₆₋₃₋ₓ]ₓ⁺[SbCl₆]ₓ

(x=1, 2, 3; L=MeCN)

Hence equimolar quantities of InCl₃ and SbCl₅ in MeCN gives the monocation (V), 3 equivalents of SbCl₅ yield the tricationic species (VI). Use of a 1:2 molar ratio of reactants (x=2, equation 2) does not give [InCl(MeCN)₅]²⁺[SbCl₆]₂⁻; instead the tricationic complex (VI) forms (equation 3). This is confirmed by analytical, spectroscopic and conductivity measurements.

2[InCl(MeCN)₅][SbCl₆]₁₂→[In(MeCN)₆][SbCl₆]₃ + [InCl₂(MeCN)₄][SbCl₆]

Crystals of (V) and (VI) were unsuitable for X-ray diffraction studies.

Indium(III) cations form complexes with many nitrogen donor ligands. The [In(NH₃)₆]³⁺ cation has been identified in liquid ammonia solution, but attempts to prepare the perchlorate salt were unsuccessful. Mixed complexes such as [In(NH₃)₅Br]²⁺ have also been postulated in liquid ammonia. Several cationic indium(III) salts with bidentate nitrogen donors have been prepared, eg [In(bipy)₃]³⁺, [In(en)₃]³⁺ as perchlorate and nitrate salts. There appears to be little reported work on the nitrile complexes of indium. Electrochemical oxidation of In metal leads to species [InL₆][BF₄]₃ (where L = DMSO, MeCN).

The use of antimony pentachloride as halide abstractor in this study provides a direct facile route to the generation of indium(III) cations. InCl₃ can also behave as a halide abstractor, in reaction with PCl₅ at 300°C to give the ionic...
product \([\text{PCl}_4][\text{InCl}_4]\). The order of halide abstracting ability is therefore \(\text{SbCl}_5 > \text{InCl}_3 > \text{PCI}_5\).

2.2.6. Scandium \([\text{ScCl}_2(\text{MeCN})_4][\text{SbCl}_6](\text{VII}). \text{Yttrium} [\text{YCl}_2(\text{MeCN})_4][\text{SbCl}_6](\text{VIII}), \text{and Lanthanum} [\text{LaCl}_3(\text{MeCN})_4][\text{SbCl}_6](\text{IX}) \text{Systems}

Halide transfer from the trivalent chlorides of Sc, Y and La generates the hexachloroantimonate(V) ion. Crystals of the three salts (VII-IX) could not be obtained, hence analytical figures are based upon solid powder products. The scandium salt (VII), formulated as \([\text{ScCl}_2(\text{MeCN})_4][\text{SbCl}_6]\), required rigorously dry conditions.

Other M-Cl shifts in the IR spectra of these complexes are obscured by the broad intense \(v(\text{SbCl})\) at \(\text{ca} \ 345 \ \text{cm}^{-1}\).

There are few reports of M(III) complexes with monodentate nitrogen ligands. Ammine complexes of scandium are known; \(^{230}\) IR studies of deuterated \(\text{ScCl}_3/\text{NH}_3\) mixtures imply the presence of \([\text{ScCl}(\text{NH}_3)_5]\text{Cl}_2\). \(^{231}\)

The ammonia complexes of lanthanide ions are not fully characterized. \(^{232}\) N-bonded thiocyanate forms octahedral \([\text{Ln}(\text{NCS})_6]\). \(^{233}\)

In this study generation of cationic species of scandium, yttrium and lanthanum has been achieved, where both halide and monodentate nitrogen donor ligands complex to the metal.
2.2.7. Titanium (III) System [TiCl\textsubscript{2}(MeCN)\textsubscript{4}][SbCl\textsubscript{6}](X)

The green crystals, which unfortunately were not of diffraction quality, analyse as [TiCl\textsubscript{2}(MeCN)\textsubscript{4}][SbCl\textsubscript{6}]. The electronic spectrum reveals a charge transfer band at 36 900 cm\textsuperscript{-1} (which corresponds to the presence of the SbCl\textsubscript{6}\textsuperscript{−} anion), and visible bands at 15 380 cm\textsuperscript{-1} and 20 000 cm\textsuperscript{-1} which correspond to a d\textsuperscript{1} metal ion in solution. The geometry of the resultant cation is likely to be trans in keeping with the trans geometry of similar [TiCl\textsubscript{2}L\textsubscript{4}]+ cations (where L = H\textsubscript{2}O, \textsuperscript{235} THF \textsuperscript{236}). The splitting of 4620 cm\textsuperscript{-1} compares a 4250 cm\textsuperscript{-1} splitting shown by trans [TiCl\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}]+ in C\textsubscript{2}TiCl\textsubscript{5} 4H\textsubscript{2}O. \textsuperscript{235} The bands at 14 970 and 19 220 cm\textsuperscript{-1} correspond to the \textsuperscript{2}E\textsubscript{g}→\textsuperscript{2}A\textsubscript{1g} and \textsuperscript{2}E\textsubscript{g}→\textsuperscript{2}B\textsubscript{1g} transitions respectively in a D\textsubscript{4h} system.

The spectrochemical series places MeCN higher than H\textsubscript{2}O; thus the band at 20 000 cm\textsuperscript{-1} for [TiCl\textsubscript{2}(MeCN)\textsubscript{4}]+(X), occurs at slightly higher energy than the corresponding band at 19 220 cm\textsuperscript{-1} shown by [TiCl\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}]\textsuperscript{+}.

Ti(III) has great tendency to form cationic species: The complex [Ti(MeCN)\textsubscript{6}][BF\textsubscript{4}\textsubscript{3}] has been prepared by direct electrochemical oxidation. \textsuperscript{228} Trans -[TiCl\textsubscript{2}(THF)\textsubscript{4}]+[ZnCl\textsubscript{3}(THF)]\textsuperscript{−} has been synthesized by reaction of mer TiCl\textsubscript{3}.3THF and ZnCl\textsubscript{2} in THF under reflux. \textsuperscript{236} Zinc dichloride here acts as chloride abstracting reagent towards TiCl\textsubscript{3}. In a similar manner SbCl\textsubscript{5} and TiCl\textsubscript{3}.3MeCN in MeCN at room temperature give [TiCl\textsubscript{2}(MeCN)\textsubscript{4}][SbCl\textsubscript{6}](X).
2.2.8 Titanium (IV) System \([\text{TiCl}_2(\text{MeCN})_4]^{2+}\cdot[\text{SbCl}_6]_2^-\) (XI)

Generation of the 1:1 salt \([\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6]\) has been effected. 199 The preparation of the dicationic species was attempted by reaction of excess \(\text{SbCl}_3\) with the isolated monocation. Analytical and spectroscopic data support the formation of the highly reactive dicationic species \([\text{TiCl}_2(\text{MeCN})_4]^{2+}\cdot[\text{SbCl}_6]_2^-\) (XI). Recrystallisation of (XI) from MeCN afforded yellow \(\text{fac} \cdot [\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6]\cdot\text{CH}_3\text{CN}\) and extremely air-sensitive green crystals of the dication. The formation of the former on recrystallisation may be rationalized by the highly reactive nature of the dication (XI). The doubly charged \(\text{Ti}^{IV}\) centre is more highly polarising than the monocation due to its higher charge density, which may well be similar to that of \(\text{SbV}\). The nature of the chloro-bridged intermediates which are proposed as precursors for the ionic halide transfer products are explained in Chapter 4, Section 4.4.

By virtue of the highly polarising nature of the \(\text{Ti}^{2+}\) centre it may be possible that one of the chloro-bridged \(\text{SbV}\) units gives up one of its chlorides to \(\text{Ti}\) to regenerate the monocation. The dication \([\text{TiCl}_2(\text{MeCN})_4]^{2+}\) is highly reactive towards ligand exchange reactions.

\(\text{TiCl}_4\) generally behaves as a halide acceptor in the formation of \([\text{TiCl}_3]^-\); \(\text{238}[\text{TiCl}_6]^{2-}\), \(\text{239}[\text{Ti}_2\text{Cl}_9]^-\) and \([\text{Ti}_2\text{Cl}_{10}]^{2-}\). 240 salts. The formation of cationic species can only take place using powerful Lewis acidic reagents such as \(\text{SbCl}_5\).
2.3 Conductivity Studies

Ionic formulation of the hexachloroantimonate(V) salts is based upon their behaviour as strong electrolytes in organic solvents, namely acetonitrile. The formation of ionic species in (I)-(XI) may actually only occur in MeCN solution. In the solid state they may exist as chloro-bridged species (which only dissociate into ions in solution) or as ionic species. A precedent for the existence of such ternary systems as ions in the solid state is found in the structure of fac-[TiCl$_3$(MeCN)$_3$][SbCl$_6$]. Therefore it would seem likely that (I)-(XI) are also ionic species in the solid state. The conductivity of [TiCl$_3$(MeCN)$_3$][SbCl$_6$] was measured in this study and is consistent with a 1:1 electrolyte in MeCN solution.

Strong electrolytes have conductivities which depend only weakly on the concentration of the solute. As the concentration of solute decreases the molar conductivity rises to a limit which is called the molar conductivity at infinite dilution, $\Lambda_0$.

By contrast weak electrolytes have molar conductivities which depend markedly on solute concentration. The value of $\Lambda_m$ is low until high dilutions are reached, at which point it increases to values which are comparable to those of strong electrolytes.

The conductivities of the salts were measured at different concentrations at 25.0 ± 0.1°C using the method described in Appendix I. Acetonitrile was selected as the solvent on the basis of its high dielectric constant (36.2 at 25°C), low viscosity (0.325 g·l⁻¹·s⁻¹ at 30°C), and low specific conductivity (5.9 x 10⁻⁸ Scm⁻¹). The use of acetonitrile as the solvent medium for
conductivity studies is appropriate for the compounds studied (which are solvated with MeCN).

The Onsager Law:

$$\Lambda_0 - \Lambda_m = (A + WBA_0) C^{1/2}$$

makes the assumption that the counterion does not enter into the coordination sphere of the complex. $^{121}$Sb nmr and UV spectroscopy indeed imply that SbCl$_6^-$ does not enter the coordination sphere and can be regarded as a non-complexing anion. Conductivity data are tabulated in Appendix 1.

$\text{[SnCl}_3(\text{MeCN})_3]^+\text{[SbCl}_6^-\text{]}$(III) and $\text{[SnCl}_2(\text{MeCN})_4]^2+\text{[SbCl}_6^-\text{]}^2-$ (IV)

Conductivity studies establish the ionic formulation of the ternary complexes SnCl$_4$.SbCl$_5$.3MeCN (III) and SnCl$_4$.2SbCl$_5$.4MeCN (IV). $\text{[SnCl}_3(\text{MeCN})_3]^+\text{[SbCl}_6^-\text{]}$ (III) behaves as a 1:1 electrolyte in acetonitrile solution. $\text{[SnCl}_2(\text{MeCN})_4]^2+\text{[SbCl}_6^-\text{]}^2-$ (IV) behaves as a 1:2 electrolyte in acetonitrile solution.

Graphs of $\Lambda_m$ (Scm$^2$mol$^{-1}$) versus $c^{1/2}$ (mol dm$^{-3}$) were plotted for $\text{[SnCl}_3(\text{MeCN})_3]^+\text{[SbCl}_6^-\text{]}$ (III) and $\text{[SnCl}_2(\text{MeCN})_4]^2+\text{[SbCl}_6^-\text{]}^2-$ (IV) (Figures 2.1 and 2.2).
Figure 2.1: $A_m$ versus $C^{1/2}$ for $[SnCl_3(MeCN)_2][SbCl_6]$ (III)

Figure 2.2: $A_m$ versus $C^{1/2}$ for $[SnCl_2(MeCN)_4][SbCl_6]_2$ (IV)
These graphs are extrapolated using linear least squares analysis to give $\Lambda_0$ (Scm$^2$mol$^{-1}$), the molar conductivity at infinite dilution (Table 2.1).

According to the Onsager Law graphs of $\Lambda_0 - \Lambda_m$ (Scm$^2$mol$^{-1}$) versus $c^{1/2}$ (mol dm$^{-3}$) give slopes ($A + W\Lambda_0$). (Figures 2.3 and 2.4).

Figure 2.3: $\Lambda_0 - \Lambda_m$ versus $c^{1/2}$ for [SnCl$_3$(MeCN)$_3$][SbCl$_6$]
Figure 2.4. $A_0 - A_m$ versus $C^{1/2}$ for [$SnCl_2(MeCN)_4][SbCl_6]_2$

The slope of the plots are obtained using linear least squares analysis and directly reflect the electrolyte types of the complexes (Table 2.1, Figure 2.5).

Table 2.1 Conductivity Data for [$SnCl_3(MeCN)_3][SbCl_6]$(III) and [$SnCl_2(MeCN)_4][SbCl_6]_2$(IV)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Lambda_0$ (S cm$^2$ mol$^{-1}$)</th>
<th>Slope</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>[$SnCl_3(MeCN)_3][SbCl_6]$</td>
<td>87.3</td>
<td>130.70</td>
<td>0.980</td>
</tr>
<tr>
<td>[$SnCl_2(MeCN)_4][SbCl_6]_2$</td>
<td>219.1</td>
<td>469.67</td>
<td>0.991</td>
</tr>
</tbody>
</table>
The slopes reflect the difference in electrolyte type between the two complexes. The 1:2 electrolyte $[\text{SnCl}_2(\text{MeCN})_4][\text{SbCl}_6]_2$ yields a greater slope, 469.67 than $[\text{SnCl}_3(\text{MeCN})_3][\text{SbCl}_6]$, 130.70. These values fall short of those obtained for comparable nickel salts in acetonitrile. Accordingly the molar conductivities, $\Lambda_m$ are also low, although of the same order for similar electrolyte types in acetonitrile (Tables 2.2 and 2.3).
### Table 2.2 $\Lambda_m$ Values for $[\text{SnCl}_3(\text{MeCN})_3][\text{SbCl}_6]$ (III) and $[\text{SnCl}_2(\text{MeCN})_4][\text{SbCl}_6]_2$ (IV)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Lambda_m$ at $10^{-3}\text{M}$ (Scm$^2$mol$^{-1}$)</th>
<th>Expected $\Lambda_m$ (at $10^{-3}\text{M}$) (Scm$^2$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{SnCl}_3(\text{MeCN})_3][\text{SbCl}_6]$</td>
<td>7.7</td>
<td>120 - 160</td>
</tr>
<tr>
<td>$[\text{SnCl}_2(\text{MeCN})_4][\text{SbCl}_6]_2$</td>
<td>20.3</td>
<td>220 - 300</td>
</tr>
</tbody>
</table>

### Table 2.3 Expected $\Lambda_m$ Ranges for Different Electrolytes in MeCN

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>$\Lambda_m$ range at $10^{-3}\text{M}$ (Scm$^2$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>120 - 160</td>
</tr>
<tr>
<td>1:2</td>
<td>220 - 300</td>
</tr>
<tr>
<td>1:3</td>
<td>340 - 420</td>
</tr>
<tr>
<td>1:4</td>
<td>(500)</td>
</tr>
</tbody>
</table>
\[ \text{Sn(MeCN)}_6\text{SbCl}_6 \text{ (II)} \]

The ionic formulation of the title compound is based on spectroscopic observations and conductivity data. A graph of \( \Lambda_m \) versus \( C^{1/2} \) yields a value of 184.9 S cm\(^2\) mol\(^{-1}\) for \( \Lambda_0 \), the molar conductivity at infinite dilution (correlation coefficient, 0.823, Figure 2.6).

**Figure 2.6.** \( \Lambda_m \) versus \( C^{1/2} \) for \[ \text{Sn(MeCN)}_6\text{SbCl}_6 \text{ (II)} \]

![Graph showing \( \Lambda_m \) vs. \( C^{1/2} \)]

This value is used to plot \( \Lambda_0 - \Lambda_m \) versus \( C^{1/2} \) (Figure 2.7), from which a slope of 280.25 is obtained. This value compares with that of 469 for the complex \[ \text{SnCl}_2\text{(MeCN)}_4\text{SbCl}_6 \text{ (IV)} \], also a 1:2 electrolyte.
As with the Sn(IV) complex (IV) the molar conductivity of (II) (170 Scm$^{-2}$mol$^{-1}$) falls below the expected $\Lambda_m$ range for a 1:2 electrolyte in acetonitrile. The low $\Lambda_0$ values obtained for the Sn(IV) and Sn(II) salts compared to the other hexachloroantimonate salts may be due to differences in the electrical conductivities of the metal cations themselves. The slopes for all three complexes are compared in Figure 2.8.
The ternary complexes InCl$_3$.SbCl$_5$.4MeCN (V) and In(MeCN)$_6$.3SbCl$_6$.3MeCN (VI) are formulated as ionic species on the basis of spectroscopic data. Conductivity measurements establishes them as 1:1 and 1:3 electrolytes respectively in acetonitrile solution. Plots of $\Lambda_m$ versus $c^{1/2}$ (Figures 2.9 and 2.10) give $\Lambda_0$ values of 181.4 Scm$^2$mol$^{-1}$ and 383.1 Scm$^2$mol$^{-1}$ for [InCl$_2$(MeCN)$_4$][SbCl$_6$] and [In(MeCN)$_6$][SbCl$_6$]$_3$ respectively. (Correlation coefficients of 0.989 and 0.958 were obtained).
Figure 2.9. \( A_m \) versus \( C^{1/2} \) for \([\text{InCl}_2(\text{MeCN})_4][\text{SbCl}_6] \) (V)

\[ 
\begin{align*}
A_m \ (\text{cm}^2 \text{ mol}^{-1}) \\
C^{1/2} \ (\text{mol dm}^{-3})
\end{align*}
\]

Figure 2.10. \( A_m \) versus \( C^{1/2} \) for \([\text{In(MeCN)}_6][\text{SbCl}_6]_3 \) (VI)

\[ 
\begin{align*}
A_m \ (\text{cm}^2 \text{ mol}^{-1}) \\
C^{1/2} \ (\text{mol dm}^{-3})
\end{align*}
\]
\( A_0 - A_m \) versus \( C^{1/2} \) plots (Figures 2.11 and 2.12) have slopes of 971.1 and 1370.1 respectively, reflecting the difference in electrolyte type of the two complexes (Figure 2.13).

**Figure 2.11.** \( A_0 - A_m \) versus \( C^{1/2} \) for [InCl₂(MeCN)₄][SbCl₆] (V)
These slopes exceed those for the Sn$^{IV}$ and Sn$^{II}$ complexes.
Molar conductivities of 150.5 and 323.7 S cm\(^{-2}\) mol\(^{-1}\) at 10\(^{-3}\) M for \([\text{InCl}_2(\text{MeCN})_4][\text{SbCl}_6]\) (V) and \([\text{In}(\text{MeCN})_6][\text{SbCl}_6]_3\) (VI) lie well within the usual range for 1:1 and 1:3 electrolytes (Table 2.3).

The formulation of (I) as \([\text{Mg}(\text{MeCN})_6][\text{SbCl}_6]_2\) is based upon spectroscopic results, and is further confirmed by conductivity data which characterise the complex as a strong 1:2 electrolyte.

A plot of \(\Lambda_m\) versus \(C^{1/2}\) (Figure 2.14) gives a \(\Lambda_0\) value of 339.01 S cm\(^{-2}\) mol\(^{-1}\) (correlation coefficient, 0.992).
The $\Lambda_0 - \Lambda_m$ versus $C^{1/2}$ plot (Figure 2.15) has a slope of 1224.6.

**Figure 2.15.** $\Lambda_0 - \Lambda_m$ versus $C^{1/2}$ for $[\text{Mg(MeCN)}_6][\text{SbCl}_6]_2$ (I)
This value compares well with slopes obtained for [InCl₂(MeCN)₄][SbCl₆] and [In(MeCN)₆][SbCl₆]₃ and again exceeds those of the tin(IV) and tin(II) salts (Table 2.4).

Table 2.4 Conductivity data for In⁺⁺⁺ and Mg⁺⁺ salts

<table>
<thead>
<tr>
<th>Complex</th>
<th>A₀   (S cm² mol⁻¹)</th>
<th>Slope (A + WBAₘ)</th>
<th>Aₘ at 10⁻³M (S cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[InCl₂(MeCN)₄]⁺⁺⁺</td>
<td>181.9</td>
<td>971.12</td>
<td>150.5</td>
</tr>
<tr>
<td>[SbCl₆]⁺⁺⁺</td>
<td>339.1</td>
<td>1224.6</td>
<td>278.9</td>
</tr>
<tr>
<td>[Mg(MeCN)₆][SbCl₆]₂</td>
<td>383.1</td>
<td>1370.1</td>
<td>323.7</td>
</tr>
<tr>
<td>[In(MeCN)₆][SbCl₆]₃</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The molar conductivity of [Mg(MeCN)₆][SbCl₆] (I), 278.9 S cm² mol⁻¹ at 25.0 ± 0.1°C, lies within the expected range for a 1:2 electrolyte (220-300 S cm² mol⁻¹) (Table 2.3).

2.4 Summary

In all the systems studied SbCl₅ shows no tendency to donate its chloride ions to form cationic SbCl₄⁺ species; but it accepts halide ions from MClₙ to give mono-, di-, or tricationic metal species, depending upon the stoichiometry of the reactants (Equation 4).

\[
\text{MCl}_n + x\text{SbCl}_5 \rightleftharpoons [\text{MCl}_{n-x}\text{L}_{6-(n-x)}]^{x⁺}[\text{SbCl}_6]_x \quad (4)
\]

(n=2, 3, 4; x=1, 2, 3; L=MeCN)

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CHAPTER 3
Halide Exchange Reactions of Bismuth(III) Chloride.

3.1. Introduction

The work described in this chapter deals with the halide transfer reactions of bismuth(III) chloride. As discussed in Chapter 2 the removal of a chloride ion from a covalent M-Cl bond (M = metal or metalloid) can be effected by antimony pentachloride. To expand on this theme of halide abstraction the behaviour of BiCl₃ in such systems has been investigated.

What is of particular interest here is that as well as showing acceptor behaviour (i.e. the formation of complex anions of several types [BiCl₅]²⁻, [BiCl₆]³⁻, [Bi₂Cl₈]²⁻, [Bi₂Cl₉]³⁻, [Bi₄Cl₁₈]⁶⁻) bismuth(III) chloride can act as a halide ion donor with the formation of cationic species, e.g. [BiCl₂(18-crown-6)]²⁺ [Bi₂Cl₈]⁺. Bismuth clusters and even 'naked' Bi⁺ cations are known. Thus bismuth trichloride exhibits duality in its behaviour; in some instances it behaves as a Lewis acid, while in others it can behave as a Lewis base.

Both anionic and cationic bismuth species can be found in the same compound; this is illustrated by (BiCl₃)₃.₇tu (tu = thiourea) and (BiCl₃)₃.₄tsc (tsc = thiosemicarbazide). These complexes comprise [Bi₂Cl₄tu₆]²⁺ [BiCl₅tu]²⁻ and [Bi₄Cl₁₀(tsc)₆]²⁺ [BiCl₆]³⁻ Cl⁻ respectively. Also the complex 2BiCl₃.1₈-crown-₆ has the ionic formulation [BiCl₂(1₈-crown-₆)]²⁺ [Bi₂Cl₈]²⁻.

Aluminium trichloride has been used to abstract chloride ions from bismuth(III) chloride, similar to the use of antimony pentachloride as Lewis acid to generate [BiCl₂(MeCN)₄][SbCl₆] (XIV) and [Bi(MeCN)₆][SbCl₆]₃ (XV). Reaction of BiCl₃ with Al₂Cl₆ in the presence of toluene or
hexamethylbenzene yields C₆H₅MeAlBiCl₆ and C₆Me₆AlBiCl₆ respectively. The arenes stabilize \([(BiCl₂)[AlCl₄]]₂\) by coordinating to the vacant site generated on the bismuth ion.

The results discussed below illustrate the generation of both cationic and anionic bismuth species, according to the following scheme:

![Diagram](image)

(xMClₙ + yBiCl₃) \[ \rightarrow \] \[MCln₋ₓ][BiCl₃₋ₓ]\] \[ \rightarrow \] \[[BiCl₃₋ₚ][MClₙ₋ₚ]\]

(where MClₙ are anhydrous metal chlorides).

All reactions were performed in acetonitrile, whose strongly coordinating properties allow occupancy of coordinatively unsaturated sites generated on metal centres (on M or Bi) following halide expulsion.
3.2 Discussion of Results: Bismuth Cations

3.2.1 [BiCl₂(MeCN)₄][SbCl₆] (XIV)

1:1 stoichiometric addition of SbCl₅ to BiCl₃ in acetonitrile provides colourless crystals of poor definition which analyse as BiCl₃·SbCl₅·4MeCN. Of several possible formulations the ionic structure [BiCl₂(MeCN)₄][SbCl₆] (XIV) is proposed on the basis of spectroscopic and conductivity data (this formulation is supported in solution phase).

The $^{121}$Sb nmr spectrum consists of a singlet $\delta=0.05$ ppm, $W_{1/2}=182\text{Hz}$. The electronic spectrum shows an intense charge transfer band, $\lambda_{\text{max}} 37 037 \text{cm}^{-1}$; both are diagnostic of SbCl₆⁻ anions in solution. Other charge transfer bands at $\lambda_{\text{max}} 44 250$ and $31 545 \text{cm}^{-1}$ in the electronic spectrum are assigned to the cationic complex [BiCl₂(MeCN)₄]⁺.

The infra-red spectrum has a sharp doublet profile $\nu$(CN) 2300 and 2260 cm⁻¹, typical for coordinated MeCN. The far IR region (400-200 cm⁻¹) has a broad intense band at $348 \text{cm}^{-1}$, $\nu$(SbCl) (cf [K][SbCl₆], 346 cm⁻¹ ($\nu_3$)). The medium-broad bands at 280 cm⁻¹ and 250-255 cm⁻¹ are tentatively assigned as Bi-N stretching and Bi-NCMe wagging modes.

Further confirmation of the ionic nature comes from conductivity measurements in acetonitrile where $\Lambda_m = 115.8$ S cm² mol⁻¹ at 25°C. 1:1 electrolytes have molar conductivities, $\Lambda_m = 120-140$ S cm² mol⁻¹ in acetonitrile under similar conditions. A cis or trans geometry for the cation in XIV (Figure 3.1) cannot be defined without structural analysis, as pertinent $\nu$(BiCl) frequencies are masked by the intense $\nu$(SbCl).
Figure 3.1. Proposed Structure of [BiCl$_2$(MeCN)$_4$]$^+$

\[ \text{cis} \quad \text{trans} \]

3.2.1,2$[\text{Bi(MeCN)}_6][\text{SbCl}_6]_2\text{MeCN}$ (XV)

Addition of 1:3 stoichiometric quantities of SbCl$_3$ to BiCl$_3$ in acetonitrile provide colourless crystals of poor definition which analyse as the ternary complex BiCl$_3$.3SbCl$_5$.8MeCN. The ionic formulation $[\text{Bi(MeCN)}_6][\text{SbCl}_6].2\text{MeCN}$ (XV) is proposed on the basis of spectroscopic and conductivity data.

The $^{121}\text{Sb}$ nmr spectrum consists of a singlet $\delta=0.16$ ppm, $W_{1/2}=190.5$ Hz, and the electronic spectrum has an intense charge transfer band at 35 714 cm$^{-1}$, both of which are diagnostic of SbCl$_6^-$ anions in solution. The other charge transfer band at 44 843 cm$^{-1}$ can be assigned to $[\text{Bi(MeCN)}_6]^3+$. The infra-red spectrum has a doublet profile $\nu$(CN) 2296, 2276 cm$^{-1}$ which corresponds to coordinated acetonitrile, a further band at $\nu$(CN) 2258 cm$^{-1}$ is assigned to uncoordinated MeCN in the lattice. The presence of a broad intense band at 340 cm$^{-1}$ is indicative of SbCl$_6^-$ in the solid state, (cf $\text{IK}[\text{SbCl}_6]$, $\nu$(SbCl), 346 cm$^{-1}$). As in $[\text{BiCl}_2(\text{MeCN})_4]^+[\text{SbCl}_6]^-$(XIV) the
bands at 280 and 240-245 cm\(^{-1}\) are tentatively assigned to Bi-N stretching and Bi-NCMe wagging modes.

Further confirmation of the ionic nature of the complex comes from conductivity measurements in acetonitrile where \(\lambda_m = 199 \text{ S cm}^2\text{mol}^{-1}\) at 25°C. Although this value is seemingly rather low for a 1:3 electrolyte, the values of \(\lambda_0\) (molar conductivity at infinite dilution, 245.6 S cm\(^{-1}\)mol\(^{-1}\) for (XV) and 142.1 S cm\(^{-2}\)mol\(^{-1}\) for (XIV)) and the slopes of the two plots (868.1 for (XV) and 486 for (XIV)) (Figure 3.7) reflect the difference in electrolyte type between the two complexes.

Use of 1:2 stoichiometric quantities of BiCl\(_3\) and SbCl\(_5\) respectively does not result in the removal of two chloride ions from BiCl\(_3\) to give [BiCl(MeCN)\(_5\)][SbCl\(_6\)]\(_2\), but gives the monocationic product, [BiCl\(_2\)(MeCN)\(_4\)][SbCl\(_6\)] (XIV).

As illustrated in Chapter 2 antimony pentachloride always behaves as a Lewis acid towards metal chlorides forming SbCl\(_6\) salts. The ionic formulations of (XIV) and (XV) are in accord with chloride ion transfer from electro-positive Bi(III). The polar solvent acetonitrile assists ion formation via occupancy of uncoordinated metal sites generated by halide abstraction.

The stoichiometry of the reactants evidently influences the number of halide ions removed. To summarize; equimolar and 1:2 stoichiometric quantities give the 1:1 electrolyte, while reaction of 1:3 stoichiometric quantities of BiCl\(_3\) with SbCl\(_5\) gives the 1:3 electrolyte [Bi(MeCN)\(_6\)][SbCl\(_6\)]\(_3\)\(_2\)MeCN as a result of triple halide abstraction.

The generation of Bi(III) chlorocations is somewhat unexpected in the light of its rather high ionization energy.
4779 KJmol⁻¹ (Bi→Bi³⁺, sum of I, II, III) yet bismuth(III) does exhibit the ability to form both cationic and anionic complexes.
Bismuth Anions

3.2.2.1 \(\text{[Mg(MeCN)}_6\text{]}_2\text{[Bi}_4\text{Cl}_{16}\text{]}\) (XII)

Treatment of \(\text{MgCl}_2\) (1 mol) with \(\text{BiCl}_3\) (2 mol) in acetonitrile provides the colourless ternary complex \(2\text{MgCl}_2.4\text{BiCl}_3.12\text{MeCN}\) (XII) identified by X-ray crystallography as the ionic salt \(\text{[Mg(MeCN)}_6\text{]}_2\text{[Bi}_4\text{Cl}_{16}\text{]}\). In this instance \(\text{Bi(III)}\) acts as the chloride abstracting agent towards the electropositive \(\text{Mg(II)}\), with subsequent formation of the tetranuclear anion \(\text{[Bi}_4\text{Cl}_{16}\text{]}^{4-}\). The magnesium cation is octahedrally coordinated by six acetonitrile ligands to yield \(\text{[Mg(MeCN)}_6\text{]}^{2+}\), whose structure has been previously described.\(^{213}\) Other members of the octahedral \(\text{[MgL}_6\text{]}^{2+}\) series which have been structurally characterised include those with \(\text{L}=\text{C}_2\text{H}_5\text{OH}, \text{THF, H}_2\text{O.}^{232}\)

In the infra-red spectrum of (XII) the characteristic sharp doublet \(v(\text{CN})\) 2322, 2290 cm\(^{-1}\), \((cf\ 2287, 2251\ \text{cm}\^{-1}\) for the free ligand), confirms strong attachment of MeCN to the \(\text{Mg}^{2+}\) ion. Bands at 405 and 340-350 are tentatively assigned as \(v(\text{Bi-Cl})\) and those at 276, 250-255 cm\(^{-1}\) to \(v(\text{Mg-N})\) str/v(\(\text{Mg-NCC}\)) wag modes respectively.

The intense charge-transfer band in the ultraviolet spectrum at \(\lambda_{\text{max}}\) 30 959 cm\(^{-1}\) is associated with the \(\text{[Bi}_4\text{Cl}_{16}\text{]}^{4-}\) anion.\(^{253}\) The molar conductivity \(\Lambda_m\) 207 Scm\(^2\) mol\(^{-1}\) in dimethylformamide solution is slightly above the range expected for 1:2 electrolytes (Table 3.3).\(^{242}\)

Formation of the hexakis solvato \(\text{Mg(II)}\) cation in (XII) and in previous studies.
MgCl₂/SbCl₅/MeCN \[\rightarrow\] [Mg(MeCN)₆][SbCl₆] \textsuperscript{2+} \textsuperscript{213} 

establishes MgCl₂ as a suitable double chloride ion source in Group 15 halide exchange systems. By careful control of the stoichiometry of the MgCl₂/BiCl₃/MeCN system (equation 1) other complex anions may be isolated,

\[ m\text{MgCl}_2 + 4\text{BiCl}_3 \rightarrow [\text{Mg(MeCN)}_6]_m[\text{Bi}_4\text{Cl}_{12}+2m]^{2m-} \]  \hspace{1cm} (1)

\( m=2 \) gives \([\text{Bi}_4\text{Cl}_{16}]^{4-} \text{(XII)}, \) whilst \( m=3 \) leads to the \([\text{Bi}_4\text{Cl}_{18}]^{6-} \) anion which has been reported in the literature. \textsuperscript{143} 

The product isolated using 3:4 stoichiometric quantities of MgCl₂ and BiCl₃ is the ternary complex 3MgCl₂.4BiCl₃.18MeCN (XIII), \textit{vide infra}.

3.2.2.2. Discussion of the Structure of [Mg(MeCN)₆]₂[Bi₄Cl₁₆] (XII)

Complete lists of bond lengths and bond angles, crystal data, collection and refinement conditions, thermal parameters and atomic coordinates is given in Appendix 2.

The unit cell of [Mg(MeCN)₆]₂[Bi₄Cl₁₆] contains discrete [Mg(MeCN)₆]²⁺ cations and discrete centrosymmetric [Bi₄Cl₁₆]⁴⁻ anions. A view of the anion with two cations is shown in Figure 3.2 with the atomic numbering scheme.

The cation has distorted octahedral geometry with Mg-N distances ranging from 2.20(2) - 2.25(3) \( \text{Å} \). These distances are slightly longer than those previously found (2.14 - 2.18\( \text{Å} \)). \textsuperscript{213}
Selected bond lengths and angles are given in Table 3.1. The \([\text{Bi}_4\text{Cl}_{16}]^{4-}\) anion contains a crystallographic centre of symmetry. Of the eight independent chlorine atoms, five are terminal, while two, \([\text{Cl}(2), \text{Cl}(6)]\), bridge two bismuth atoms, and one, \([\text{Cl}(1)]\), bridges three.

Each bismuth atom achieves a coordination number of six. Bi(1) is bonded to two terminal chlorine atoms [mutually \(\text{cis}\) at 2.453(18), 2.516(20) Å], two \(\mu^2\) chlorine atoms [\(\text{trans}\) at 2.678(13), 2.730(14) Å], and two \(\mu^3\) chlorine atoms [\(\text{cis}\) at 3.009(16), 3.034(16) Å]. On the other hand Bi(2) is bonded to three terminal chlorine atoms in the \(\text{fac}\) configuration [2.426(16), 2.528(14), 2.552(16) Å], as well as two \(\mu^2\) chlorine atoms [\(\text{cis}\) at 2.974(17), 2.976(13)Å] and one \(\mu^3\) chlorine atom at 2.930(14) Å. The terminal Bi-Cl bonds (to the atoms Cl(3), Cl(4), Cl(5), Cl(7) and Cl(8)) are shorter than any of the bridging bonds. They are similar to the corresponding lengths observed in BiCl3 \(\text{46} [2.468(4) - 2.518 (7)\text{Å}].\)

The Bi-Cl-Bi bridges are asymmetric. Distances to Bi(1) are significantly shorter, 2.678(13) Å, than those to Bi(2), 2.976(13) Å. This may reflect the fact that Bi(2) is bonded to three terminally bound chlorine atoms, while Bi(1) has only two such bonds.

With this wide variation in the bond lengths around each Bi(III) centre the Cl-Bi-Cl angles deviate by up to 10° from those of a regular octahedron (Table 3.1).
Figure 3.2. Crystal Structure of $[\text{Mg(MeCN)}_6]_2[\text{Bi}_4\text{Cl}_{16}]$
Table 3.1. Selected Bond Lengths and Angles for \([\text{Me(McCN)}_6]_2\text{Bi}_4\text{Cl}_{16}\), (esd's in Parentheses).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(1)-Cl(1)</td>
<td>3.009(16)</td>
</tr>
<tr>
<td>Bi(1)-Cl(6)</td>
<td>2.678(13)</td>
</tr>
<tr>
<td>Bi(1)-Cl(7)</td>
<td>2.453(18)</td>
</tr>
<tr>
<td>Bi(1)-Cl(8)</td>
<td>2.516(20)</td>
</tr>
<tr>
<td>Bi(1)-Cl(11)</td>
<td>3.034(16)</td>
</tr>
<tr>
<td>Bi(2)-Cl(1)</td>
<td>2.930(14)</td>
</tr>
<tr>
<td>Bi(2)-Cl(2)</td>
<td>2.974(17)</td>
</tr>
<tr>
<td>Bi(2)-Cl(3)</td>
<td>2.528(14)</td>
</tr>
<tr>
<td>Bi(2)-Cl(4)</td>
<td>2.426(16)</td>
</tr>
<tr>
<td>Bi(2)-Cl(5)</td>
<td>2.552(16)</td>
</tr>
<tr>
<td>Bi(2)-Cl(6)</td>
<td>2.976(13)</td>
</tr>
</tbody>
</table>

Bi-Cl bonds trans to terminal halogens are weaker (longer) than those trans to bridging halogens. A more strongly bound group (with a shorter bond length) limits the amount of electron density available for the bonding of the position trans to itself. This is illustrated as follows: the terminal Bi(2)-Cl(5), 2.552(16) Å is trans to \(\mu^3\)-Cl(1), length 2.930(14) Å. The terminal Bi-Cl bond, Bi(2)-Cl(4), of length 2.426(16) Å is trans to \(\mu^2\)-Cl(2), length 2.974(17) Å. Also the terminal Bi(2)-Cl(3), 2.528(14) Å is shorter than the \(\mu^2\)-bridging Bi(2)-Cl(6) bond, 2.976(13) Å which is trans to it. It is also noted that the longer bridging bonds of 2.976(13) and 2.974(17) Å are trans to the shorter terminal bonds of 2.528(14) and 2.426(16) Å respectively, and vice versa that
the shortest bridging bond of 2.930(14) Å is trans to the longest terminal bond, 2.352(16) Å. The lengthening of a bond trans to a somewhat shorter bond is consistent with the population of antibonding orbitals. Force constants calculated from low frequency vibrational spectra imply similar differences between bond lengths observed in the bromo- and iodobismuthates, BiX₄⁻, BiX₅²⁻, BiX₆³⁻ and Bi₂X₉³⁻.²⁵⁴

3.2.2.3.1Mg(MeCN)₆][Bi₄Cl₁₈] (XIII)

The ternary complex 3MgCl₂.4BiCl₃.18MeCN is formulated as the ionic title compound (XIII) on the basis of analytical, spectroscopic and conductivity data.

The infra-red spectrum contains two sharp ν(MeCN) bands at 2320, 2289 cm⁻¹ characteristic of the Mg(II) cation, two bands at 230-240 and 273 cm⁻¹ assigned to ν(Mg-N) stretch/ν(Mg-NCC) wag modes and two strong bands at 401, 335-345 which can be assigned to ν(Bi-Cl) modes.

The intense charge transfer band in the vis-uv spectrum at λₘₐₓ 31 055 cm⁻¹ is associated with the [Bi₄Cl₁₈]⁶⁻ anion. The molar conductivity in dimethylformamide Λₘ=251.8 S cm² mol⁻¹ is within the usual range (Λₘ=200-250 S cm² mol⁻¹) for 1:3 electrolytes in DMF.

The anion in (XIII) [Bi₄Cl₁₈]⁶⁻ is likely to have a similar structure to that in [pyr]₆[Bi₄Cl₁₈]⁶⁻,¹⁴³ which comprises two pairs of edge-shared octahedra joined symmetrically by apex-apex fusion of their axial chlorides (TYPE E, Figure 3.11).
Further reactions have been carried out to investigate the effect of stoichiometry upon the MgCl$_2$/BiCl$_3$ system.

Using 0.25 equivalents of MgCl$_2$ (m=1, equation 1) the reaction flask contained unreacted bismuth(III) chloride. Thin-layer chromatography of the product revealed the presence of unreacted BiCl$_3$ and a product with $R_f=0$ in MeCN and DMF on SiO$_2$ and Al$_2$O$_3$. This product is [Mg(MeCN)$_6$][Bi$_4$Cl$_{16}$] on the basis of analytical, spectroscopic, conductivity and m.p. data. Formation of [Bi$_4$Cl$_{14}$]$_2^-$ (according to equation 1) would clearly involve generation of halide deficient bismuth centres. Aggregation to form such a cluster is impossible if their six coordinate geometry is maintained.

According to equation 1 reaction of equimolar quantities of MgCl$_2$ and BiCl$_3$ (m=4) gives [Mg(MeCN)$_6$][Bi$_4$Cl$_{20}$]$^8^-$. Instead, unreacted BiCl$_3$ is found in the reaction flask. Thin layer chromatography revealed the presence of unreacted BiCl$_3$ and a product with zero $R_f$. On the basis of analytical, conductivity, spectroscopic and m.p. data, this second product is the 3:1 electrolyte [Mg(MeCN)$_6$][Bi$_4$Cl$_{18}$] (XIII) instead of the 4:1 salt [Mg(MeCN)$_6$][Bi$_4$Cl$_{20}$]$^8^-$. (The latter anion would comprise four BiCl$_6$ octahedra fused apex-apex, each bismuth centre having four terminal chlorines and two $\mu^2$ bridging chlorines, type G, Figure 3.11. Its high negative charge of $-8$ is probably too much to hold together).

Treatment of MgCl$_2$ (1 mol) with BiCl$_3$ (3 mol) gives a colourless semi-crystalline material; excess unreacted bismuth(III) chloride is found in the reaction vessel. Thin-
layer chromatography of the product revealed the presence of unreacted BiCl₃ and a product with zero \( R_f \). This product is \([\text{Mg(MeCN)₆}]₂[\text{Bi₄Cl₁₆}]\) on the basis of analytical, spectroscopic, conductivity and m.p. data. Reaction at this stoichiometry could potentially give \([\text{Bi₃Cl₁₁}]²⁻\), but a discrete trimeric structure of this sort is forbidden due to the apparent desire of bismuth(III) to attain six coordination. The minimum number of chlorides required to retain six coordinate Bi centres would be twelve, this would lead to a cluster of three highly distorted face-sharing octahedra which share a common \( \mu^3 \)-chloro apex, or three face-sharing BiCl₆ octahedra each joined by three \( \mu^3 \) chlorines. This \([\text{Bi₃Cl₁₂}]³⁻\) anion could potentially form by reaction of 2:3 molar ratios of MgCl₂ and BiCl₃. But in a reaction of this stoichiometry excess unreacted BiCl₃ was found in the reaction vessel. Thin layer chromatography, analytical, spectroscopic, conductivity and m.p. data revealed the presence of unreacted BiCl₃ and \([\text{Mg(MeCN)₆}]₂[\text{Bi₄Cl₁₆}]\).

Although the trimeric anions \([\text{Bi₃Cl₁₄}]⁵⁻\) and \([\text{Bi₃Cl₁₆}]⁷⁻\) have been postulated on the basis of the stoichiometry of the reactants used and analytical data, their existence has not been proved.

There is no apparent reason why only tetramers form in these reactions: Monomeric \([\text{Mg(MeCN)₆}]₂[\text{BiCl₄}]₂\) and \([\text{Mg(MeCN)₆}]₂[\text{BiCl₅}]\) and dimeric \([\text{Mg(MeCN)₆}]₂[\text{Bi₂Cl₈}]\) bismuth anions could potentially form with these stoichiometries, but only the formation of tetrameric anions was observed. This can be associated with the large size of the \([\text{Mg(MeCN)₆}]²⁺\) cation in these complexes.
3.2.4. Other \( \text{MCl}_n \) reactions with Bismuth(III) Chloride

**TiCl\(_4\) System (XVI)**

Equimolar quantities of bismuth trichloride and titanium tetrachloride in acetonitrile yield a mixture of \( \text{TiCl}_4.2\text{MeCN} \) and \( \text{BiCl}_3.3\text{MeCN} \). The infra-red spectrum reveals the presence of coordinated acetonitrile. There is a distinct doublet profile to each of the sharp \( \nu(\text{CN}) \) bands at 2305 and 2295 cm\(^{-1}\), which presumably results from some site irregularity concerning the ligand environment.

In the electronic spectrum the charge-transfer band at 30 769 cm\(^{-1}\) corresponds to the presence of \( \text{BiCl}_3 \). Thin-layer chromatography revealed the presence of bismuth trichloride.

Recrystallisation from MeCN isolates yellow crystals of \( \text{TiCl}_4.2\text{MeCN} \). Charge transfer bands in the ultra-violet visible spectrum at 45 662, 39 682 and 33 557 cm\(^{-1}\) are almost identical to those (at 45 871, 39 682 and 33 783 cm\(^{-1}\)) for the synthesized adduct. Bands at 2310 and 2290 cm\(^{-1}\) in the infra-red spectrum correspond to coordinated acetonitrile, whose doublet profile is observed at \( \nu(\text{CN}) \) 2310 and 2285 cm\(^{-1}\) in the synthesized adduct. Bands at 380 and 315 cm\(^{-1}\) in the far infra-red region also closely correspond to those at 387 and 315 cm\(^{-1}\) in \( \text{TiCl}_4.2\text{MeCN} \).

\( \text{BiCl}_3 \) is therefore not a powerful enough Lewis acid to cleave the covalent Ti-Cl bond to form a bismuth-chloro anion and \( \text{TiCl}_4 \) does not abstract Cl\(^{-} \) from \( \text{BiCl}_3 \). This contrasts the behaviour of \( \text{SbCl}_5 \) which has adequate Lewis acidic strength to abstract a chloride ion from \( \text{TiCl}_4 \), giving the ionic species \( [\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6] \).
BiCl₃ likewise fails to act as a Lewis acid towards TiCl₃. The purple solid obtained is a mixture of the two adducts, TiCl₃.3MeCN and BiCl₃.3MeCN. The infra-red spectrum reveals the presence of coordinated acetonitrile, ν(CN) at 2305 and 2290 cm⁻¹. The charge transfer band at 31 515 cm⁻¹ is due to BiCl₃. The band at 17 029 cm⁻¹ in the visible region corresponds to the ²B₁g→²B₂g transition of a d¹ ion in solution.

VCl₃ (XVIII), CrCl₃ (XIX) and SnCl₄ (XXI) show similar behaviour to TiCl₄ and TiCl₃ towards BiCl₃. In all three cases the acetonitrile adducts VCl₃.3MeCN, CrCl₃.3MeCN and SnCl₄.2MeCN respectively form, which were identified spectroscopically.
Reaction of equimolar quantities of FeCl$_3$ and BiCl$_3$ yields an orange coloured solid which is a mixture of FeCl$_3$.2MeCN and BiCl$_3$.3MeCN. The presence of coordinated acetonitrile is observed in the infra-red spectrum, which has ν(CN) bands at 2305 and 2290 cm$^{-1}$. The weak band at 2260 cm$^{-1}$ reveals the presence of some uncoordinated acetonitrile.

Inspection of the electronic spectrum reveals charge transfer bands at 47 778, 41 946, 35 087(sh), 32 154, and 28 011 cm$^{-1}$. These bands are almost identical to those observed at 47 400, 41 600, 37 400(sh), 32 000 and 27 000 cm$^{-1}$ for |Et$_4$N|][FeCl$_4$] in acetonitrile, which correspond to charge transfer bands of the tetrahedral tetrachloro-ferrate anion, [FeCl$_4$]$^-$. The formation of [FeCl$_4$] from the acetonitrile adduct of FeCl$_3$ has occurred. Hathaway and Holah have noted that the ultraviolet spectrum of FeCl$_3$.2MeCN is identical to that of |Et$_4$N|][FeCl$_4$], and that solvolysis occurs to produce the [FeCl$_4$]$^-$. A series of equilibria, summarised as:

$$2\text{FeCl}_3 + n(\text{solvent}) \rightleftharpoons \text{Fe}^{III}\text{Cl}_2\text{L}_n + \text{Fe}^{III}\text{Cl}_4^- \tag{2}$$

has been suggested to account for the formation of [FeCl$_4$]$^-$ in acetonitrile solution. The presence of [FeCl$_4$]$^-$ has resulted from solvolysis of FeCl$_3$.2MeCN, not by halide transfer from bismuth trichloride to give [BiCl$_2$(MeCN)$_4$][FeCl$_4$].
3.3. Conductivity Data

Conductivity measurements on \([\text{Mg(MeCN)}_6]_2[\text{Bi}_4\text{Cl}_{16}]\) (XII), \([\text{Mg(MeCN)}_6]_3[\text{Bi}_4\text{Cl}_{18}]\) (XIII), \([\text{BiCl}_2(\text{MeCN})_4][\text{SbCl}_6]\) (XIV) and \([\text{Bi(MeCN)}_6][\text{SbCl}_6]_3\) (XV) confirm their existence as ionic species in solution. The existence of these species as ions may only occur in solution. But the structural evidence for \([\text{Mg(MeCN)}_6]_2[\text{Bi}_4\text{Cl}_{16}]\) (XII) as an ionic product implies that \([\text{Mg(MeCN)}_6]_3[\text{Bi}_4\text{Cl}_{18}]\) (XIII) also exists as an ionic product in the solid state. The conductivities of individual complexes were measured at different concentrations (at 25.0 ± 0.1°C) using the method described in Appendix 1.

Both acetonitrile and dimethylformamide were used as solvents for the bismuth complexes. The use of acetonitrile as a solvent for conductivity measurements has been described (Chapter 2). Due to the low solubilities of (XII) and (XIII) in acetonitrile, dimethylformamide was selected as the solvent for conductivity studies of these compounds. DMF has a high dielectric constant (36.7 at 25°C) and low specific conductivity (0.6 - 2.0 x 10^{-7} S cm^{-1}) but it has a greater viscosity than acetonitrile (0.796 g^{-1} s^{-1} at 25°C).
Conductivity of \([\text{BiCl}_2(\text{MeCN})_4][\text{SbCl}_4]\) (XIV) and \([\text{Bi(MeCN)}_6][\text{SbCl}_6]\) (XV)

Ionic formulation of the ternary compounds \(\text{BiCl}_3.\text{SbCl}_5.4\text{MeCN}\) and \(\text{BiCl}_3.3\text{SbCl}_5.8\text{MeCN}\) as (XIV) and (XV) is based upon spectroscopic and conductivity measurements. The conductivity of these salts were measured in acetonitrile. The title compounds were found to behave as strong electrolytes whose conductivities vary with concentration according to the Onsager Law (Appendix 1).

The conductivities of both salts were measured as a function of increasing concentration. Graphs of \(\Lambda_m\) (Scm\(^2\) mol\(^{-1}\)) versus \(c^{1/2}\) (mol dm\(^{-3}\)) for each salt appear in Figures 3.3 and 3.4.

*Figure 3.3. Graph of \(\Lambda_m\) versus \(c^{1/2}\) for \([\text{BiCl}_2(\text{MeCN})_4][\text{SbCl}_6]\) (XIV)*
Using linear least squares analysis, values of molar conductivity at infinite dilution, $\Lambda_0$, of 142.18 and 245.65 $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ were obtained for the title compounds XIV and XV respectively. These values were used to plot graphs of $\Lambda_0 - \Lambda_m$ versus $c^{1/2}$ for both salts (Figures 3.5 and 3.6).
Figure 3.5. Graph of $\Delta \eta$ versus $C^{1/2}$ for (XIV)
These graphs yield slopes characteristic of the electrolyte type of the complexes (see Table 3.2 and Figure 3.7).
Figure 3.7. Comparison of $\Lambda_0 - \Lambda_m$ versus $C^{1/2}$ for (XIV) and (XV)

Table 3.2. Conductivity Data for (XIV) and (XV)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Lambda_0$ (Scm$^2$mol$^{-1}$)</th>
<th>Slope</th>
<th>$\Lambda_m$ (Scm$^2$mol$^{-1}$)</th>
<th>Corr Coeff</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XIV)</td>
<td>142.2</td>
<td>486.6</td>
<td>115.7</td>
<td>0.99</td>
</tr>
<tr>
<td>(XV)</td>
<td>245.6</td>
<td>868.6</td>
<td>199</td>
<td>0.90</td>
</tr>
</tbody>
</table>

The molar conductivity 115.7 Scm$^2$mol$^{-1}$ for [BiCl$_2$(MeCN)$_4$][SbCl$_6$] (XIV) lies within the range expected for a 1:1 electrolyte (120-160 Scm$^2$mol$^{-1}$) in acetonitrile. The value for $\Lambda_m$ obtained for [Bi(MeCN)$_6$][SbCl$_6$]$_3$ (XV) is low for a 1:3 electrolyte (expected range= 340-420 Scm$^2$mol$^{-1}$).
Figure 3.8 shows a comparison of $A_0 - A_m$ versus $c^{1/2}$ graphs for (XV) and another 1:3 electrolyte studied, namely [In(MeCN)$_6$][SbCl$_6$]$_3$ (VI).

**Figure 3.8. Comparison of $A_0 - A_m$ versus $c^{1/2}$ for the 1:3 electrolytes (VI) and (XV)**

The graphs have comparable slopes, although conductivity values obtained for the indium$^{III}$ salts, (V) and (VI), (Chapter 2) have markedly higher values than their bismuth$^{III}$ congeners (XIV) and (XV). This is associated with the lower electrical conductivity of Bi(III) ($0.00867 \times 10^6$ Scm$^{-1}$) compared to In(III) ($0.116 \times 10^6$ Scm$^{-1}$), which is attributed to the larger size of Bi(III). There is scant data available on the conductivity of bismuth cations in solution for comparative purposes.
Conductivity of \([\text{Mg(MeCN)}_6]_2[\text{Bi}_4\text{Cl}_{16}]\) (XII) and \([\text{Mg(MeCN)}_6]_3[\text{Bi}_4\text{Cl}_{18}]\) (XIII)

Conductivity measurements of both these complexes were made in dimethylformamide, as both were found to be insoluble even in refluxing acetonitrile. We assumed that DMF replaces MeCN as coordinating ligand in DMF solution based upon its greater donor capacity towards metal ions. However the molar weight of \([\text{Mg(MeCN)}_6]_2[\text{Bi}_4\text{Cl}_{16}]\) was used to calculate the concentration in DMF.

The molar conductivity, \(\Lambda_m\), of \([\text{Mg(DMF)}_6]_2[\text{Bi}_4\text{Cl}_{16}]\) (XII) in DMF is 172 Scm\(^2\)mol\(^{-1}\) (at 10\(^{-3}\)M). This value based on a single conductivity measurement.

Conductivity of \([\text{Mg(DMF)}_6]_3[\text{Bi}_4\text{Cl}_{18}]\) (XIII)

Formation of the above species in DMF solution is assumed, however, the molecular weight of \([\text{Mg(MeCN)}_6]_3[\text{Bi}_4\text{Cl}_{18}]\) was used to calculate the concentration in DMF. A graph of \(\Lambda_m\) versus \(C^{1/2}\) for (XIII) is given in Figure 3.9.
A value of 326.17 Scm$^2$ mol$^{-1}$ obtained for $\Lambda_0$ (correlation coefficient, 0.97) was then used to plot a graph of $\Lambda_0 - \Lambda_m$ versus $C^{1/2}$. The slope has a value 2022.6 (Figure 3.10).
The molar conductivity of the title compound (XIII), 202 S cm$^2$ mol$^{-1}$, lies within the range observed for a 1:3 electrolyte in dimethylformamide (Table 3.3).

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>$\Lambda_m$ range (S cm$^2$ mol$^{-1}$) in DMF ($10^{-3}$M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>65 - 90</td>
</tr>
<tr>
<td>1:2</td>
<td>130 - 170</td>
</tr>
<tr>
<td>1:3</td>
<td>200 - 240</td>
</tr>
<tr>
<td>1:4</td>
<td>300?</td>
</tr>
</tbody>
</table>
3.4 The Structural Relationship of the [Bi₄Cl₁₆]⁴⁻ Anion with Other Complex Bismuth(III)-Chloro Anions

Figure 3.11 places the structure of [Bi₄Cl₁₆]⁴⁻ in context with other known (and idealised) structures of tetranuclear halo-bismuth(III) anions. For such species, all Bi(III) centres are invariably six coordinate, with or without a formal lone pair of electrons showing stereochemical activity. It is possible to rationalise some of the structures as aggregates of the dinuclear [Bi₂Cl₈]²⁻ 243,245 unit. This basic building block can be regarded as an edge-edge dimer of formal ψ-square based pyramidal [BiCl₄]⁻ units with retention of lone pair activity. [TYPE A]

Transverse dimerisation of two such units leads to a structure [TYPE B] which, curiously, is unknown for [Bi₄Cl₁₆]⁴⁻. Examples of this structural type from Group 15 are, however, provided by [Et₄N]₄[Sb₄Cl₁₆]⁴⁻ 260 and the [As₄Cl₁₆]⁴⁻ unit in (S₅N₅)₄[As₈Cl₂₈]·2S₄N₄. 142 Other examples include [TeCl₄]₄, 261 [SeBr₄]₄ 262 and [Et₃PtCl₄]₄. 263 In this cubic structure each MX₆ octahedron shares three edges and the formal lone pairs associated with the M(III) centres can be accommodated in the tetrahedral 'hole' in the centre of the cubic array. Each metal atom binds three terminal and three µ³ halide atoms.

An alternative structural arrangement for [Bi₄Cl₁₆]⁴⁻ is based upon a tetrahedral Bi₄ array in which each metal centre has three terminal Bi-Cl bonds with the four remaining halogen atoms located as triply bridging groups in the centres of the four faces [TYPE C]. This structural type is unknown.

Direct super-positioning (apex-apex, eclipsed) of two [Bi₂Cl₈]²⁻ units would provide the hypothetical [Bi₄Cl₁₆]⁴⁻ [TYPE
D1 featuring a rectangular Bi4 array incorporating both single and double halogen bridges, but with retention of two lone pairs. Removal of these lone pairs of electrons (formal) by the addition of first one and then another halide ion gives the hypothetical [Bi4Cl17]5- and the symmetrical [Bi4Cl18]6- [TYPE E] species respectively. An example of the latter is provided by [pyrH]6[Bi4Cl18]6-143 in which two pairs of edge-edge octahedra are joined symmetrically by apex-apex fusion of their axial chlorines. As mentioned previously the ternary complex 3MgCl2.4BiCl3.18MeCN (XIII) most likely contains this anion structure.

An alternative structure for [Bi4Cl18]6- is based on a tetrahedral Bi4 array [TYPE F]. In addition to three terminal Bi-Cl bonds per metal centre there are single halogen bridge bonds along the six edges of the tetrahedron as depicted. Type F is unknown.

Further halide addition leads to [Bi4Cl20]8- with the idealised tetranuclear array [TYPE G] in which the four MX6 octahedra are fused apex-apex with a full complement of four single halogen bridge bonds and four terminal halogens for each Bi centre (cf the tetrameric penta-fluorides [MF5]4 M=Mo, Nb, Ta). 264

The structure of [Bi4Cl16] in (XII) can be regarded as the super-positioning of two [Bi2Cl8]2- units but with lateral displacement such that the Bi centres do not sit directly over one another (TYPE H, Figure 3.12). This cluster of four BiCl4 octahedra has two pairs of non-equivalent Bi atoms (1 and 2) resulting from fused octahedra which share two (Bi(2)) or three (Bi(1)) common edges. There are three types of halogen
environment: 10 Cl atoms bind only one Bi centre (terminal); four more bind two Bi centres ($\mu^2$) and two bind three Bi centres ($\mu^3$). This discrete centrosymmetric structure is adopted by [Ti(O\text{Me})_4]_4, $^{265}$ [HL]$_4^+[$Sb$_4$Br$_{16}$]$_4^-$ $^{266}$ (L=2-amino-1,3,4-thiadiazole) and [Cp$_2$Fe]$_4[$Bi$_4$Br$_{16}$]$_4^-$. $^{267}$ But this is the first report of any [Bi$_4$Cl$_{16}$]$_4^-$ anion structure. [Bi$_4$Br$_{16}$]$_4^-$ and [Sb$_4$Br$_{16}$]$_4^-$ also consist of four edge-sharing distorted octahedra, joined by six bridging halogens, two of which bridge three metal centres ($\mu^3$) while the other four bridge two metal centres ($\mu^2$).

There is a general consensus that the condensation of MX$_4^-$ units (M=As, Sb, and Bi) into dimers, trimers, tetrarimers, oligomers or polymers (and the retention or loss of lone pair activity) is dependent upon the nature of the cation present. Bi(III) complex anions can be regarded as archetypal in this respect; large cations promote the formation of large anions. $^{268}$ All previous cases however, have involved alkyl ammonium or related cations for which N-H$_{\text{cation}}$-$X_{\text{anion}}$ hydrogen bonding is invariably present. To what extent, if any, such auxiliary H-bonding influences the resulting structure is an open question. Unquestionably the bulky 'metallo' cation [Mg(MeCN)$_6$]$_2^+$ undergoes no H-bonding or direct ion-ion interactions in [Mg(MeCN)$_6$]$_2$[Bi$_4$Cl$_{16}$].

A more relevant factor is the stoichiometry of the MgCl$_2$/BiCl$_3$/MeCN reaction systems. $^{2}$MgCl$_2$/4BiCl$_3$ results in the formation of the [Bi$_4$Cl$_{16}$]$_6^-$ anion. Other stoichiometric ratios give only [Mg(MeCN)$_6$]$_2$[Bi$_4$Cl$_{16}$]$_4^-$ or [Mg(MeCN)$_6$]$_3$[Bi$_4$Cl$_{18}$]$_6^-$. 

100
Figure 3.11. Structures of Tetranuclear Halo-Bismuth Anions
Figure 3.12. Schematic Structure of the [Bi₄Cl₁₆]⁴⁻ Anion
3.5. Other Bismuth(III) Halo Anions

Condensation of BiX₄⁻ units seems to be influenced by the nature of the cation present: and large anions seem to form in the presence of large cations. For example the tetraneuclear anion structures [Bi₄X₁₆]⁴⁻ and [Bi₄X₁₈]⁶⁻, where X=Cl, Br, occur in association with "bulky" counterions, such as [Cp₂Fe], [Mg(MeCN)₆]²⁺ (XII), (XIII) and [PyrH]⁺. Monomeric [BiX₄]⁻ units do not exist; instead infinite chains of [BiX₄]ₙ⁻ units are present in the structures of stoichiometrically formulated species. For example, quinolinium tetraiodobismuthate consists of infinite zigzag chains of [BiI₄]⁻ with [C₉H₇NH]⁺ cations situated between them. The bismuth atoms have a distorted octahedral coordination. Similar skew-octahedral chains are observed in the 2-picolinium salts of [BiBr₄] and [BiI₄], individual [BiX₄]⁻ units being linked by double halogen bridges. Infinite chains of distorted edge-sharing BiCl₆ octahedra are found in ferricenium tetrachlorobismuthate, the cations stack between the polymeric anions.

The [BiX₅]²⁻ unit is found in [C₅H₁₀NH₂]₂[BiBr₅]²⁻, and is present as the tetragonal BiCl₅²⁻ group in bismuth subchloride. The [BiCl₆]³⁻ anion is found in Cs₂Na[BiCl₆] as a discrete regular octahedral group.

Dimerization also occurs to form [Bi₂X₈]²⁻, [Bi₂X₉]³⁻ and [Bi₂X₁₀]⁴⁻ units. The [Bi₂Cl₈]²⁻ unit consists of two square-pyramidal BiCl₄⁻ units, which share a basal edge. The lone pairs are fully active giving a 4₉-octahedral geometry to each bismuth atom. Face-sharing triply-bridged biocathedral units Bi₂X₉³⁻ are found in complexes such as Cs₃Bi₂Cl₉.
comparison \([\text{Bi}_2\text{Br}_{10}]^{4-}\) found in \(K_4[\text{Bi}_2\text{Br}_{10}].4\text{H}_2\text{O}\), \(\text{Sr(H}_2\text{O})_8\)\[\text{Bi}_2\text{Br}_{10}\] and \(\text{Na}_7[\text{BiBr}_6][\text{Bi}_2\text{Br}_{10}]\) consist of two edge sharing \(\text{BiX}_6\) octahedra, with no evidence of lone-pair activity. There is no Cl analogue of the \([\text{Bi}_2\text{Br}_{10}]^{4-}\) unit.

There is no crystallographic evidence for the formation of trinuclear anions, and the tetranuclear anions tend to be found in combination with larger cations than Group 1 and 2 metal ions.

3.6. Summary

Halide abstraction from electropositive magnesium dichloride has been effected by bismuth trichloride. Previous studies of complex bismuth anions have used aqueous HBr and HCl as the source of halide ion and bismuth oxide or hydroxide as the source of Bi(III). This study represents the first example of bismuth(III) chloride acting as a Lewis acid (halide abstracting reagent) to generate cationic metal species directly from \(\text{MCln}\). By virtue of its electropositive nature \(\text{MgCl}_2\), is a suitable double chloride ion source for \(\text{BiCl}_3\). Failure of \(\text{BiCl}_3\) to remove chloride ions from the other transition metal halides to form ionic species confirms that \(\text{BiCl}_3\) is a weaker Lewis acid than \(\text{SbCl}_3\). This point is well illustrated by the generation of cationic bismuth species upon treatment with \(\text{SbCl}_3\).
CHAPTER 4
Sb(III) and As(III) as Lewis Acids

4.1. Introduction

The use of Sb(V) and Bi(III) as Lewis acids towards metal chlorides has been reported in Chapters 2 and 3. To expand on this theme of halide abstraction, arsenic and antimony trihalides have been used in conjunction with various metal halides in an attempt to generate cationic metal species by a direct route.

The ability of antimony(III) and arsenic(III) to act as halide acceptors is a recognised feature of their chemistry. A range of complex halide ions have been isolated and structurally characterised, whose structures often depend upon the source of halide ion which necessarily reflects the cation choice. The following complex anions have been isolated. \([\text{MX}_4]^\text{−}\), \(137, 140, 274-276, 213\) in each case the metal ion is octahedrally coordinated by halide ions due to the formation of a polymeric anion chain in which monomeric units are joined by halogen bridges. The \([\text{MX}_4]^\text{−}\) unit is not monomeric \((C_{2v})\).

\([\text{MX}_3]^2\text{−}\) \(137, 277-280\), the geometry of this anion is based upon a square pyramid. Secondary interactions can occur between neighbouring anions to form infinite chains of \([\text{SbCl}_5]^2\text{−}\), for example, in dianilinium pentachloroantimonate(III), \(137\) while in the 4,4'-dipyridylium complex \(279\) the anions build up dimers, with average Sb-Cl bridging distances of 3.19Å. In \(\text{K}_2\text{SbCl}_5\) \(278\) the equivalent Sb-Cl distance is 3.881Å. By contrast such interionic interactions are further reduced in \([\text{NH}_4]_2[\text{SbCl}_5]\) \(277\) where \([\text{SbCl}_5]^2\text{−}\) exists as a discrete ion, the lone pair on antimony occupies one of the octahedral sites in the antimony(III) coordination sphere.

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\[ \text{[MX}_6\text{]}^{3-} \] anions are also known, they are found in \( \text{[Co(NH}_3\text{)}_6\text{]}^{3+}[\text{SbCl}_6]^{3-} \) and (C\( _5\)H\( _5\)NH\( _6\)Sb\( ^{III}\)Sb\( ^{V}_3\)Br\( _2\text{]}^{3-} \). There appears to be very little or no stereocchemical lone pair activity on the trivalent group 15 atom, instead it can be regarded as occupying a spherical \( s \) orbital, not available for describing primary bonds. If no \( d \)-orbital participation is invoked the bonds can be described approximately as three-centre four-electron bonds formed from \( p \) orbitals only. Conspicuous absentees from the \( \text{MX}_5^{2-} \) and \( \text{MX}_6^{3-} \) anions are those of the arsenic halides.

As observed in the case of Bi(III) dimerization of "monomeric" \( \text{MX}_4^{-} \) units occurs to produce \( \text{[M}_2\text{X}_8\text{]}^{2-} \) and \( \text{[M}_2\text{X}_9\text{]}^{3-} \). Examples of these anion types are observed for both antimony(III) and arsenic(III) halides. The \( \text{[M}_2\text{X}_8\text{]}^{2-} \) ion types are similar for the Sb(III) \( 260,284 \) and As(III) \( 140 \) halides. The metal atoms have \textit{pseudo}-octahedral coordination, one octahedral site being occupied by the lone pair to form two square-based pyramids joined by a basal edge.

The \( \text{[M}_2\text{X}_9\text{]}^{3-} \) anions can be found as discrete or polymeric \( 140,244 \) dimer units with limited lone pair activity on M. In certain structures they are observed as two discrete, face-sharing distorted octahedra, \( 140 \) while in others they form a chain of infinite apex-apex fused octahedra, which are connected to the cations by N-H--Cl hydrogen bonds. \( 141 \)

A rather more unusual complex anion is found by reaction of tris(dimethylamino)cyclopropenium iodide with antimony triiodide, producing the polymeric \( \text{[Sb}_3\text{I}_10\text{]}^{m-} \). The distorted Sb\( _6 \) octahedra are linked edge to edge to form a polyanion. Distortion is due to differences in the magnitude of
the stereochemical effect of the non-bonding pairs at the three independent Sb atoms.

Finally, tetrameric units \([\text{M}_4\text{X}_{16}]^{4-}\) have been structurally characterised for both As(III) \(^{142}\) and Sb(III) \(^{260}\) halides. Both have a cubane type \(\text{M}_4\) unit of four edge-bridged octahedra; each metal centre is octahedrally coordinated to three terminal and three \(\mu_3\) bridging chlorides. The bromide analogue \([\text{HL}]_4[\text{Sb}_4\text{Br}_{16}]\) \(^{266}\) (L=2-amino-1, 3, 4-thiadiazole), by comparison does not have the same anion structure. Lateral displacement of \(\text{Sb}_2\text{Br}_8^{2-}\) dimer units has occurred in the formation of the tetramer, similar to that observed in \([\text{Mg(MeCN)}_6]_2[\text{Bi}_4\text{Cl}_{16}]\) (XII). Intramolecular hydrogen bonding, N-H···Br occurs between NH\(_2\) and NH groups of the cation and eight Br atoms of the anion. Stabilisation of the \([\text{As}_4\text{Cl}_{16}]^{4-}\) anion \(^{142}\) occurs by the additional bonding of four \(\{\text{AsCl}_3\}\) units via Cl bridges to form four additional distorted octahedra, while in \([\text{Et}_4\text{N}]_4[\text{Sb}_4\text{Cl}_{16}]\) \(^{260}\) there appears to be no intramolecular bonding between the cations and anions. The structure \([\text{Fe(Cp)}(\text{CO})_2\text{Cl}]_4[\text{SbCl}_3]_4\) \(^{286}\) has a \(\text{Sb}_4\text{Cl}_4\) cubanelike framework, with four antimony and four chlorine atoms occupying alternate corners of a tetragonally distorted cube. The iron atoms of the cation bond to chlorine atoms of the \(\text{Sb}_4\text{Cl}_4\) anion. In all these tetrancular anion structures the lone pair on the \(\text{M}^{\text{III}}\) atom is thought to point to the central cavity of the cube.

The majority of these arsenic and antimony(III) halide anions are synthesized by direct mixing with a quaternary ammonium (or related) salt. Many have hydrogen bonds, N-H···X between cations and anions which have a stabilising effect on the complex anion. \(^{141,276}\)
As an alternative approach, the use of metal halides as the source of halide ion for the production of antimonate(III) and arsenate(V) species has been investigated. Preliminary observations indicate that arsenic trichloride is not capable of removing a halide ion from metal halides to form ionic species such as:
\[
\text{MCl}_n + \text{AsCl}_3 \rightarrow \text{[MCl}_{n+1}][\text{AsCl}_4] \quad (1)
\]

Where M=Ti(IV) the above reaction in acetonitrile results in the formation of the bis(acetonitrile) adduct TiCl\(_4\).2MeCN. Therefore it was an obvious step to attempt the oxidation of As(III) to As(V), using chlorine as oxidising agent, in order to generate cationic metal species resulting from halide transfer to As(V) and formation of the hexachloroarsenate anion AsCl\(_6^-\).

Arsenic pentachloride has only been isolated at -105°C by the ultraviolet irradiation of AsCl\(_3\) in liquid Cl\(_2\). A number of its complexes are known, which represent the use of complexing agents to stabilise high oxidation states:

\[
\text{AsCl}_3 + \text{Cl}_2 + \text{MCl}_n \rightarrow [\text{AsCl}_4]^+|[\text{MCl}_{n+1}]^- \quad (2)
\]

M=Al, Ga, Sb

\[
\text{AsCl}_3 + \text{Cl}_2 + \text{Q}^+\text{Cl}^- \rightarrow [\text{Q}]^+[[\text{AsCl}_6]^- \quad (3)
\]

Q+=Et\(_4\)N, PPh\(_4\)

\[
\text{AsCl}_3 + x\text{D} + \text{Cl}_2 \rightarrow \text{AsCl}_5.y\text{D} + [x-y]\text{D} \quad (4)
\]

The instability of AsCl\(_5\) is due to the instability of the highest valence state of p-block elements following completion
of the first (3d) transition series. Incomplete shielding of the nucleus leads to the "d-block contraction", which causes a lowering of the 4s orbital in AsCl₃. Hence the large promotional energy required by the 4s² electrons to enter a vacant d orbital makes the formation of AsCl₅ difficult.

Isolation of the tetraphenylphosphonium hexachloroarsenate(V) salt was achieved by ozonation or chlorination of \([\text{PPh}_4]_2[\text{As}_2\text{Cl}_8]\) at -40°C, i.e. an intermediate trivalent As(III) anion was isolated before oxidation to the pentavalent state.

The behaviour of antimony pentachloride and bismuth trichloride with antimony trichloride provides observations on the relative Lewis strengths of the chlorides of the group.

4.2. Oxidation of As(III) to As(V)

As previously mentioned, preliminary observations indicate the failure of AsCl₃ to remove a halide ion from TiCl₄. Therefore the oxidation of As(III) to As(V) was carried out using chlorine as oxidising agent.

Titanium and tin tetrachlorides were chosen as covalent chlorides, while zinc and magnesium chlorides were selected as rather more electropositive metal chlorides. Tetramethylammonium chloride was also used as a source of halide ion in these oxidation reactions in an attempt to produce an AsCl₆⁻ standard for ⁷⁵As nmr purposes. The following results were obtained.
Discussion of Results: Oxidation of As(III) to As(V)

4.2.1. [Me₄N][AsCl₆] (XXII)

Isolation of the title compound (XXII) from reaction of Me₄NCl with AsCl₃ in Cl₂ follows a very similar procedure to the synthesis of Et₄N+AsCl₆⁻. Full dissolution of tetramethylammonium chloride in acetonitrile is indicative of its incorporation into an ionic product which is soluble in MeCN.

Formulation of the compound as (XXII) is based upon analytical, conductivity, infra-red and electronic spectroscopic data. The high melting point 230-233°C (with decomposition) is indicative of the incorporation of the tetramethylammonium cation into the product (compare Me₄NCl; m.p. > 300°C). The presence of the broad intense band at 350 cm⁻¹ in the far infra-red spectrum is assigned to v₃(AsCl)[F₁u bending mode]. Charge transfer bands at 38 759, 37 453 and 36 900 cm⁻¹ in the electronic spectrum are associated with the hexachloroarsenate(V) anion.

The conductivity of this salt was measured in dimethylformamide, due to its greater solubility in this solvent compared with that in acetonitrile: its existence as a 1:1 electrolyte i.e. \( \Lambda_m = 99.14 \ \text{Scm}^2\text{mol}^{-1} \) at 10⁻³M at 25.0 ± 0.1°C is confirmed. The molar conductivity range for a 1:1 electrolyte in DMF is 65-90 Scm²mol⁻¹.

4.2.2. [Mg(MeCN)₆][AsCl₆] (XXIII)

Immediate precipitation of solid material was observed upon addition of MgCl₂.2MeCN to a chlorine saturated solution of AsCl₃ in MeCN, this solid is proposed as the title compound (XXIII) on the basis of infra-red and electronic spectroscopy;
analytical and conductivity data. A clear m.p. of 66.68°C distinguishes the compound from the bis(acetonitrile) adduct MgCl$_2$.2MeCN m.p. > 300°C.

The doublet profile in the infra-red spectrum at $\nu$(CN) 2316 and 2286 cm$^{-1}$ is characteristic of acetonitrile coordinated to a metal centre (compare the corresponding bands at 2287 and 2251 cm$^{-1}$ for the free ligand). Other hexakis(acetonitrile) magnesium(II) cations isolated in these studies have $\nu$(CN) doublets, for example, at 2320 and 2289 cm$^{-1}$. Acetonitrile coordination to magnesium raises the $\nu$(CN) by 29 and 35 cm$^{-1}$ due to coupling of the M-N and C$\equiv$N stretching frequencies. This can be compared to increases in $\nu$(CN) stretching frequencies, upon ligand coordination, of 23, 29 and 25, 29 cm$^{-1}$ observed for the Ti(IV) and Sn(IV) species respectively. This is due to the electropositive nature of magnesium compared to Ti(IV) and Sn(IV). Zinc, also electropositive causes an increase of 29 and 33 cm$^{-1}$ to $\nu$(CN), which is similar to that observed for magnesium.

The band at 406 cm$^{-1}$ is assigned to the $\delta$(CCN) bending mode $v_3$ of coordinated acetonitrile. (Compare bands at 407, 405 and 401 cm$^{-1}$ for other hexakis(acetonitrile) magnesium(II) cations). The broad intense band at 345 cm$^{-1}$ is tentatively assigned to $\nu$(AsCl), this band is close to the corresponding band at 350 cm$^{-1}$ for (XXII). The similar bands at 333 cm$^{-1}$ and 352 cm$^{-1}$ for [Et$_4$N][AsCl$_6$] have been assigned as the $F_{1u}$ bending mode ($v_3$) of the As-Cl bond. [MgCl$_2$.2MeCN has $\nu$(MCl) at 315 and 250 cm$^{-1}$].

The charge transfer bands at 36 764, 37 453 and 38 759 cm$^{-1}$ in the electronic spectrum are associated with the
hexachloroarsenate(V) anion, and are very similar to those observed at 38 759, 37 453 and 36 900 cm\(^{-1}\) in \([\text{Me}_4\text{N}]\text{[AsCl}_6]\).

The conductivity was measured in DMF solution, due to the insolubility of the compound in acetonitrile. Low solubility in acetonitrile of (XXIII) compares with the low solubility of the hexakis(acetonitrile) magnesium(II) salts with tetranuclear bismuth chloro-anions (Chapter 3). The molar conductivity, \(\lambda_m=157.67 \text{ S cm}^2\text{mol}^{-1}\) (at \(10^{-3}\text{M at 25.0 \pm 0.1°C}\)) of (XXIII) confirms its existence as a 1:2 electrolyte. Similar electrolyte types have molar conductivities in the range 130-170 S cm\(^2\) mol\(^{-1}\) in DMF solution.

4.2.3. ZnCl\(_2\) Reaction (XXIV)

The oxidation of AsCl\(_3\) to AsCl\(_5\) with chlorine was carried out but halide transfer to AsCl\(_5\) from ZnCl\(_2\) proved to be unsuccessful. The white solid obtained from this reaction is the bis(acetonitrile) adduct, ZnCl\(_2\)2MeCN. The melting point, 95-98°C is very similar to that of 108-109°C for the synthesized adduct. The doublet profile in the infra-red spectrum at 2316 and 2284 cm\(^{-1}\) is characteristic of acetonitrile coordinated to a metal centre. The sharp band at 402 cm\(^{-1}\) corresponds to the \(\delta\)(CCN) bending mode of coordinated acetonitrile. Bands at 383, 347, 310 and 245 cm\(^{-1}\) are assigned to \(\nu\)(MCl) stretching and bending modes, compare those observed at 400, 390, 355, 320, 265 and 240 cm\(^{-1}\) for the synthesized adduct.
4.2.4. TiCl₄ Reaction (XXV)

The oxidation of AsCl₃ to AsCl₅ using Cl₂ as oxidising agent was carried out but halide transfer from TiCl₄ to AsCl₅ was unsuccessful. The bright yellow crystals isolated from this reaction correspond analytically to the bis(acetonitrile) adduct, TiCl₄.2MeCN. The m.p. of these crystals, 150-152°C is very similar to the m.p.'s of the bis adducts isolated from the reactions of TiCl₄/BiCl₃/MeCN; 148-151°C and TiCl₄/SbCl₃/MeCN; 158-160°C. The synthesized adduct itself has a m.p. of 150-152°C. Bands in the IR and UV spectrum are very similar to those observed in the synthesized adduct.

4.2.5. SnCl₄ Reaction (XXVI)

The oxidation of AsCl₃ to AsCl₅ using Cl₂ as oxidising agent was carried out but halide transfer from SnCl₄ to AsCl₅ has proved to be unsuccessful. The colourless crystals isolated from this reaction analyse for chloride as the bis(acetonitrile) adduct, SnCl₄.2MeCN. Halide abstraction by arsenic has not occurred. The m.p., 110-112°C is very close to that of the synthesized adduct, 112-114°C. ²⁹¹

The v(CN) bands in the infra-red spectrum at 2312 and 2280 cm⁻¹ correspond to acetonitrile coordinated to a metal centre. The band at 410 cm⁻¹ is assigned to the δ(CCN) bending mode of coordinated MeCN. The bands at 392, 366, 334 and 303 cm⁻¹ in the far infra-red region are very similar to those observed at 397, 303, 367, 333-345 and 305 cm⁻¹ for SnCl₄.2MeCN. ²⁵⁹
4.2.6. $^{75}\text{As NMR Studies}$

Several attempts were made to identify the $^{75}\text{As nmr}$ signal in DMSO solution, using $\text{AsO}_4^{3-}$ as external reference in solutions of [Me$_4$N]$^+\text{[AsCl}_6^-$(XXII) and [Mg(MeCN)$_6$][AsCl$_6$]$^2-$ (XXIII). Failure to locate any signal using a $^{75}\text{As nmr}$ probe does not rule out the presence of the hexachloroarsenate(V) anion, but is more likely a result of the relatively large electric quadrupole moment of the nucleus, which causes $^{75}\text{As}$ linewidths to be rather broad, and the short relaxation times of this nucleus. Dove et al. have reported the $^{75}\text{As}$ resonance of AsCl$_6^-$ as a singlet at $\delta=391.8$ ppm (ca 0.1M concentration) relative to Et$_4\text{NAsF}_6$ at $\delta=0$ ppm in MeCN (at an operating frequency of 42.83 Hz). The signal is seen to reduce in intensity in a MeCN solution containing AsF$_6^-$ and is replaced by the resonances of AsCl$_n$F$_6-n^-$, $n<5$, indicative of the instability of the AsCl$_6^-$ anion.

4.2.7. Conclusions

The results of these reactions indicate that AsCl$_3$ can be oxidised to AsCl$_5$, but halide transfer from Ti(IV), Sn(IV) and Zn(II) chlorides to AsCl$_5$ does not take place. Instead the products of these reactions are simply the bis(acetonitrile) adducts. By contrast, oxidation of AsCl$_3$ to AsCl$_5$ by chlorine and generation of AsCl$_6^-$ by halide transfer occurs in the presence of Me$_4$NCl and MgCl$_2$ at room temperature. AsCl$_3$ is oxidised to AsCl$_5$ in the presence of Cl$_2$. AsCl$_5$ is unstable at RT and halide transfer from these two chloride ion donors to AsCl$_5$ takes place to give AsCl$_6^-$. The symmetrical AsCl$_6^-$ anion stabilizes the $^{+5}$ oxidation state of arsenic. The failure of Ti, Sn and Zn
chlorides to donate chloride ions to AsCl$_5$ compared to the ability of MgCl$_2$ to do so illustrates the superior role of MgCl$_2$ as a source of halide ion in these reactions.

The use of Me$_4$NCl as source of chloride ion for transfer to As(V) was to produce an AsCl$_6^-$ standard for $^{75}$As nmr purposes, and follows previous methods for the generation of hexachloroarsenate(V) by the addition of an ionic chloride containing a bulky cation. 288a Stabilisation of the higher oxidation state of As primarily relies upon a large lattice energy contribution to the stability of the arsenic(V) salt. The stability of the AsCl$_6^-$ anion is also increased by complexation, but this contribution to the stability of the salt is minor compared to lattice energy effects. Similar strategy for isolation and structural determination of AsCl$_6^-$ is observed by the use of the bulky tetraphenylphosphonium cation. 289

Another method for the stabilisation of arsenic(V) relies on the use of neutral ligands which are capable of $\pi$ bonding and of increasing the electron density on the metal. This reduces the oxidising strength of arsenic in the +5 state. Ligands such as R$_3$PO have been used to this end. 288a

Lewis acid halides FeCl$_3$, AlCl$_3$, GaCl$_3$ 294 and SbCl$_5$ 295 have been used to form cationic arsenic(V) species according to conductivity measurements. Stabilisation of the As(V) state by generation of the tetrachloroarsenate(V) cation has been achieved. By contrast the compound PCl$_5$.AsCl$_5$ has been formulated as PCl$_4^+$AsCl$_6^-$. 295 although later studies propose that its formula lies between PCl$_5$ and PCl$_5$.AsCl$_5$, [x AsCl$_6^-$.(1-x)PCl$_6^-$.] 290. Raman studies 296 indicate that this compound decomposes to AsCl$_3$, Cl$_2$ and PCl$_5$. 115
The oxide chloride of arsenic(V), AsOCl₃ has been isolated by ozonolysis of AsCl₃. At room temperature it decomposes to 
\((\text{As}_2\text{O}_3\text{Cl}_4)_n\) of unknown structure. In the same study arsenic trichloride reacts with fluorine at -78°C to give AsCl₄⁺AsF₆⁻. 297

The use of MgCl₂ as a source of chloride ion to stabilise the pentavalent state of arsenic following oxidation of AsCl₃ with Cl₂ in our studies represents a novel route to the generation of the hexachloroarsenate(V) anion. In this present study and in previous studies 213 MgCl₂ is established as a suitable double chloride ion source in Group 15 halide exchange systems, i.e.

\[
\begin{align*}
\text{MgCl}_2 + 2\text{SbCl}_5 \rightarrow \text{MeCN} \quad & [\text{Mg}(\text{MeCN})_6][\text{SbCl}_6]\_2 \quad (\text{I}) \\
\text{MgCl}_2 + 2\text{BiCl}_3 \rightarrow \text{MeCN} \quad & [\text{Mg}(\text{MeCN})_6][\text{Bi}_4\text{Cl}_{16}] \quad (\text{XII}) \\
3\text{MgCl}_2 + 4\text{BiCl}_3 \rightarrow \text{MeCN} \quad & [\text{Mg}(\text{MeCN})_6][3\text{Bi}_4\text{Cl}_{18}] \quad (\text{XIII}) \\
\text{MgCl}_2 + 2\text{SbCl}_3 \rightarrow \text{MeCN} \quad & [\text{Mg}(\text{MeCN})_6][\text{SbCl}_6]\_2 \quad (\text{213})
\end{align*}
\]

Thus the use of MgCl₂ to generate cationic metal species seemed an obvious choice, due to its electropositive nature. Solvent choice is also an important factor in the generation of the bulky [Mg(MeCN)₆]²⁺ cation to stabilise the [AsCl₆]⁻ anion. The stability of As(V) in [Mg(MeCN)₆][AsCl₆]₂ is therefore enhanced by complexation and a large lattice energy contribution, whereby As(V) behaves as a Lewis acid towards MgCl₂ generating ionic species.

\[
\text{MgCl}_2 + \text{AsCl}_3 + \text{Cl}_2 \rightarrow \text{MeCN} \quad [\text{Mg}(\text{MeCN})_6][\text{AsCl}_6]
\]
To our knowledge this represents the first example of the use of an electropositive metal halide as the source of halide to generate the hexachloroarsenate anion.
4.3. Sb(III) as a Lewis Acid

The usual preparation of antimonate(III) salts involves direct mixing with a quaternary ammonium (or related) salt. As an alternative approach we have investigated the use of metal halides as the source of halide ion in an attempt to generate antimonate(III) salts involving cationic metal species. Previous studies have resulted in the formation of the ternary complex MgCl$_2$.2SbCl$_3$.6MeCN, identified as [Mg(MeCN)$_6$][SbCl$_4$]$_2$. This was obtained from the reaction of SbCl$_3$ with MgCl$_2$ in acetonitrile solution.

A variety of different metal chlorides have been used as the source of halide ion in reactions with SbCl$_3$ in acetonitrile. Several covalent chlorides were used, namely: TiCl$_4$, SnCl$_4$ and TiCl$_3$. Iron(III) and In(III) chlorides were selected on the basis of their Lewis acidic tendencies. While Sb(V) and Bi(III) chlorides were chosen as a means of demonstrating the relative Lewis acidic strengths of the group 15 chlorides. The following results were obtained.

4.3.1. Discussion of Results: Sb(III) as Lewis Acid

**TiCl$_4$ Reaction (XXVII)**

Reaction of TiCl$_4$ with SbCl$_3$ in acetonitrile results in the formation of the adducts TiCl$_4$.2MeCN and SbCl$_3$.3MeCN, which have been spectroscopically identified using IR and UV techniques. Halide transfer from Ti$^{IV}$ to Sb$^{III}$ has not occurred.

Recrystallisation from MeCN gave bright yellow crystals of TiCl$_4$.2MeCN, m.p. 158-160°C. TiCl$_4$.2MeCN. Bands observed in the electronic and infra-red spectrum confirm the formation of the bis(acetonitrile) adduct.
**TiCl₃ Reaction (XXVIII)**

Reaction of TiCl₃ with 2SbCl₃ in MeCN results in the formation of the two acetonitrile adducts, TiCl₃·3MeCN and SbCl₃·3MeCN, which have been identified using IR and UV-Visible spectroscopy. Halide transfer from Ti(III) to Sb(III) has not occurred.

**FeCl₃ Reaction (XXIX)**

Reaction of equimolar FeCl₃ with SbCl₃ in MeCN gives a yellow solid which is a mixture of FeCl₃·2MeCN and SbCl₃·3MeCN. Halide transfer from Sb(III) to Fe(III) or vice versa has not occurred.

Peaks at 2320 and 2295 cm⁻¹ in the infra-red spectrum correspond to coordinated acetonitrile. In the far infra-red region the broad intense band at 378 cm⁻¹ is assigned to \( \nu(FeCl) \). The bands at 350 and 250 cm⁻¹ are assigned to \( \nu(SbCl) \) (compare bands at 352 and 259 cm⁻¹ in SbCl₃ itself).

The charge transfer bands at 41841, 37313(sh), 32051 and 27700 cm⁻¹ in the electronic spectrum are attributed to the \([FeCl₄]^-\) anion in solution, they correspond closely to bands observed at 41600, 37400, 32000 and 27700 cm⁻¹ in \([Et₄N][FeCl₄]\).²⁵⁸

The dissociation of FeCl₃·2MeCN to FeCl₂·FeCl₄⁻ in MeCN accounts for the presence of FeCl₄⁻ in the electronic spectrum.

**InCl₃ Reaction (XXX)**

Reaction of InCl₃ with 3SbCl₃ in acetonitrile results in the formation of a mixture of the tris(acetonitrile) adducts of SbCl₃ and InCl₃. Halide transfer has not occurred between In(III) and
Group 13 halides generally behave as Lewis acids, the trihalides interact with other metal chlorides to form mixed halides with halogen bridges, many of which are quite volatile.

**SnCl₄ Reaction (XXXI)**

Reaction of SnCl₄ with 2SbCl₃ in MeCN results in the formation of the two acetonitrile adducts SnCl₄.2MeCN and SbCl₃.3MeCN. Halide transfer from Sn⁴⁺ to Sb¹¹⁺ has not occurred.

Bands at 2304 and 2276 cm⁻¹ in the infra-red spectrum correspond to coordinated acetonitrile. In the far infra-red spectrum bands at 408, 392 and 360 cm⁻¹ assigned to v(SnCl) and those at 334 and 304 cm⁻¹ assigned to v(SnN) are very similar to those observed in SnCl₄.2MeCN. Recrystallisation from MeCN gave colourless crystals SnCl₄.2MeCN.

**SbCl₅ Reaction (XXXII)**

Reaction of equimolar SbCl₅ with SbCl₃ in acetonitrile solution results in the formation of the highly air-moisture sensitive ternary complex SbCl₃.SbCl₅.4MeCN. This product is formulated as an ionic product on the basis of infra-red, electronic and nmr spectroscopic data.

The bands at 2310 and 2280 cm⁻¹ in the infra-red spectrum correspond to coordinated MeCN. These ligands necessarily bond to the Sb¹¹⁺ centre as there is strong evidence for the formation of the six coordinate hexachloroantimonate(V) anion.

The presence of a broad intense band at 346 cm⁻¹ in the far infra-red spectrum is indicative of SbCl₅⁻. Compare the exceptionally strong v(SbCl) 346 cm⁻¹ [F₁u bending mode (v₃)]
observed for [K][SbCl₆]. The intense charge transfer band at λ_max 37313 cm⁻¹ is diagnostic of SbCl₆⁻ species in solution. The clearly resolved singlet at δ = 0.17 ppm (W_1/2=175Hz) in the ¹²¹Sb nmr spectrum provides further confirmation of SbCl₆⁻. (Compare the external reference [Et₄N][SbCl₆] δ = 0, W_1/2=190Hz). The intense band at 260 cm⁻¹ in the far infra-red spectrum is assigned to ν(SbCl); compare the similar band at 259 cm⁻¹ of SbCl₃ itself.

In the knowledge that the presence of the SbCl₆⁻ ion arising from the self-ionisation of SbCl₅ is unlikely, halide transfer has occurred from SbIII to SbV: the ternary complex (XXXII) may be formulated as [SbIIICl₂(MeCN)₄][SbVCl₆]⁻. However this simple stoichiometric formulation is rather unlikely. The cation species may well be multinuclear, analogous to the fluoro species derived from SbF₃·SbF₅ adducts of differing stoichiometries (Chapter 1). These have no coordinated solvent molecules and synthesis usually involves the reduction of SbF₅ by PF₃ in arsenic trifluoride. The solid-state nature of the ternary species SbCl₃·SbCl₅·4MeCN is an obvious candidate for an X-ray structural study, but suitable crystals could not be obtained.

Conductivity measurements in acetonitrile solution imply that the product is a 1:1 electrolyte, Λ_m=141.75 Scm²mol⁻¹ at 10⁻³M.

A similar reaction is found in that of Ph₃SbCl₂ with SbCl₅ in carbon tetrachloride. Chloride ion transfer to SbCl₅ occurs to give the ionic species [Ph₃SbCl]⁺[SbCl₆]⁻, although the cation contains antimony in the pentavalent state.
There are very few examples where Sb$^{III}$Cl$_3$ behaves as a Lewis base, this more unusual feature of its chemistry is observed in the unstable, light-sensitive products [Ni(CO)$_3$SbCl$_3$] and [Fe(CO)$_3$(SbCl$_3$)$_2$].

Antimony(III) chloride behaves as a chloride ion donor in the 1:1 adduct SbCl$_3$.GaCl$_3$ (synthesis in liquid SO$_2$). This comprises very distorted tetrahedral GaCl$_4^-$ anions which strongly interact with SbCl$_2^+$ cations via Ga-Cl...Sb bridges to give a polymeric chain. In this instance halide transfer has occurred from Sb$^{III}$ to Ga$^{III}$ but a strong covalent interaction exists between the ions [SbCl$_2^+$.GaCl$_4^-$]. The product cannot be formally regarded to contain the SbCl$_2^+$ cation.

This study represents the behaviour of Sb$^{III}$ as a chloride ion donor in the presence of the very powerful Lewis acid SbCl$_5$.

**BiCl$_3$ Reaction (XXXIII)**

Reaction of equimolar BiCl$_3$ with SbCl$_3$ in acetonitrile results in the formation of the two tris(acetonitrile) adducts BiCl$_3$.3MeCN and SbCl$_3$.3MeCN. Halide transfer from Sb$^{III}$ to Bi$^{III}$ or vice versa has not occurred.

The bands at 2300 and 2260 cm$^{-1}$ in the infra-red spectrum correspond to coordinated MeCN. In the far infra-red spectrum bands at 350 and 250 cm$^{-1}$ are tentatively assigned to v(BiCl)$_3$. The charge transfer bands at 45 045, 42 918, 34 965 and 31 847 cm$^{-1}$ are due to the presence of BiCl$_3$.3MeCN. Similar bands are observed at 46 882, 43 478, 35 014 and 32 258 cm$^{-1}$ in the electronic spectrum of BiCl$_3$ in MeCN.
4.3.2. Conductivity Studies

Acetonitrile was chosen as the solvent for conductivity studies. Using the technique described in Appendix 1 the conductivity of (XXXII) was measured over a series of dilutions at 25.0 ± 0.1°C to allow application of the Onsager Law for solutions of strong electrolytes.

Reaction of SbCl$_5$/SbCl$_3$/MeCN (XXXIII)

The ternary complex SbCl$_5$.SbCl$_3$.4MeCN is formulated as an ionic product in solution on the basis of spectroscopic data which identify the SbCl$_6^-$ anion, also conductivity studies imply that the complex behaves as a 1:1 electrolyte in MeCN.

Initially the graph of $\Lambda_m$(Scm$^2$mol$^{-1}$) versus $c^{1/2}$(mol dm$^{-3}$) was plotted (Figure 4.1).

Figure 4.1. $\Lambda_m$ versus $c^{1/2}$ for SbCl$_3$.SbCl$_5$.4MeCN
This graph was extrapolated to give \( \Lambda_0 \), the molar conductivity at infinite dilution, using linear least squares analysis (\( \Lambda_0 = 177.50 \text{ Scm}^2\text{mol}^{-1} \) at 25.0 ± 0.1°C, correlation coefficient, 0.984). This value is used to plot a graph of \( \Lambda_0 - \Lambda_m \) versus \( c^{1/2} \) (Figure 4.2) to give a slope which necessarily reflects the electrolyte type of the complex. The slope has a value of 428.1.

**Figure 4.2.** \( \Lambda_0 - \Lambda_m \) versus \( c^{1/2} \) for SbCl₃.SbCl₅.4MeCN

\[ \Lambda_m, \text{ the molar conductivity at } 10^{-3}\text{M is } 141.75 \text{ Scm}^2\text{mol}^{-1}. \text{ This value is within the range, } 120-160 \text{ Scm}^2\text{mol}^{-1}, \text{ expected for a } 1:1 \text{ electrolyte in acetonitrile solution.} \]
4.3.3. Conclusions

The results of these reactions in most cases illustrate the failure of SbCl₃ to generate cationic metal species by halide abstraction, by contrast with SbCl₅ which removes at least one halide ion from the corresponding metal chlorides. The rapacious Lewis acidity of SbV is illustrated by the generation of cationic Sb₃⁺ and Bi₃⁺ species and the stable SbCl₆⁻ anion by halide removal from SbCl₃ and BiCl₃ i.e.

\[
\text{SbCl}_3 + \text{SbCl}_5 \rightarrow \text{SbCl}_3\cdot\text{SbCl}_4\cdot4\text{MeCN} \quad (\text{XXXII})
\]

\[
\text{BiCl}_3 + \text{SbCl}_5 \rightarrow [\text{BiCl}_2(\text{MeCN})_4][\text{SbCl}_6] \quad (\text{XIV})
\]

The reaction of Sb₃⁺ with Bi₃⁺ in MeCN gives the acetonitrile adducts. This serves to illustrate their similar Lewis acidic strengths, which is further confirmed by their identical behaviour towards the various metal chlorides chosen.

4.4. Mechanism of Halide Transfer

Many of the reactions investigated in this study illustrate the transfer of chloride ions from MClₙ to a group 15 chloride and the formation of ionic species. Comparisons of the behaviour of AsCl₃, SbCl₃, BiCl₃ and SbCl₅ towards different MClₙ provides insight into the relative Lewis acidic strengths of these chlorides.

The choice of acetonitrile as solvent for these reactions is based upon its strongly coordinating aprotic properties: M-Cl/Sb-Cl solvolysis side reactions are avoided. Its powerful donor properties ensures occupation of coordinatively
unsaturated sites generated on the metal centres following halide removal, and the attainment of a six coordinate geometry for M. The resultant formation of ionic products is assisted by this polar solvent.

The transfer of halide ion(s) from M to E (E=AsIII, SbIII, BiIII, SbV) is thought to proceed by a molecular mechanism which involves halogen bridged intermediates. The generation of \[[\text{Mg(MeCN)}_6][\text{SbCl}_6]\] is used as an example. In this MgCl2/SbCl5/MeCN system halogen-bridged intermediates of binuclear (A) and/or trinuclear (B) nature can be proposed (Figure 4.3) involving the edge or face sharing fusion of octahedral units.

In MeCN solution asymmetric cleavage of chloride bridges at 1 generates (I) which implies that Sb(V) is the preferred halogen acceptor. Vacant sites on \[[\text{Mg}]^{2+}\] are occupied by six MeCN ligands. The solvent plays a very important role in the stabilisation of the cationic species; it assists ionic formation via occupancy of co-ordinatively unsaturated metal species implicit with halide expulsion. The unlikely situation where asymmetric cleavage at 3 occurs would result in the formation of \([\text{SbCl}_4]^+\). This is dismissed on the basis of the rapacious Lewis acidity of SbCl5. (Symmetric cleavage at 2 gives the starting materials).

In this case multiple halide abstraction has occurred, so both binuclear and trinuclear halogen bridged intermediates can be proposed. With a binuclear species sequential removal of chloride from MgCl2 to give MgCl+(solvated) is implied, a second molecule of SbCl5 approaches the MgCl+(solvated) species to abstract its chloride to give the fully solvated
[Mg(MeCN)₆]²⁺ cation. The MgCl⁺ cation has actually been structurally identified in [MgCl(THF)₅][AlCl₄].

Figure 4.3. Proposed Intermediates of [Mg(MeCN)₆][SbCl₆]₂

(The number and arrangement of coordinated ligands, L=MeCN around the Mg centre is variable).

By contrast, a trinuclear intermediate as in B may be involved, whereby simultaneous removal of both chlorides from MgCl₂ occurs to give (I). In complexes where triple halide abstraction takes place, i.e. [In(MeCN)₆][SbCl₆]₃ (VI) and [Bi(MeCN)₆][SbCl₆]₃ (XV), more complex multinuclear bridged
species can be envisaged to enable simultaneous chloride abstraction from MCl₃.

Another consideration of the halide transfer mechanism is associated with the positions of the MeCN ligands on the metal centre. Whether chloride ligands trans to MeCN are removed in preference to those trans to another chloride is an open question. Compare the "trans effect" and similar "trans influence" of ligands on metal centres. The expected trans geometry of the [TiCl₂(MeCN)₄]⁺ cation in (X) implies that the MeCN ligands exert such a trans effect on the removal of chloride from mer TiCl₃.3MeCN.

The use of covalent chlorides as chloride ion donors in the reactions investigated rules out the preformation of any ionic species in MeCN. In fact most of these chlorides form molecular adducts in MeCN. Even MgCl₂, which is an ionic compound, has limited solubility in MeCN. Its conductivity was measured and was found to be negligible in MeCN. Therefore the dissociation of MgCl₂ into ions does not occur. The autoionization of these group 15 chlorides is also negligible; the formation of ionic species in these reactions has occurred by halide transfer from MClₙ to the group 15 Lewis acid EClₙ by a molecular mechanism.

Where halide transfer to BiCl₃ has occurred similar halogen bridged intermediate species are envisaged, the lone pair on Bi⁺⁺⁺ may or may not be active before oligomerization to a tetraneutral Bi₄ unit occurs.
4.5 Variations in the Lewis Acidity of Group 15 Chlorides

From these studies it is apparent that there are variations between the acceptor strength of arsenic, antimony and bismuth chlorides. Antimony pentachloride is by far the most powerful Lewis acid of the chlorides of this group. In all reactions (I-XI) SbCl₅ removes at least one chloride ion from MClₙ to generate partially or fully solvated metal cations and SbCl₆⁻. The formation of cationic Sb⁺³ and Bi⁺³ species upon reaction with SbCl₅ in (XIV), (XV) and (XXXII) shows that SbCl₅ exceeds SbCl₃ and BiCl₃ in chloride acceptor strength. The failure of BiCl₃, SbCl₃ and AsCl₃ to abstract chloride ions from those chlorides which form cations with Sb⁺⁵ provides further confirmation of their weaker Lewis acidity. The only chloride from which As⁺³⁺, Sb⁺³ and Bi⁺³ will remove chloride ions is MgCl₂, to give [Mg(MeCN)₆][AsCl₆]₂ (XXIII), [Mg(MeCN)₆][SbCl₄]₂, [Mg(MeCN)₆]₂[Bi₄Cl₁₆] (XII) and [Mg(MeCN)₆]₃[Bi₄Cl₁₈] (XIII) respectively. All other chlorides used gave the acetonitrile adducts (A) rather than halide transfer products (HT) (Table 4.1).
Table 4.1. The Formation of Halide Transfer Products with MClₙ and the Group 15 Chlorides

<table>
<thead>
<tr>
<th>MClₙ</th>
<th>As(V)</th>
<th>Sb(V)</th>
<th>Sb(III)</th>
<th>Bi(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂</td>
<td>HT</td>
<td>HT</td>
<td>HT</td>
<td>HT</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>A</td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>TiCl₃</td>
<td></td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>A</td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>VCl₃</td>
<td></td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>CrCl₃</td>
<td></td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>FeCl₃</td>
<td></td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>InCl₃</td>
<td></td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>A</td>
<td>HT</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>SbCl₅</td>
<td></td>
<td>HT</td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>BiCl₅</td>
<td></td>
<td>HT</td>
<td>A</td>
<td></td>
</tr>
</tbody>
</table>

Such variations between the chloride donor ability of MgCl₂ compared to MClₙ (n=2, M=Zn; n=3, M=Ti, V, Cr, Fe, In; n=4, M=Ti, Sn) is attributed to a number of factors: The electronegativity of M, the size and charge of Mn⁺ (polarizability). According to Pauling's electronegativity scales magnesium has by far the lowest electronegativity compared to other M, such that it is more likely to donate chloride to ECln to become a cation. There is a correlation between the size (using Shannon and Prewitts effective ionic radii, 22 coordination number 6) and the charge of Mn⁺ and its chloride donor ability. This is also related to the chloride ion acceptor ability of ECln (Table 4.2).
Table 4.2. Ratio of Charge to Effective Ionic Radii (charge density) for Mn+:

<table>
<thead>
<tr>
<th>M</th>
<th>Charge</th>
<th>Ionic Radii (pm)</th>
<th>Charge Density (charge/ionic radii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>2</td>
<td>86</td>
<td>0.023</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>88</td>
<td>0.022</td>
</tr>
<tr>
<td>Ti</td>
<td>3</td>
<td>81</td>
<td>0.037</td>
</tr>
<tr>
<td>V</td>
<td>3</td>
<td>78</td>
<td>0.038</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>75.5</td>
<td>0.0397</td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
<td>69 (low spin)</td>
<td>0.0434 (L.S)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78.5 (high spin)</td>
<td>0.0382 (H.S)</td>
</tr>
<tr>
<td>In</td>
<td>3</td>
<td>94</td>
<td>0.0319</td>
</tr>
<tr>
<td>Ti</td>
<td>4</td>
<td>74.5</td>
<td>0.0536</td>
</tr>
<tr>
<td>Sn</td>
<td>4</td>
<td>83</td>
<td>0.048</td>
</tr>
<tr>
<td>As</td>
<td>3</td>
<td>72</td>
<td>0.0416</td>
</tr>
<tr>
<td>As</td>
<td>5</td>
<td>60</td>
<td>0.0833</td>
</tr>
<tr>
<td>Sb</td>
<td>3</td>
<td>90</td>
<td>0.033</td>
</tr>
<tr>
<td>Sb</td>
<td>5</td>
<td>74</td>
<td>0.067</td>
</tr>
<tr>
<td>Bi</td>
<td>3</td>
<td>117</td>
<td>0.0256</td>
</tr>
</tbody>
</table>

It must be remembered that these values relate to the effective ionic radii and size of Mn+, so are appropriate for the formation of [Mg(MeCN)₆]²⁺, [In(MeCN)₆]³⁺ and [Bi(MeCN)₆]³⁺ but are used as guidelines for predicting the behaviour of MClₙ.
in the formation of \([\text{MC}_{n-x}\text{L}_{6-(n-x)}]^x+\), when the charge of \([\text{M}]^x+\)
is not the same as its oxidation state.

The chloride ion donor and acceptor ability of M deduced from these studies parallels the trends observed in electronegativity and charge density data, i.e. the higher the charge density and electronegativity the greater is the Lewis acidity (acceptor ability) of M. This is a direct measure of the "hardness" of M.

On the basis of these data it is understood why MgCl\(_2\) is a suitable source of chloride ion for Group 15 halide transfer reactions compared to other MC\(_n\); the electronegativity and charge density of trivalent As, Sb and Bi all exceed that of Mg, while their charge densities are lower than those of other M. This latter point explains the failure of As\(^{III}\), Sb\(^{III}\) and Bi\(^{III}\) to behave as Lewis acids towards MC\(_n\) other than MgCl\(_2\).

To compare, Sb\(^V\) has a high charge density which is greater than all the metals used and explains its behaviour as a powerful Lewis acid towards them, and equally to Sb\(^{III}\) and Bi\(^{III}\). In addition to the reduced electron density around Sb\(^V\), which causes an increased acceptor strength, the superiority of SbCl\(_5\) over SbCl\(_3\) as a Lewis acid is associated with an increase in stability in changing from a trigonal bipyramidal to an octahedral geometry after chloride acceptance. The formation of ionic products is favoured due to a lattice energy contribution.

It is apparent from this study that BiCl\(_3\) and SbCl\(_3\) have very similar chloride acceptor strengths, the following series can be drawn up in order of decreasing Lewis acidity:

\[
\text{SbCl}_5 \gg \text{SbCl}_3 = \text{BiCl}_3 > \text{AsCl}_5 > \text{AsCl}_3
\]
Chloride ion removal from MgCl₂ by AsCl₅ and the formation of a stable product [Mg(MeCN)₆][AsCl₆] (XXIII) requires the presence of Cl₂ to oxidise AsCl₃ to AsCl₅. Its Lewis acidity is not adequate to effect halide ion transfer in the trivalent state, unlike SbCl₃ and BiCl₃.

It was observed that the reaction of AsCl₃/Cl₂ with ZnCl₂ (XXIV) fails to give halide transfer products: Zn and Mg have very similar charge density (Table 4.2) but the electronegativity of Zn (1.65) is greater than that of Mg (1.31). Also the 2nd ionization energy of Zn (1726 kJmol⁻¹) is higher than for Mg (1450 kJmol⁻¹).
CHAPTER 5
Titanium Tetrachloride (a) Lewis Acid and b) Cation Formation

TiCl₄ is a colourless liquid which is rapidly hydrolysed in the air. The role of TiCl₄ as a Lewis acid is well established; it complexes with chloride ions to form a series of chloro-anions and forms a large number of addition compounds with other ligand types. The most common coordination number of Ti(IV) is six, although compounds of different coordination number are known. For example, \((\eta^5-C_5H_5)_2TiCl_2\) \(302\) distorted tetrahedral (if the centre of the ring is considered as the coordination site), TiO(porphyrin), \(303\) square pyramidal and TiCl₄(diars)₂ \((\text{diars}=\sigma\text{-phenylenebis(dimethylarsine)})\) \(304\) dodecahedral.

a) TiCl₄ as a Lewis Acid

5.1.1. Introduction

The formation of Ti(IV) complex chloro-anions is an established feature of its chemistry; TiCl₅⁻ and TiCl₆²⁻ anions have been isolated \(305,306\) by reaction of Et₄NCl with TiCl₄ in thionyl chloride.

The dinuclear anions [Ti₂Cl₁₀]²⁻ and [Ti₂Cl₉]⁻ have been prepared by reaction of PCl₃ and PCl₅ with TiCl₄ in SOCl₂ and POCI₃ respectively. \(240\) The [Ti₂Cl₁₀]²⁻ anion comprises an edge-bridged biocathedral unit. This anion is also formed as a by-product of the reaction of trithiazyl chloride, (NSCl)₃ with TiCl₄ in CCl₄. \(307\) By comparison the [Ti₂Cl₉]⁻ anion provided the first example of a first row transition metal in the +4 formal oxidation state to assume the geometry of a face-shared biocathedron (Figure 5.1).

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Isolation of the double salt \[ \text{[PCl}_4\text{]}_3\text{[TiCl}_6\text{]}\text{[PCl}_6\text{]} \] was achieved by reaction of a large excess of PCl\(_5\) with TiCl\(_4\) in CH\(_3\)NO\(_2\) and POCl\(_3\). Attempts to prepare the simple salt \[ \text{[PCl}_4\text{]}\text{[TiCl}_6\text{]} \] have been unsuccessful.

Interest in the chemistry of TiCl\(_4\)/MgCl\(_2\) systems stems from the knowledge that Ziegler-Natta catalysts of the type MgCl\(_2\)/electron donor/TiCl\(_4\)/AlEt\(_3\) are very effective in the polymerization of ethylene and propylene. Extremely active catalysts can be prepared by milling MgCl\(_2\) and TiCl\(_4\) together, polymerization is then effected using AlEt\(_3\) as an activator. MgCl\(_2\) acts as the catalyst support, its unique behaviour as such has been attributed to the similarity of its crystal structure to that of \(\alpha\) or \(\gamma\) TiCl\(_3\), and the similar ionic radii (Pauling) of Ti\(^{4+}\) and Mg\(^{2+}\) (0.68 and 0.65\(\text{Å}\) respectively), which illustrates the compatibility of these two catalyst components. Sobota et al have suggested that the key to the unusual role played by MgCl\(_2\) as a support for super-high-activity Ziegler-Natta catalysts lies in the reaction:
\[
\text{AlCl}_3 + [\text{MgCl}_2(\text{THF})_2] \rightarrow [\text{MgCl(THF)}_2][\text{AlCl}_4]\cdot\text{THF} \quad (1)
\]

Elimination of AlCl\(_3\) from the catalyst composition (equation 2) prevents the formation of AlEtCl\(_2\), which is thought to poison the catalyst. AlEtCl\(_2\) is formed during the catalyst synthesis, as a by-product of the alkylation of TiCl\(_3\).

\[
\text{AlEt}_2\text{Cl} + \text{AlCl}_3 \rightarrow 2\text{AlEtCl}_2 \quad (2)
\]

Several groups have investigated the chemistry of TiCl\(_4\)/MgCl\(_2\) systems in different oxygen donor solvents as models for Ziegler/Natta catalyst sites: Bassi et al. have used EtOAc, \(^{310}\) and ClCH\(_2\)CO\(_2\)Et (ethylchloroacetate). \(^{311}\) Sobota's group have carried out similar reactions in THF. \(^{217}\) These studies gave bimetallic complexes which incorporate halogen-bridging. Although titanium(IV) is very oxophilic the solvent molecules bind to the magnesium centre, which implies that Ti(IV) is the preferred halogen acceptor in these halogen bridged structures.

Reaction of MgCl\(_2\) in EtOAc with equimolar TiCl\(_4\) in EtOAc at 60°C yields TiMgCl\(_6\)(EtOAc)\(_4\) \(^{310}\) which has the following chloro-bridged structure (Figure 5.2).
Complex formation has changed the metal geometry of titanium from tetrahedral to octahedral.

Reaction of MgCl₂ with equimolar TiCl₄ in ethylchloroacetate gives TiMgCl₅(O₂CCH₂Cl).(ClCH₂CO₂Et)₃ (Figure 5.3). 311
In this structure the Ti(IV) atom is octahedrally coordinated by five chlorine atoms and an oxygen atom of a ClCH₂CO₂ residue. This unit has resulted from the loss of the ethyl group from ethylchloroacetate. Six coordination is observed for Mg(II) which is surrounded by two bridging chlorine atoms, the carbonyl oxygen atoms of three ClCH₂CO₂Et and an oxygen atom of the ClCH₂CO₂ residue. The two octahedra share an edge via the two chlorine bridges and are further connected by the CO₂ group of the ClCH₂CO₂ residue.

Reaction of Mg(OH)Cl with TiCl₄ in EtOAc gives TiMgCl₅OH(EtOAc)₄ (Figure 5.4).

**Figure 5.4. Structure of TiMgCl₅OH(EtOAc)**

This structure consists of two slightly distorted octahedra; Ti(IV) being coordinated by five chlorines and a hydroxyl ligand, and Mg(II) by the carbonyl oxygens of four EtOAc molecules and two bridging Cl atoms. The two octahedra share an edge defined by the double chlorine bridge between Ti and Mg as in TiMgCl₆(EtOAc)₄. The presence of both OH and Cl ligands on the titanium centre is unusual due to the hydrolytic nature of Ti-Cl bonds.
Reactions of MgCl₂ with TiCl₄ in THF, in varying stoichiometries results in the formation of a variety of products: 217

\[
2[\text{TiCl}_4(\text{THF})_2] + [\text{MgCl}_2(\text{THF})_2] \xrightarrow{\text{THF}, 20^\circ C} [\text{Mg(THF)}_6][\text{TiCl}_5(\text{THF})_2] \quad (3)
\]

\[
a + [\text{MgCl}_2(\text{THF})_2] \xrightarrow{\text{THF}, 20^\circ C} [(\text{THF})_4\text{Mg}(\mu\text{-Cl})_2\text{TiCl}_4] \quad (4)
\]

\[
b + [\text{MgCl}_2(\text{THF})_2] \xrightarrow{\text{THF}, 20^\circ C} [(\text{THF})_3\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_3][\text{TiCl}_5(\text{THF})] \quad (5)
\]

Complete halide transfer from Mg⁺ to Ti⁺ has occurred in reaction of a 1:2 molar ratio of [MgCl₂(THF)₂] with [TiCl₄(THF)₂] (equation 3) to give the [Mg(THF)₆]²⁺ cation and [TiCl₅(THF)]⁻ anions. Reaction of this product, a, with equimolar MgCl₂ (equation 4) gives the binuclear chlorine-bridged structure b (Figure 5.5), which is similar to that found in TiMgCl₆(EtOAc)₄. 310 With an equimolar ratio of [MgCl₂(THF)₂] and b (equation 5) the product is c which comprises the homobimetallic cation [(THF)₃Mg₂(μ-Cl)₃(THF)]⁺ (Figure 5.6) and the pseudo octahedral [TiCl₅(THF)]⁻ anion. 238 This cation consists of two face-sharing octahedra joined by three chlorine bridges, a similar cation structure is observed with [MoOCl₄THF]⁻. 216
Other bimetallic halogen-bridged magnesium species are known; direct reaction between MgCl$_2$(THF)$_2$ and FeCl$_3$ in THF yields [MgCl(THF)$_5$][FeCl$_4$]$^{309}$ and [FeCl$_2$(μ-Cl)$_2$Mg(THF)$_4$].$^{313}$ The former species is light sensitive and undergoes reduction to the bimetallic compound. Structural characterisation of [MgCl(THF)$_5$]$^{+}$$^{309}$ provides evidence for the existence of the previously postulated MgCl$^+$ cation. Reduction of Fe$^{III}$ to Fe$^{II}$ is thought to be caused by THF, which reacts with FeCl$_3$, with ring-opening and polymerization.

All reactions in this research have used MeCN as solvent for halide transfer. Reasons for this choice of solvent are based upon its strongly coordinating aprotic properties (Chapter 4, Section 4.4). The results presented in Chapters 2, 3 and 4
indicate the success of MeCN as solvent media for halide transfer reactions involving arsenic, antimony and bismuth chlorides. Solvolysis side reactions are avoided and unsaturated sites generated on the metal centres following halide removal are occupied by MeCN ligands. It was therefore an obvious choice to study the reaction of MgCl$_2$ with TiCl$_4$ in MeCN to investigate what effect, if any, the use of a more polar nitrogen donor solvent has upon the reaction. Complete or single halide transfer may take place, or the formation of bridged species, similar to those observed in EtOAc, CICH$_2$CO$_2$Et and THF, may occur.
5.1.2. Discussion of Results

Reaction of TiCl₄ with MgCl₂ in MeCN (XXXIV)

Isolation of air sensitive bright yellow crystals from the reaction of equimolar TiCl₄ with MgCl₂ in MeCN gave the ternary complex TiCl₄·MgCl₂·6MeCN (X-ray structural determination pending).

The doublet at 2304 and 2276 cm⁻¹ in the infra-red spectrum corresponds to coordinated acetonitrile. In the far infra-red region the band at 412 cm⁻¹ is assigned to δ(CCN) of coordinated MeCN. The broad intense peak at 330 cm⁻¹ is assigned to a Ti-Cl stretching mode. Similar peaks are observed at 324 and 321 cm⁻¹ in [Me₄N]₂[TiCl₆] and [Et₄N]₂[TiCl₆] respectively, 305 and at 330 cm⁻¹ in aqueous H₂[TiCl₆]. 306 (Compare ν(TiCl) peaks at 387a, br and 318w for TiCl₄·2MeCN).

In the electronic spectrum the intense band at 43 666 cm⁻¹ (shoulder at 38 461 cm⁻¹) is associated with Cl(n)→Ti charge transfer transitions. The peak observed at 43 800 cm⁻¹ for TiCl₆²⁻ 301 is similar (Compare peaks at 45 871, 39 682 and 33 783 cm⁻¹ for TiCl₄·2MeCN).

Conductivity studies show that the product behaves as a 1:1 electrolyte in MeCN solution (Λₐ=73 Scm²mol⁻¹ at 10⁻²M; Λ₀=110.8 Scm²mol⁻¹).

Conductivity of MgCl₂·TiCl₄·6MeCN

The conductivity of this ternary species was measured at 25.0 ± 0.1°C over a range of concentrations, using the method detailed in Appendix 1. A graph of Λₐ (Scm²mol⁻¹) versus c¹/₂ (moldm⁻³) was plotted (Figure 5.7) from which a value for Λ₀ of 110.8 Scm²mol⁻¹ was obtained by extrapolation.
This value was used to plot $A_0 - A_m$ versus $c^{1/2}$ which gives a slope of 298.11 (Figure 5.8).
Figure 5.8. Graph of $\Lambda_0 - \Lambda_m$ versus $c^{1/2}$ for $\text{MgCl}_2\cdot\text{TiCl}_4\cdot6\text{MeCN}$

$\Lambda_m = 73$ Scm$^2$mol$^{-1}$ at 10$^{-2}$M. These values are low by comparison with the expected range for 1:1 electrolytes in MeCN ($\Lambda_m = 120-160$ Scm$^2$mol$^{-1}$), but are of similar magnitude to those observed for the 1:1 electrolytes $[\text{SnCl}_3(\text{MeCN})_3][\text{SbCl}_6]$ (III) and $[\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6]$. A molar conductivity of 98 Scm$^2$mol$^{-1}$ at 10$^{-3}$M was recorded ($\Lambda_0 = 116.26$ Scm$^2$mol$^{-1}$) for the latter complex.

The exact nature of the ternary species $\text{MgCl}_2\cdot\text{TiCl}_4\cdot6\text{MeCN}$ is unknown. There are three possible structures for a species of this stoichiometry:

i) a neutral chloro-bridged product $[\text{LaMg}(\mu-\text{Cl})_2\text{TiCl}_4]$ (Figure 5.9, $L=\text{MeCN}$) like those where $L=\text{THF}$ and EtOAc. Analytical figures indicate six solvent molecules rather than four, so in this case two uncoordinated solvent molecules must
be present in the lattice. It can be envisaged that such a bimetallic species could undergo some degree of dissociation in MeCN to give a conducting solution.

ii) single halide transfer from Mg$^{11}$ to Ti$^{IV}$ would involve symmetric cleavage of chloro-bridges according to 2 (Figure 5.9) to give [MgCl(MeCN)$_5$][TiCl$_5$(MeCN)].

iii) double halide transfer from Mg$^{11}$ to Ti$^{IV}$ would involve asymmetric cleavage of the chloro-bridges at 1 (Figure 5.9) to give [Mg(MeCN)$_6$][TiCl$_6$]. Similarly Sobota et al. $^{217}$ suggest an ionic formulation [Mg(MeCN)$_6$][ZrCl$_6$] for ZrCl$_4$.MgCl$_2$.6THF based upon elemental analysis.

**Figure 5.9. Chloro-Bridged TiCl$_4$/MgCl$_2$/MeCN Species**

It is unlikely that asymmetric cleavage of the bridges according to 3 occurs, as this would imply that Mg$^{11}$ is the preferred halogen acceptor.

These Ti/Mg chloro-bridged species are models for the halogen bridged intermediates of the ionic products resulting
from halide transfer to a Group 15 chloride (Chapters 2, 3 and 4).

The solvent used may play a crucial role in the type of product formed i.e. equimolar quantities of reactants in EtOAc and THF give the chloro-bridged products \([L_4Mg(\mu-Cl)_2TiCl_4]\), \(L=\text{THF, EtOAc}\). Both these ligands have oxygen donor atoms, while MeCN contains nitrogen as its donor atom (all three ligands can be classed as "hard" by virtue of their donor atoms).

Differences in polarity of these solvents could reflect the different products formed. Dipole moments increase in the order THF < EtOAc < MeCN (1.63, 1.78 and 3.92 Debye respectively). Thus MeCN is more likely than THF and EtOAc to give ionic rather than bridged species where transfer of chloride(s) from \(\text{Mg}^{II}\) to \(\text{Ti}^{IV}\) occurs (solvent assisted cleavage of the chloro bridges may take place as shown in Figure 5.9, and vacant sites in the metal coordination spheres are occupied by polar MeCN following halide transfer).

5.2. Ti-Cl Bond Lengths

Table 5.1 shows variations in the Ti-Cl bond lengths of various \(\text{Ti}^{(IV)}\) chloro species.
Several points can be made from the lengths observed in Table 5.1.

Terminal Ti-Cl\textsubscript{t}, lengths are consistently shorter than bridging, Ti-Cl\textsubscript{b}, lengths. This is consistent with the expected
weakening of the bridging bonds, causing an increase in their length.

Bridging and terminal bond lengths are similar in both anionic and neutral bridged species.

Both the bridging and terminal lengths in the face-shared bioctahedral complex \([\text{PCI}_4][\text{Ti}_2\text{Cl}_9]\) are shorter than in the edge-sharing bioctahedral anion \([\text{Ti}_2\text{Cl}_{10}]^2-\); this is associated with the shorter metal-metal interionic distances in \([\text{Ti}_2\text{Cl}_9]^-\), causing a general tightening of all the bonds in the molecule.

Cationic Ti-Cl lengths are not dissimilar from those observed in gaseous and solid TiCl_4, but are markedly shorter than those observed in the mononuclear anionic species \([\text{TiCl}_5(\text{THF})]^+\) and \([\text{TiCl}_6]^2-\). Loss of a chloride ion in the cationic \([\text{TiCl}_3(\text{MeCN})_3]^+\) species causes a reduction in the electron density around the Ti centre. The stability is maintained by a reduction in the length of the remaining Ti-Cl bonds and coordination of solvent at the vacant sites.

Removal of a further chloride from \([\text{TiCl}_3(\text{MeCN})_3]^+\) to form \([\text{TiCl}_2(\text{MeCN})_4]^{2+}\) (XI) is likely to cause an even greater decrease in the observed Ti-Cl bond length associated with a more positive charge on the metal centre and a reduction in the number of chlorine atoms bonded to Ti\(^{IV}\). Crystallographic data for (XI) is not available to clarify this.

The anionic species \([\text{TiCl}_5(\text{THF})]^+\) has shorter Ti-Cl lengths than those observed in \([\text{TiCl}_6]^2-\), which is consistent with an increase in the electron density on Ti associated with an increased number of coordinated chlorines.
5.3. Ti(IV) Cations

Evidence for the behaviour of TiCl₄ as a chloride ion donor in the literature is scant, therefore its role as a source of cations is unusual; the formation of the cationic species [TiCl₃(MeCN)₃][SbCl₆] and [TiCl₂(MeCN)₄][SbCl₆]₂ (XI) (Chapter 2) represents this rather undeveloped area of its chemistry.

Preliminary observations indicate that both are highly reactive species for ligand exchange and chloride replacement reactions; the following results illustrate this. Both neutral and anionic donors were selected in attempts to generate mixed ligand Ti⁴⁺ cationic complexes. Chloride and bromide anions were used as ligands, and the neutral phosphine, triphenylphosphine (PPh₃).

5.3.1. Discussion of Results: Anionic Ligands

Reaction of [TiCl₃(MeCN)₃][SbCl₆] with Me₄NCl (XXXV)

It is possible to remove chloride ions from TiCl₄ to form cations; therefore it must be possible to regenerate TiCl₄ by the addition of chloride ions to a cation. Me₄NCl was used as the source of chloride ion and TiCl₄·2MeCN has been regenerated using a 1:1 molar ratio of reactants according to:
The bis(acetonitrile) adduct was identified by analytical, IR and UV spectroscopic and m.p. measurements. The band at 37 313 cm\(^{-1}\) in the UV spectrum of the mother liquor (from recrystallization of the solid product initially isolated) is diagnostic of SbCl\(_6\)\(^-\) in solution. The singlet at δ-0.1123 ppm in the \(^{121}\)Sb nmr spectrum also confirms the presence of SbCl\(_6\)\(^-\) in solution.

In a similar vein addition of chloride ion to cationic bismuth, [BiCl\(_2\)(MeCN)\(_4\)][SbCl\(_6\)] (XIV), gave BiCl\(_3\).

Bromide ligand (from Me\(_4\)NBr) was added to [TiCl\(_3\)(MeCN)\(_3\)][SbCl\(_6\)] in an attempt to generate mixed halide titanium species, [TiCl\(_3\)Br.2MeCN] in MeCN. Instead this reaction liberated bromine (detected as MeCN-Br-Br-NCMe in the UV spectrum, \(\lambda_{\text{max}}=38 022\) cm\(^{-1}\)). Oxidation of Br\(^-\) to Br\(^0\) has taken place. The most likely oxidising agent is Sb(V), [SbCl\(_6\)\(^-\) + 2e\(\rightarrow\)SbCl\(_4\)\(^-\), \(E^0=+0.818\) V in 6M HCl (SCE)], \(^{317}\) which is subsequently reduced to Sb(III) considering the potential of the Sn\(^4+/Sn^2+\) couple. [Sn\(^4+/2e\rightarrow Sn^2+, E^0=+0.154\)V in aqueous HCl]. The oxidation of Br\(^-\) to Br\(^0\) in MeCN proceeds by a two step process: \(^{318}\)
1st anodic wave: $3\text{Br}^- \rightarrow \text{Br}_3^- + 2e^- \quad E_{1/2} = +0.42V \quad \text{Ag}^+/\text{Ag} \quad 0.01M \text{MeCl}_2$

[+$0.748V \text{ (SCE)}$]

2nd anodic wave: $2\text{Br}_3^- \rightarrow 3\text{Br}_2^+ + 2e^- \quad E_{1/2} = +0.71V \quad \text{as above}$

[+$1.038V \text{(SCE)}$]

The first process is thermodynamically favourable with Sb(V) as oxidant. The 2nd process occurs to give Br$_2$ due to the formation of Br$_3^-$ as intermediate.

There are precedents for the behaviour of SbCl$_5$ as oxidising agent towards organic molecules and transition metals.
5.3.2. Titanium-Phosphine Systems

5.3.2.1. Introduction

Coordination compounds which contain neutral phosphorus donors are abundant for the majority of the elements in the Periodic Table. Certain elements have relatively little phosphine derivative chemistry, notably the early transition elements of groups 3 and 4 and the lanthanides and actinides. One reason for this lies in their electropositive and oxophilic nature; most complexes of these elements are formed with nitrogen and oxygen based donors.

The comparatively small number of phosphine donor complexes of these elements has also been attributed to the behaviour of P-donors as "soft" ligands, while the metals themselves are "hard" acids. The unsuitability of such interactions in the presence of hard donors may well account for the absence of M-P bonded complexes, but if no preferentially bonding ligands are present in the reaction medium phosphine complexes should form. It is therefore necessary to choose the appropriate ligand and solvent and to ensure that "hard" ligands are not present in excess.

Backbonding is important for the stability of phosphine complexes, the electron deficient nature of the high oxidation states of these metal centres also accounts for the lack of stability of their phosphine complexes. In fact many such complexes are reactive due to the lability of the phosphine ligands.

A number of Ti(IV) phosphine complexes have been reviewed. Phosphine adducts of TiCl₄ have received reasonably extensive coverage in the literature; mono TiCl₄.L
and bis TiCl₄.L₂ species have been made (L=monodentate phosphine); the chelating bidentate phosphine complexes TiCl₄.L₂ (L₂=bidentate phosphine, dppe, dmpe etc) are stable adducts. Synthesis is usually effected by mixing the ligand and TiCl₄ in benzene in appropriate stoichiometries.

Some cationic Ti(IV) phosphine complexes \([\text{Cp}_2\text{TiMe(L)}]^+\text{BPh}_4^-\) (L=PMé₃, PMe₂Ph, PMePh₂, PBu₃) have been prepared. 324

\[
\text{THF} \quad \text{Cp}_2\text{TiMeCl} + L + \text{NaBPh}_4 \rightarrow [\text{Cp}_2\text{TiMe(L)}]^+\text{BPh}_4^- - \text{NaCl}
\]

It is noted that even the bulky phosphine PBu₃ forms the above complex, and that these species are formed in the presence of a large excess of THF. This indicates that the phosphines compete effectively with the oxygen donor THF for the vacant site generated on the titanium centre. The above reaction does not take place when L=PPh₃, dppe and dmpe; this is associated with their lower pKₐ values compared to those of PMe₃, PMe₂Ph, PMePh₂ and PBu₃ (Table 5.2). 5

**Table 5.2. Some pKₐ Values of Tertiary Phosphines**

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBu₃</td>
<td>11.40</td>
</tr>
<tr>
<td>PMe₃</td>
<td>8.65</td>
</tr>
<tr>
<td>PMe₂Ph</td>
<td>6.49</td>
</tr>
<tr>
<td>PPh₃</td>
<td>2.73</td>
</tr>
<tr>
<td>P(4-ClC₆H₄)₃</td>
<td>1.03</td>
</tr>
</tbody>
</table>
The species \((\eta^\text{-C}_9\text{H}_7)_2\text{TiMe}(\text{L}))^+\text{BPh}_4^-\) have also been prepared as before \((\text{L}=\text{PMe}_3, \text{PMePh}_2)\), and the acyl complex \([\text{Cp}_2\text{Ti}(\text{COMe})\text{PMe}_2\text{Ph}]^+\text{BPh}_4^-\), by phosphine displacement of MeCN. Again this illustrates the ability of Ti(IV) to accept phosphine ligands in preference to hard donor ligands. The cationic species \([\text{Cp}_2\text{TiCl}(\text{PMe}_2\text{Ph})]^+\) is believed to be generated during the electrochemical oxidation of \(\text{Cp}_2\text{TiCl}(\text{PMe}_2\text{Ph})\), although it has not been isolated as a salt.

5.3.2.2. Discussion of Results

The following results do not have any accompanying analytical data, the identification of the reaction products is based upon spectroscopic measurements.

Reaction of \([\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6]\) with PPh$_3$ in MeCN

Reaction of \([\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6]\) with PPh$_3$ in varying stoichiometries (XXXVI-XXXVIII) gives a mixture of the starting materials and \([\text{TiCl}_3(\text{PPh}_3)_3][\text{SbCl}_6]\).

Reaction of 1:2 and 1:3 stoichiometric quantities of \([\text{TiCl}_3(\text{MeCN})_3][\text{SbCl}_6]\) with PPh$_3$ (XXXVII and XXXVIII) respectively causes immediate precipitation of an orange solid of m.p. 209-210°C. Inspection of the IR spectrum reveals the presence of bands associated with the PPh$_3$ ligand at 1440, 1120, 1060, 1025, 995, 750, 730, 690 and 537 cm$^{-1}$. (Compare peaks at 1435, 1150, 1090, 1020, 990, 740, 690, 510 and 490 cm$^{-1}$ of PPh$_3$ itself (Nujol). The bands at 455 and 437 cm$^{-1}$ are assigned to v(Ti-P). Those at 360 and 340 cm$^{-1}$ are v(M-Cl); the broad intense band at 340 cm$^{-1}$ may be tentatively assigned to v(SbCl), while the band at 360 cm$^{-1}$ may be assigned to v(TiCl). The absence of the characteristic v(CN) doublet (at c.a. 2287-
2325 cm⁻¹) and the δ(CCN) (at 429 cm⁻¹) in the IR spectrum indicates the loss of coordinated acetonitrile from [TiCl₅(MeCN)₃][SbCl₆] and their replacement by three PPh₃ ligands to maintain an octahedral geometry around Ti(IV).

The bands at 45 248, 39 062 and 36 764 cm⁻¹ in the UV spectrum can be assigned to π→π* charge transfer transitions of the phenyl rings of PPh₃, or to Cl(π)→Ti transitions. Similar bands are observed at 44 200 and 36 100 cm⁻¹ in TiCl₅Me.PPh₃. The presence of the band expected at 37 037 cm⁻¹ for SbCl₆⁻ is masked by the charge transfer peaks associated with PPh₃.

In the proton nmr spectrum a broad multiplet is found at δ=7.75 ppm (relative to TMS), this is assigned to aromatic protons of the PPh₃ ligands. A similar shift is observed at δ=+7.56 ppm in TiCl₅Me.PPh₃.

A singlet is observed at δ=-0.4994 ppm in the ³¹P nmr spectrum. The chemical shift of free PPh₃ is observed at δ=+5.5 ppm in CH₂Cl₂ at RT (H₃PO₄ as external reference). This upfield shift relative to the free ligand corresponds to coordinated PPh₃. In (PhO)₂TiCl₂.2PPh₃ a singlet is observed in the ³¹P nmr spectrum at δ=+1.8 ppm, relative to H₃PO₄. In the adduct TiCl₄.PPh₃ with 1:4 and 1:8 excess of PPh₃ ³¹P shifts are observed at δ=-20.5 ppm. The presence of a singlet implies a fac geometry for the species formed, i.e. all PPh₃ groups are chemically equivalent, this follows the fac configuration of [TiCl₅(MeCN)₃][SbCl₆].

The following reaction takes place:
The complex is thought to have the following structure (Figure 5.10).

**Figure 5.10. Proposed Structure for $[\text{TiCl}_3(\text{PPh}_3)_2][\text{SbCl}_4]$**

\[
\text{MeCN} \\
[TiCl_3(\text{MeCN})_3][\text{SbCl}_6] + 3\text{PPh}_3 \rightarrow [TiCl_3(\text{PPh}_3)_3][\text{SbCl}_6] \ (\text{XL}) \\
20^\circ C \quad \text{orange product}
\]
CHAPTER 6
General Experimental

Except where otherwise stated all of the compounds were air or moisture sensitive. All operations were therefore carried out under a N₂ atmosphere using a conventional 'dry box' or under nitrogen on a Schlenk line using standard techniques. Anhydrous metal halides and SbCl₅ were used as obtained commercially. SbCl₃ was sublimed prior to use on an all glass vacuum-line rig. Phosphine ligands were used directly as supplied. All solvents were dried prior to use. Acetonitrile was freshly distilled and purified following the procedure of Walter and Ramaley. Dichloromethane was freshly distilled from calcium hydride, benzene and hexane from sodium/benzophenone. Dimethylformamide and dimethylsulphoxide were freshly distilled under vacuum. N.m.r solvents were dried over 3Å molecular sieve.

Instrumentation

Infra-red Spectra (4000-200 cm⁻¹) were recorded as nujol mulls located between CsI plates using a Perkin-Elmer 580B spectrometer.

Proton (¹H) Nuclear Magnetic Resonance Spectra (220 MHz) were recorded on a Perkin-Elmer R34 spectrometer, with samples in sealed tubes using TMS as internal reference.

³¹P (¹H) Nuclear Magnetic Resonance Spectra (162 MHz) were recorded on a Bruker WH400 spectrometer, with samples in sealed tubes as CDCl₃ solutions, using 85% H₃PO₄ as external reference.

¹²¹Sb Nuclear Magnetic Spectra (95.72 MHz) were recorded on a Bruker WH400 spectrometer. Samples were sealed in tubes.
as MeCN solutions doped (10% by volume) with CD$_3$CN, relative to [Et$_4$N][SbCl$_6$] (δ=0, $\Delta\nu$= 190 Hz) as external reference.

$^2$H NMR Spectra were recorded on a Bruker WH400 spectrometer, with samples as MeCN solutions doped (10% by volume) with CD$_3$CN, relative to AsO$_4$$^-$ as external reference.

Visible-Ultraviolet spectroscopic measurements were made with a Shimadzu UV35 spectrophotometer using MeCN solutions sealed in quartz cells with a light path of 1 cm.

Atomic Absorption measurements were made with a Varian Techtron AA6 spectrometer.

Arsenic, antimony and bismuth were determined by Atomic Absorption Spectrometry. Bismuth analyses were carried out on dilute hydrochloric acid solutions (ca 5x10$^{-4}$ mol dm$^{-3}$) of the compounds. The wavelength used was 222.8 nm. The spectrometer was calibrated each time of use on standard solutions of bismuth of concentrations in the range 50-200 ppm. These standard solutions were prepared by dissolving a known weight of bismuth metal in a minimum volume of 1:4 hydrochloric acid followed by dilution with distilled water to a known volume in a volumetric flask. A calibration curve was then plotted of concentration against absorption. This plot is slightly curved, however, for the range of concentrations of unknown samples used (typically 75-150 ppm) it is reasonable to approximate this to a straight line. Antimony analyses were carried out on dilute hydrochloric acid solutions of the compounds, using a wavelength of 231.2 nm (concentration of unknown samples 30-80 ppm). Calibration of the spectrometer was effected with standard solutions of antimony of
concentrations in the range 10-150 ppm. These were prepared by dissolving a known mass of potassium antimonyl tartrate in 10% HCl. Arsenic analyses were carried out on dilute sodium hydroxide, nitric acid solutions of the compounds, using a wavelength of 193.7 nm (concentration of unknown samples 75-175 ppm). Calibration of the spectrometer was effected with standard solutions of arsenic of concentrations in the range 50-200 ppm. These were prepared by dissolving a known mass of arsenic(III) oxide in 20% NaOH, which was neutralized with nitric acid and diluted with distilled water to a known volume in a volumetric flask.

Spot tests for arsenic and antimony were carried out by gently warming zinc in dilute sulphuric acid to cause a regular evolution of hydrogen. Approximately 1 cm$^3$ of the test solution was added and a cotton wool plug moistened with aqueous AgNO$_3$ placed in the top of the test tube. A black spot of metallic Ag confirms the presence of As and Sb, due to the production of AsH$_3$ and SbH$_3$.

Elemental analyses of Carbon, Hydrogen and Nitrogen were performed by Butterworth Laboratories Ltd., Teddington, Middlesex, TW11 8LJ and Medac Ltd., Department of Chemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH. For this, small samples were sealed in glass tubes under vacuum, to prevent deterioration of the compounds while in transit.

Chloride was determined by the Volhard titration method described in Vogel. 330

Titanium was determined as the yellow peroxo species [TiO(SO$_4$)$_2$]$^{2-}$ obtained from aqueous solutions of Ti$^{III}$ and Ti$^{IV}$
in 2M sulphuric acid and 10% hydrogen peroxide. The colour intensity was measured at 410 nm and compared with a standard Ti(IV) sulphate calibration curve.

6.1. Experimental Section for Chapter 2

6.1.1: Reaction of \text{MgCl}_2 with \text{SbCl}_5 (I)

A solution of \text{MgCl}_2 (2.20g, 23.10mmol) in MeCN (70cm³) was obtained by direct Soxhlet extraction. This solution was chilled (0°C) and to it was added dropwise a solution of \text{SbCl}_5 (6.00cm³, 46.20mmol) in MeCN (30cm³). The resulting pale yellow solution was allowed to warm to room temperature and stirred for a further 24h under nitrogen. Removal of solvent in vacuo provided a white solid which was collected by filtration and washed with n-hexane (3 x 50cm³) then pumped dry for 1h (Yield 14.12g, 65.1%). The product was recrystallised from MeCN as colourless air-moisture sensitive crystals of diffraction quality. A structural determination was not performed as neither cation nor anion structures are novel species.

6.6.2: Reaction of \text{SnCl}_2 with \text{SbCl}_5 (II)

A solution of \text{SbCl}_5 (5cm³, 38.45mmol) in MeCN (50cm³) was added dropwise to a chilled, stirred solution of \text{SnCl}_2 (3.64g, 19.2mmol). The resulting colourless solution was stirred for 24h at RT under N₂. Solvent removal in vacuo provided a white solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 3h (Yield 13.5g, 68%). Recrystallisation from MeCN gave very air-moisture sensitive colourless crystals. Attempts to mount these crystals in 0.25mm diameter Lindemann tubes failed due to their highly air-moisture sensitive nature; hydrolysis
occurred during manipulation of single crystals under sodium-dried nujol prior to their insertion into the Lindemann tube.

**6.1.3: Reaction of SnCl₄ with SbCl₅ (III)**

A solution of SbCl₅ (5.54 cm³, 42.67 mmol) in MeCN (50 cm³) was added dropwise to a chilled (0°C) and stirred solution of SnCl₄ (5.00 cm³, 42.72 mmol) in MeCN (50 cm³). The resulting pale yellow solution was allowed to warm to room temperature and stirred for a further 24h under nitrogen. Removal of solvent *in vacuo* gave an off-white solid which was collected by filtration. The resultant solid was washed with *n*-hexane (3 x 50 cm³) and pumped dry for 2h (Yield 17.92 g, 75%). The product was recrystallised from MeCN affording colourless needle crystals of diffraction quality. Attempts to mount a single crystal in a 0.25 mm diameter Lindemann tube under argon for diffraction purposes failed due to the highly air-moisture sensitive nature of the product.

**6.1.4: Reaction of SnCl₄ with 2SbCl₅ (IV)**

A solution of SbCl₅ (1.73 cm³, 13.3 mmol) in MeCN (50 cm³) was added dropwise to a chilled (0°C) and stirred solution of (III) (9.09 g, 13.3 mmol) in MeCN (100 cm³). The resulting pale yellow solution was allowed to warm to room temperature and stirred for a further 24h under nitrogen. Removal of solvent *in vacuo* gave an off-white solid which was collected by filtration. The resultant solid was washed with *n*-hexane (3 x 50 cm³) and pumped dry for 3h (Yield 9.5 g, 70%). Recrystallisation from MeCN gave very unstable colourless crystals of diffraction quality. Attempts to mount a single crystal in a 0.25 mm diameter Lindemann tube under argon for
diffraction purposes failed due to their extremely unstable nature.

6.1.5: Reaction of InCl₃ with SbCl₅ (V)

A solution of InCl₃ (1.15 g, 5.2 mmol) in MeCN (100 cm³) was obtained by direct Soxhlet extraction under N₂. This solution was allowed to cool to RT and chilled (0°C), to it a solution of SbCl₅ (0.67 cm³, 5.2 mmol) in MeCN (50 cm³) was added. The resulting pale yellow solution was allowed to warm to RT and stirred for a further 24 h. Solvent removal in vacuo gave a white solid which was collected by filtration, washed with n-hexane (3 x 50 cm³) and pumped dry for 2 h (Yield 2.66 g, 75%). Recrystallisation from MeCN gave colourless air-moisture sensitive crystals which were not of diffraction quality.

6.1.6: Reaction of InCl₃ with 2SbCl₅

A solution of InCl₃ (2.1 g, 9.49 mmol) in MeCN (100 cm³) was obtained by direct Soxhlet extraction under N₂. This solution was allowed to cool to RT and chilled (0°C). To it a solution of SbCl₅ (2.46 cm³, 18.98 mmol) in MeCN (50 cm³) was added. The resulting pale yellow solution was allowed to warm to RT and stirred for a further 24 h under N₂. Solvent removal in vacuo gave a white solid which was collected by filtration, washed with n-hexane (3 x 50 cm³) and pumped dry for 2 h (Yield 6.73 g, 52%; based on [In(MeCN)₆][SbCl₆]₃). m.p. 197-198°C. Recrystallisation from MeCN gave colourless air-moisture sensitive crystals which were not of diffraction quality.
6.1.7: Reaction of InCl$_3$ with 3SbCl$_5$ (VII)

A solution of InCl$_3$ (1.9g, 8.59mmol) in MeCN (100cm$^3$) was obtained by direct Soxhlet extraction under N$_2$. This solution was allowed to cool to RT and chilled(0°C). To it a solution of SbCl$_5$ (3.35cm$^3$, 25.7mmol) in MeCN (50cm$^3$) was added. The resulting pale yellow solution was allowed to warm to RT and stirred for a further 24h. Solvent removal in vacuo gave a white solid which was collected by filtration, washed with n-hexane (3 x 50cm$^3$) and pumped dry for 2h (Yield 8.4g, 71%). Recrystallisation from MeCN gave colourless air-moisture sensitive crystals which were not of diffraction quality.

6.1.8: Reaction of ScCl$_3$ with SbCl$_5$ (VIII)

A solution of SbCl$_5$ (5cm$^3$, 38.45mmol) in MeCN (100cm$^3$) was added dropwise to a chilled (0°C) and stirred solution of ScCl$_3$ (2.72g, 18mmol) in MeCN (100cm$^3$). The resulting pale yellow solution was allowed to warm to room temperature and stirred for a further 24h under nitrogen. Removal of solvent in vacuo gave an off-white oily product which was washed with n-hexane (4 x 50cm$^3$), left to stand overnight in n-hexane (100cm$^3$) and pumped dry for 3h to give a sticky white solid. Repeated washing with n-hexane and final drying in vacuo for 4h gave an extremely air-moisture sensitive product of low yield.

6.1.9: Reaction of YCl$_3$ with SbCl$_5$ (VIII)

A solution of SbCl$_5$ (5cm$^3$, 38.45mmol) in MeCN (100cm$^3$) was added dropwise to a chilled (0°C) cloudy solution of YCl$_3$ (3.18g, 16.3mmol) in MeCN (100cm$^3$). After approximately 3h the cloudy yellow solution became clear yellow and was allowed to stir for a further 24h under nitrogen at RT. Removal
of solvent in vacuo gave a white solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 3h (Yield 6.75g, 63%). This air-moisture sensitive solid could not be obtained as crystalline material.

6.1.10: Reaction of LaCl₃ with SbCl₅ (IX)

A solution of SbCl₅ (5cm³, 38.45mmol) in MeCN (100cm³) was added dropwise to a chilled (0°C) cloudy solution of LaCl₃ (4.36g, 17.8mmol) in MeCN (100cm³). The resulting cloudy yellow solution was allowed to stir under N₂, full dissolution of LaCl₃ occurred to give a clear yellow solution, which was allowed to stir for a further 24h under nitrogen at RT. Removal of solvent in vacuo gave a white solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 3h (Yield 8.1g, 65%). The resulting air-moisture sensitive solid could not be obtained as crystalline material using standard recrystallisation techniques.

Table 6.1.1 shows the data obtained for the series of complexes I-IX.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.p.(°C)</th>
<th>Analyses: % found (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mg\text{II}(\text{MeCN})\text{6}][\text{SbCl}_\text{6}]\text{2}</td>
<td>White</td>
<td>-</td>
<td>C: 15.33, H: 1.91, N: 8.92, Cl: 45.50, Sb: 25.92</td>
</tr>
<tr>
<td>(I)</td>
<td>(15.34)</td>
<td>(1.93)</td>
<td>(8.95)</td>
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<td>115-118</td>
<td>13.07</td>
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<td>(II)</td>
<td>(13.93)</td>
<td>(1.74)</td>
<td>(8.12)</td>
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<tr>
<td>[Sn\text{IV}Cl_\text{3}(\text{MeCN})\text{3}][\text{SbCl}_\text{6}]</td>
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<td>74-76</td>
<td>11.8</td>
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<tr>
<td>(III)</td>
<td>(10.6)</td>
<td>(1.3)</td>
<td>(6.2)</td>
</tr>
<tr>
<td>[SnCl_\text{2}(\text{MeCN})\text{4}][\text{SbCl}<em>\text{6}]</em>\text{2}\cdot\text{CH}_\text{3}CN</td>
<td>White</td>
<td>96-99</td>
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</tr>
<tr>
<td>(IV)</td>
<td>(11.28)</td>
<td>(1.41)</td>
<td>(6.58)</td>
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<tr>
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<td>167-168</td>
<td>13.96</td>
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<tr>
<td>(V)</td>
<td>(14.03)</td>
<td>(1.75)</td>
<td>(8.18)</td>
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<tr>
<td>[In(\text{MeCN})\text{6}][\text{SbCl}<em>\text{6}]</em>\text{3}</td>
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<td>196-197</td>
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<td>(VI)</td>
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<td>(1.31)</td>
<td>(6.15)</td>
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<td>180-185</td>
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<td>(VII)</td>
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<td>(1.95)</td>
<td>(9.11)</td>
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<td>229-231</td>
<td>18.19</td>
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<td>(2.29)</td>
<td>(10.69)</td>
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<td>[LaCl_\text{2}(\text{MeCN})\text{4}][\text{SbCl}_\text{6}]</td>
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<td>198-200</td>
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<td>(IX)</td>
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<td>(1.7)</td>
<td>(7.9)</td>
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<td>Compound</td>
<td>$\delta_{\text{Sb}NMR}$ (ppm)</td>
<td>$W_{1/2}$ (Hz)</td>
<td>Electronic $\lambda_{\text{max}}$ (cm$^{-1}$)</td>
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<td>37 037</td>
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<td>45 662</td>
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<td>171</td>
<td>36 900</td>
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<td>-0.15</td>
<td>162</td>
<td>36 900</td>
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<td>37 037</td>
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<tr>
<td>VII</td>
<td>-0.54</td>
<td>192</td>
<td>37 037</td>
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<tr>
<td>VIII</td>
<td>-0.55</td>
<td>192</td>
<td>37 037</td>
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<tr>
<td>IX</td>
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<td>287</td>
<td>37 037</td>
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</tr>
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</table>
Several attempts were made to isolate Ti(III) and Ti(IV) hexachloroantimonate salts as follows:

6.1.11: Reaction of TiCl₃ with SbCl₅ (X)

A solution of TiCl₃ (2.69 g, 17.4 mmol) in MeCN (70 cm³) was obtained by direct Soxhlet extraction. The resultant deep blue solution was allowed to cool to room temperature, then chilled (0°C), a small portion was removed for analytical purposes. TiCl₃·3MeCN m.p. 137-138°C. Found: Ti, 17.36%; C₆H₉N₉Cl₃Ti calc Ti, 17.27; vₘₐₓ (CN) 2325 and 2292 cm⁻¹ (lit., 2305 and 2280 cm⁻¹); λₘₚₓ (MeCN) 14 705 and 17 182 cm⁻¹ (lit., 257 14 700(sh) and 17 200 cm⁻¹). To the remaining chilled solution a solution of SbCl₅ (2.26 cm³, 17.4 mmol) in MeCN (30 cm³) was added dropwise. Upon addition of SbCl₅ the solution changed from a deep blue to a green colour. The resulting solution was allowed to warm to room temperature and stirred for a further 3 h. Removal of solvent in vacuo provided a green solid which was collected by filtration. The resultant solid was washed with benzene (3 × 50 cm³) and then n-hexane (3 × 50 cm³) and pumped dry for 2 h. (Yield 6.44 g, 60%). The product was recrystallised from MeCN affording very air-moisture sensitive green crystals, m.p. 85-87°C. Found: C, 15.88; H, 2.34; N, 5.90; Cl, 46.14; Ti, 7.41%. C₈H₁₂N₄Cl₈TiSb requires C, 15.55; H, 1.94; N, 9.07; Cl, 45.94; Ti, 7.75%; vₘₐₓ (CN) 2320, 2290, and 2250 cm⁻¹; vₘₐₓ (M-Cl) 422 s, sh, 342 vs, br, 275 w; λₘₐₓ (MeCN) 36 900, 20 000 and 15 384 cm⁻¹.

6.1.12: Reaction of TiCl₄ with excess SbCl₅ (XL)

A solution of SbCl₅ (3.0 cm³, 23.1 mmol) in MeCN (50 cm³) was added dropwise to a chilled, stirred solution of TiCl₄ (2.51 cm³, 22.8 mmol). The resultant yellow solution was stirred
for 24 h at room temperature, solvent removal in vacuo provided a bright yellow solid which was collected by filtration and pumped dry for 3 h. Recrystallisation from MeCN yielded bright yellow crystals, m.p 96-97°C (lit., 95-96°C).

A solution of [TiCl₃(MeCN)₃][SbCl₆] (10.2 g, 16.6 mmol) in MeCN (50 cm³) was added dropwise to a chilled, stirred solution of SbCl₅ (3.9 cm³, 30 mmol) in MeCN (50 cm³). The resultant orange-yellow solution was allowed to warm to room temperature and stirred for a further 24 h. Solvent removal in vacuo provided a yellow solid which was collected by filtration. The solid was washed with n-hexane (3 x 50 cm³) and pumped dry for 3 h (Yield 8.7 g, 55%). M.p. 88-90°C (Found: C, 10.4; H, 1.5; N, 5.8; Cl, 51.8; Ti, 4.8; Sb, 25.1%. C₈H₁₂N₄Cl₁₄TiSb₂ requires C, 10.8; H, 1.3; N, 5.9; Cl, 52.1; Ti, 5.0; Sb, 25.5%). νmax. (CN) 2322 and 2295 cm⁻¹; νmax. (M-Cl) 432 vs, 412 w, 375 sh, 352 sh, and 344 vs br; δSb(MeCN)-0.48 (s, SbCl₆⁻) W 1/2, 177; λmax (MeCN) 37 453 cm⁻¹. Recrystallisation from MeCN afforded yellow crystals, structural determination of which gave [TiCl₃(MeCN)₃][SbCl₆].CH₃CN and a mass of green crystals of poor quality. m.p. 84-86°C; νmax(CN) 2320, 2292 and 2252 cm⁻¹; νmax (M-Cl) 424 s,sh, 400 w, and 340 vs,br cm⁻¹; λmax (MeCN) 37 037 and 14 705 cm⁻¹.
6.2. Experimental Section For Chapter 3

6.2.1. 2MgCl₂₄BiCl₃₁₂MeCN (XII)

An intimate mixture of BiCl₃ (19.55g, 61.7mmol) and MgCl₂ (3.0g, 31.7mmol) was extracted with hot MeCN (150cm³) using standard Soxhlet apparatus under nitrogen. The resulting clear colourless solution was concentrated to half its volume and placed in a refrigerator overnight, whereupon colourless needle crystals of the title compound separated. These were filtered and washed with n-hexane (2 x 25cm³). Yield (19.4g, 64.8%).

6.2.2. 3MgCl₂₄BiCl₃₁₈MeCN (XIII)

An intimate mixture of BiCl₃ (3.6g, 11.6mmol) and MgCl₂ (0.8g, 8.7mmol) was extracted with hot MeCN (150cm³) using standard Soxhlet apparatus under nitrogen. Removal of approximately half the solvent in vacuo gave a colourless clear solution, which was placed in a refrigerator overnight. This provided a matte of colourless fibrous crystals of the title compound. These were filtered, washed with n-hexane (2 x 25cm³) and dried by pumping in vacuo at room temperature for 2h. Yield (4.1g, 62.2%) Table 6.2.1 shows the spectroscopic and analytical data obtained for these complexes.
### Table 6.2.1. Analytical and Principal Spectroscopic Data for (XII) and (XIII)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(XII)</th>
<th>(XIII)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>m.p. (°C)</td>
<td>127-128</td>
<td>decomp (&gt;208)</td>
</tr>
<tr>
<td>Analyses (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C, H, N, Bi</td>
<td>14.7, 1.9, 8.6, 42.1</td>
<td>19.1, 2.8, 10.6, 35.4</td>
</tr>
<tr>
<td>found (calc)</td>
<td>(14.8)(1.9)(8.6)(42.9)</td>
<td>(18.9)(2.4)(11.0)(36.5)</td>
</tr>
<tr>
<td>Electronic</td>
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<td></td>
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<tr>
<td>$\lambda_{max}$ (cm$^{-1}$)</td>
<td>30 959</td>
<td>48 500 (sh)</td>
</tr>
<tr>
<td></td>
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<td>43 600 (sh)</td>
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<td></td>
<td></td>
<td>31 055</td>
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<tr>
<td>Infra-red</td>
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<td></td>
</tr>
<tr>
<td>$\nu$(CN) cm$^{-1}$</td>
<td>2322</td>
<td>2320</td>
</tr>
<tr>
<td></td>
<td>2290</td>
<td>2289</td>
</tr>
<tr>
<td>[450-200] cm$^{-1}$</td>
<td>405 vs</td>
<td>401 vs</td>
</tr>
<tr>
<td></td>
<td>340-350 vs, br</td>
<td>335-345 s, br</td>
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<tr>
<td></td>
<td>276 m</td>
<td>273 (sh)</td>
</tr>
<tr>
<td></td>
<td>250-255 s, br</td>
<td>230-240 s, br</td>
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<tr>
<td>Conductivity</td>
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<td></td>
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<tr>
<td>$\lambda_m$ (S cm$^{-2}$ mol$^{-1}$)</td>
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<td>251.8</td>
</tr>
</tbody>
</table>
6.2.3. Reaction of other Stoichiometric Ratios of MgCl₂ with BiCl₃

Intimate mixtures of BiCl₃ and MgCl₂ in varying molar ratios were extracted with hot MeCN (150cm³) using standard Soxhlet apparatus under nitrogen, as before. The following stoichiometric ratios of MgCl₂: BiCl₃ were used (1:4, 1:3, 2:3, and 1:1) in the Soxhlet filter stick. In reactions where a large excess of BiCl₃ was used i.e. 1:4, and 1:3 unreacted BiCl₃ was left on the sides of the Soxhlet flask. The remaining colourless solution was decanted and reduced to approximately half its volume in vacuo and placed in a refrigerator overnight, whereupon colourless crystals separated. These were filtered, washed with n-hexane (2 x 25cm³) and dried by pumping in vacuo at room temperature for 2h. (50-55% yields were obtained).

6.2.4. BiCl₃SbCl₄MeCN (XIV)

SbCl₅ (1.26cm³, 9.6mmol) in MeCN (20cm³) was added dropwise to an ice-cold solution of BiCl₃ (30g, 9.6mmol) in MeCN (50cm³). The resulting pale yellow solution was stirred at room temperature for 12h. Removal of solvent in vacuo provided a white solid which was collected by filtration, washed with n-hexane (2 x 25cm³) and pumped dry for 1h. The white solid was recrystallised from MeCN/CH₂Cl₂ as colourless crystals of poor definition (Yield 6.11g, 81.3%). See Table 6.2.2.

6.2.5. BiCl₃ 3SbCl₄ 8MeCN (XV)

SbCl₅ (1.85cm³, 14.7 mmol) in MeCN (30cm³) was added dropwise to an ice-cold stirred solution of BiCl₃ (1.5g, 4.75mmol) in MeCN (50cm³). The resulting pale yellow solution was stirred at room temperature for 12h. Removal of
solvent \textit{in vacuo} provided a white solid which was collected by filtration, washed with \textit{n}-hexane (3 x 25cm$^3$) and pumped dry for 3h. The white solid was recrystallised from MeCN as colourless crystals of poor definition (Yield 5.26g, 72%).

<table>
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<tr>
<th>Complex</th>
<th>(XIV)</th>
<th>(XV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
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<td>White</td>
</tr>
<tr>
<td>m.p. (°C)</td>
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<td>134-136</td>
</tr>
<tr>
<td>C, H, N, Sb, Bi found(calc)</td>
<td>(12.3) (1.5) (7.2) (15.7) (16.8)</td>
<td>(12.4, 1.6, 7.2, 23.7, 13.5)</td>
</tr>
</tbody>
</table>

| 121Sb NMR |
|-----------|-------|------|
| δ(ppm), $\Delta$ (Hz) | 0.05 182 | -0.16 190.5 |
| Electronic | 44250, 37037, | 44843, 35714 |
| $\lambda_{max}$ (cm$^{-1}$) | 31545 (sh) | |

<table>
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<tr>
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<tr>
<td>[450-200] cm$^{-1}$</td>
</tr>
<tr>
<td>Conductivity</td>
</tr>
<tr>
<td>$\Lambda_0$ (Scm$^2$mol$^{-1}$)</td>
</tr>
</tbody>
</table>
6.2.6. Reaction of TiCl₄ with BiCl₃ in MeCN (XVI)

TiCl₄ (2 cm³, 18.2 mmol) in MeCN (50 cm³) was added dropwise to an ice-cold solution of BiCl₃ (5.8 g, 18.2 mmol) in MeCN (100 cm³). The resulting bright yellow solution was stirred at room temperature for 24 h under nitrogen. Removal of solvent in vacuo provided a bright yellow solid which was collected by filtration, washed with n-hexane (3 x 25 cm³) and pumped dry for 2 h. Yield (7.9 g, 62%) (Found: C, 16.41; H, 2.13; N, 9.41; Ti, 7.8; Bi, 29.1%; C₁₀H₁₅N₅Cl₇BiTi requires C, 16.9; H, 2.1; N, 9.85; Ti, 7.62; Bi, 29.43%); \( \nu_{\text{max}} \) 2305, 2300, 2295, 2290 (MeCN), 385 vs, br, 320 and 280, m, br cm⁻¹ (Nujol); \( \lambda_{\text{max}} \) (MeCN), 40 000 and 30 769 cm⁻¹. The yellow solid was recrystallised from MeCN as yellow crystals, m.p. 158-160°C (Found: Ti, 17.2; Cl, 52.8%; calc. for C₄H₆N₂TiCl₄; Ti, 17.6; Cl, 52.19); \( \lambda_{\text{max}} \) (MeCN), 45 662, 39 682, and 33 557 cm⁻¹; \( \nu_{\text{max}} \) 2310, 2300, 2290, 2280 (MeCN), 380 vs, br, 315 m, 270 m, br cm⁻¹ (Nujol).

6.2.7. Reaction of TiCl₃ with BiCl₃ in acetonitrile (XVII)

A solution of TiCl₃ (1.93 g, 12.5 mmol) in MeCN (50 cm³) was obtained by Soxhlet extraction, and added dropwise to an ice-cold solution of BiCl₃ (395 g, 12.5 mmol) in MeCN (100 cm³). The resulting purple solution was stirred at room temperature for 24 h under nitrogen. Solvent removal in vacuo provided a light purple solid which was collected by filtration, washed with n-hexane (3 x 25 cm³) and pumped dry for 3 h. Crystalline material could not be obtained. (Yield 5.1 g, 65%) m.p. 99-102°C. (Found: C, 15.9; H, 2.2; N, 9.0; Ti, 7.4; Bi, 32.3%; C₄H₁₂N₄Cl₆BiTi requires C, 15.15; H, 1.90; N, 8.83; Ti, 7.55; Bi, 32.9%). \( \nu_{\text{max}} \) 2305, 2290 (MeCN), 420 s, sh, 390 s, sh, 330 s, sh.
and 270m, br cm\(^{-1}\) (Nujol); \(\lambda_{\text{max}}\) (MeCN) 31 515 and 17 029 cm\(^{-1}\).

**6.2.8. Reaction of VCl\(_3\) with BiCl\(_3\) in MeCN (XVIII)**

A solution of VCl\(_3\) (3g, 19.1mmol) in MeCN (50cm\(^3\)) was added dropwise to an ice-cold solution of BiCl\(_3\) (6.0g, 19.1mmol) in MeCN (100cm\(^3\)). The resulting purple solution was stirred at room temperature for 24h under nitrogen. Solvent removal in vacuo provided a purple solid which was collected by filtration, washed with n-hexane (3 x 25cm\(^3\)) and pumped dry for 3h. The purple solid could not be obtained as crystalline material (Yield 7g, 58%) m.p. 130°C (decomp). (Found: C, 13.9; N, 1.93; N, 8.0; Bi, 32.12%; \(\text{CgH}_{12}\text{N}_{4}\text{Cl}_{6}\text{BiV}\) requires C, 15.0; H, 1.9; N, 8.7; Bi, 32.8%). \(\nu_{\text{max}}\) 2320, 2290, 2245 (MeCN), 435m, sh, 415w, 378m, sh, 355w, 330w, 285w, 260m, br cm\(^{-1}\) (Nujol); \(\lambda_{\text{max}}\) (MeCN) 31 017, 20 391 and 17 857 (sh) cm\(^{-1}\).

**6.2.9. Reaction of CrCl\(_3\) with BiCl\(_3\) in MeCN (XIX)**

A solution of CrCl\(_3\) (2g, 12.62mmol) in MeCN (50cm\(^3\)) was added dropwise to an ice-cold solution of BiCl\(_3\) (4g, 12.68 mmol) in MeCN (100cm\(^3\)). The resulting solution was stirred at room temperature for 24h under nitrogen. Solvent removal in vacuo provided a grey-purple coloured solid which was collected by filtration, washed with n-hexane (3 x 25cm\(^3\)) and pumped dry for 3h. Crystalline material could not be obtained. (Yield 5.6g, 65.4%) m.p. 90-92°C. (Found: C, 17.4; H, 2.29; N, 9.5; Bi, 31.5%; \(\text{C}_{10}\text{H}_{12}\text{N}_{5}\text{Cl}_{6}\text{BiCr}\) requires C, 17.6; H, 2.21; N, 10.3; Bi, 30.8%). \(\nu_{\text{max}}\) 2315, 2300, 2260 (MeCN) 440 m, sh, 420 m, sh.
6.2.10. Reaction of FeCl₃ with BiCl₃ in MeCN (XX)

A red-orange solution of FeCl₃ (3.35g, 20.6mmol) in MeCN (50cm³) was obtained by Soxhlet extraction under nitrogen and added dropwise to an ice-cold solution of BiCl₃ (6.51g, 20.6mmol) in MeCN (100cm³). This became a red-brown colour which was stirred at room temperature for 24h under nitrogen. Solvent removal in vacuo provided an orange coloured solid, which was collected by filtration, washed with n-hexane (3 x 25cm³) and pumped dry for 3h. Crystalline material could not be obtained. (Yield 8.9g, 67.3%) m.p. 54-56°C. (Found: C, 10.61; H, 1.49; N, 6.02, Bi, 33.1%; C₈H₁₂N₄Cl₆BiFe requires C, 14.9; H, 1.87; N, 8.72; Bi, 32.5%). \( \nu_{\text{max}} \) 2305, 2290, 2260 (MeCN) 385vs, br, 280m, br, 250 m, br cm⁻¹ (Nujol); \( \lambda_{\text{max}} \) (MeCN) 47 778, 41 946, 35 087(sh), 32 154 and 28 011 cm⁻¹.

6.2.11. Reaction of SnCl₄ with BiCl₃ in MeCN (XXI)

A solution of SnCl₄ (2cm³, 17.1mmol) in MeCN (50cm³) was added dropwise to an ice-cold solution of BiCl₃ (5.4g, 17.1mmol) in MeCN (100cm³). The resulting colourless solution was stirred at room temperature for 24h under nitrogen. Solvent removal in vacuo provided a white solid, which was collected by filtration, washed with n-hexane (3 x 25cm³) and pumped dry for 3h (Yield 8.6g, 68%). (Found: C, 12.52; H, 1.6; N, 7.25; Bi, 28.4%; C₈H₁₂N₄Cl₇BiSn requires C, 12.97; H, 1.62; N, 7.56; Bi, 28.27%); \( \nu_{\text{max}} \) 2310, 2280 (MeCN) 410w, 400w, 395w, 365m, 340s, br, 305m, 250m cm⁻¹ (Nujol); \( \lambda_{\text{max}} \) (MeCN) 34 722, 31 347 cm⁻¹. The white solid was recrystallised from MeCN affording colourless crystals, m.p. 95-97°C; \( \nu_{\text{max}} \) 2310, 2285
6.3. Experimental Section for Chapter 4

6.3.1: Oxidation of As(III) to As(V)

6.3.1.1: Me₄NCl Reaction (XXII)

Me₄NCl (5.28 g, 48.23 mmol) and AsCl₃ (4.1 cm³, 48.9 mmol) were dissolved in MeCN (300 cm³) and the solution chilled to 0°C. Chlorine gas was passed into the colourless solution until it became saturated with the gas and turned orange. The Me₄NCl dissolved fully in MeCN to give an orange solution. Cl₂ was periodically passed into the solution to maintain a saturated environment, which was then stirred for 24 h under N₂ at RT. Removal of solvent and excess Cl₂ in vacuo gave a yellow coloured solid which was collected by filtration, washed with n-hexane (3 x 50 cm³) and pumped dry rapidly. Recrystallization from MeCN gave a semi-crystalline yellow solid (Yield 12 g, 69%) m.p. 230-233°C with decomposition. (Found: Cl, 59.12; As, 20.42%; C₄H₁₂NCl₆As requires Cl, 58.82; As, 20.71%); ν max 387 m, sh and 350 vs, br cm⁻¹ (Nujol); λ max (MeCN) 38 759, 37 453 (sh) and 36 900 cm⁻¹; λₐₘ 99.14 Scm²mol⁻¹ at 25.0 ± 0.1°C in DMF solution.

6.3.1.2: MgCl₂ Reaction (XXIII)

Chlorine gas was passed into a chilled (0°C) solution of AsCl₃ (11.45 cm³, 136.7 mmol) in MeCN (200 cm³) until the solution became saturated with gas. A solution of MgCl₂ (6.51 g, 68.36 mmol) in MeCN (100 cm³) was obtained by direct Soxhlet extraction, then added dropwise under N₂ to the chlorine saturated solution of AsCl₃ in MeCN. Immediate precipitation of
a yellow-orange coloured solid occurred. Chlorine gas was periodically passed into the orange solution, which was allowed to warm to RT and stirred for a further 24h under N₂. Removal of solvent and excess Cl₂ in vacuo gave a pale yellow coloured solid, which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry rapidly. Recrystallization from MeCN gave a semi-crystalline material (Yield 40g, 69%) m.p. 66-68°C. (Found: Cl, 51.1; As, 17.93%; C₁₂H₁₈N₆Cl₂As₂ requires Cl, 50.312; As, 17.72%); v_{max} 2316, 2286 (MeCN), 406m (CCN), 385s, sh and 345vs, br cm⁻¹ (MCl) Nujol; λ_{max} 36764, 37453(sh) and 38759cm⁻¹; A_m=157.67 Scm²mol⁻¹ at 25 ± 0.1°C in DMF solution.

6.3.1.3: ZnCl₂ Reaction (XXIV)

Chlorine gas was passed into a chilled (0°C) solution of AsCl₃ (10.12cm³, 120.7mmol) in MeCN (200cm³) until the solution became saturated with gas. To this a solution of ZnCl₂ (8.23g, 60.3mmol) in MeCN (50cm³) was added dropwise under N₂. Chlorine gas was periodically passed into the resulting yellow solution to maintain a level of saturation, which was then allowed to warm to room temperature and stirred for a further 24h under N₂. Solvent removal in vacuo afforded a white solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry rapidly. The white solid was not obtained as crystalline material. (Yield 9.21g, 70%). m.p. 95-98°C. (Found: Cl, 32.51%; C₄H₆N₂Cl₂Zn requires Cl, 32.48%); v_{max} 2316, 2284 (MeCN), 402m, sh (CCN), 383m, 347s, br, 310s, br and 245m, br cm⁻¹ (MCl).
6.3.1.4: TiCl₄ Reaction (XXV)

Chlorine gas was passed into a chilled (0°C) solution of AsCl₃ (3.82cm³, 45.6mmol) in MeCN (200cm³) until the solution became saturated with gas. To this a solution of TiCl₄ (5.0cm³, 45.6mmol) in MeCN (100cm³) was added dropwise under N₂. Chlorine gas was periodically passed into the resulting bright orange solution to maintain a level of saturation, which was then allowed to warm to room temperature and stirred for a further 24h under N₂. Solvent removal in vacuo afforded a bright yellow solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry rapidly. Recrystallization from MeCN afforded bright yellow crystals (Yield 7.4g, 60%). m.p. 150-152°C. (Found: Cl, 52.61%; Ti, 17.81%; C₄H₆N₂Cl₄Ti requires Cl, 52.19%; Ti 17.62%); ν₅ax 2310, 2300, 2280 and 2270 cm⁻¹(MeCN), 410m, 380vs, br, and 315m,sh cm⁻¹ (Nujol); λ₅ax(MeCN) 44 444, 37 037 and 32 679 cm⁻¹.

6.3.1.5: SnCl₄ Reaction (XXVI)

Chlorine gas was passed into a chilled (0°C) solution of AsCl₃ (3.6cm³, 42.9mmol) in MeCN (200cm³) until the solution became saturated with gas. To this a solution of SnCl₄ (5.0cm³, 42.7mmol) in MeCN (50cm³) was added dropwise under N₂. The resulting colourless solution was periodically saturated with Cl₂ to give an orange coloured solution, which was then allowed to warm to room temperature and stirred for a further 24h under N₂. Solvent removal in vacuo afforded a white solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry rapidly. Recrystallization from MeCN afforded colourless crystals (Yield 8g, 55%). m.p. 110-112°C.(Lit,²⁹ 112-114°C). (Found: Cl, 41.7%; C₄H₆N₂Cl₄Sn
6.3.2: Sb(III) as a Lewis Acid

6.3.2.1: Reaction of TiCl₄ with SbCl₃ (XXVII)

A solution of sublimed SbCl₃ (3.6g, 24.6mmol) in MeCN (100cm³) was added dropwise to an ice-cold solution of TiCl₄ (1.35cm³, 12.3mmol) in MeCN (100cm³). The resultant bright yellow solution was allowed to warm to room temperature and stirred for a further 24h under N₂. Solvent removal in vacuo afforded a bright yellow solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 2h. (Yield 11.03g, 72%; based on TiCl₄·SbCl₃·5MeCN). (Found: Ti, 7.62; Sb, 19.77; Cl, 39.2%; C₁₀H₁₅N₅Cl₇TiSb requires Ti, 7.68; Sb, 19.55; Cl, 39.84%); vmax 2310, 2300, 2280 and 2270 (MeCN), 420vw, 402vw, 378vs,br, 352m,br, 316vs,br cm⁻¹ (Nujol); λmax(MeCN) 45 871 and 38 610 cm⁻¹. Recrystallization from MeCN gave bright yellow crystals m.p. 158-160°C. (Found: Ti, 17.51; Cl, 51.95%; C₄H₆N₂Cl₄Ti requires Ti, 17.62; Cl, 52.19%); vmax 2310, 2300, 2280, 2280 (MeCN), 378vs,br, 316s,br cm⁻¹ (Nujol); λmax(MeCN) 45 871 and 38 610 cm⁻¹.

6.3.2.2: Reaction of TiCl₃ with SbCl₃ (XXVIII)

A solution of TiCl₃ (4.76g, 30.85mmol) in MeCN (100cm³) was obtained by direct Soxhlet extraction. The resulting deep blue solution was filtered and allowed to cool to RT. This solution was chilled (0°C) and to it was added a solution of sublimed SbCl₃ (14.07g, 61.6mmol) in MeCN (100cm³). The resulting purple coloured solution was allowed to warm to RT and stirred for a further 24h under N₂. Solvent removal in vacuo afforded a purple solid which was collected by filtration,
washed with n-hexane (3 x 50cm$^3$) and pumped dry for 2h. (Yield 13.56g, 70%; based on TiCl$_3$.SbCl$_3$.6MeCN), m.p. 52-54°C. Crystalline material could not be obtained. (Found: Ti, 7.03; Sb, 19.51; Cl, 33.29%; C$_{12}$H$_{18}$N$_6$Cl$_6$TiSb requires Ti, 7.61; Sb 19.37; Cl, 33.85%); $\nu_{\text{max}}$ 2310, 2282 (MeCN), 409s,sh, 375s,br, 344w, 323s,br and 308w cm$^{-1}$ (Nujol); $\lambda_{\text{max}}$(MeCN) 46 728, 40 485, 30 959, 20 080(sh) and 17 182 cm$^{-1}$.

6.3.2.3; Reaction of FeCl$_3$ with SbCl$_3$ (XXIX)

A solution of FeCl$_3$ (3.25g, 20.05mmol) in MeCN (100cm$^3$) was obtained by direct Soxhlet extraction. The resulting deep red solution was filtered and allowed to cool to RT. This solution was chilled (0°C) and to it was added a solution of sublimed SbCl$_3$ (4.87g, 21.3mmol) in MeCN (50cm$^3$). The resulting orange-red coloured solution became bright orange within minutes, continued stirring at RT under N$_2$ allowed observation of a further colour change to that of bright yellow. Solvent removal in vacuo afforded a yellow-orange coloured solid which was collected by filtration, washed with n-hexane (3 x 50cm$^3$) and pumped dry for 2h. The solid was washed with benzene (3 x 50cm$^3$) to remove further impurities, n-hexane (3 x 50cm$^3$) and pumped dry for 2h. (Yield 7.22g, 65%; based on FeCl$_3$.SbCl$_3$.4MeCN) m.p. 90-92°C. (Found: C, 17.12; H, 2.55; N, 10.75; Cl, 38.57; Sb, 21.25%; C$_8$H$_{12}$N$_4$Cl$_6$SbFe requires C, 17.31; H, 2.16; N, 10.10; Cl, 38.37; Sb, 21.96%); $\nu_{\text{max}}$ 2320, 2295 (MeCN), 378vs,br, 350m and 250m,br cm$^{-1}$ (Nujol); $\lambda_{\text{max}}$(MeCN) 41 841, 37 313(sh), 32 051 and 27 700 cm$^{-1}$.

6.3.2.4; Reaction of InCl$_3$ with SbCl$_3$ (XXX)

A solution of InCl$_3$ (1.54g, 6.94mmol) in MeCN (100cm$^3$) was obtained by direct Soxhlet extraction. The solution was
filtered and allowed to cool to RT and was chilled (0°C). To it a solution of sublimed SbCl₃ (4.2g, 18.4mmol) in MeCN (50cm³) was added dropwise. The resulting cloudy white solution was allowed to warm to RT and stirred for a further 24h under N₂. Solvent removal in vacuo afforded a white oily product which was pumped dry for 3h, washed with n-hexane (5 x 50cm³) and pumped dry for a further 3h to give a sticky white solid. (Yield 2.46g, 51%; based on InCl₃.SbCl₃.6MeCN). (Found: Cl, 30.45; Sb, 17.39%; C₁₂H₁₈N₆Cl₆SbIn requires Cl, 30.59; Sb, 17.51%); νₘₐₓ 2312, 2284 (MeCN), 389m, sh, 312s, br, 290s, and 258s cm⁻¹; λₘₐₓ (MeCN) 39682 cm⁻¹.

6.3.2.5: Reaction of SnCl₄ with SbCl₃ (XXXI)

A solution of sublimed SbCl₃ (7.83g, 34.3mmol) in MeCN (50cm³) was added dropwise to an ice-cold solution of SnCl₄ (2.0cm³, 17.1mmol) in MeCN (100cm³). The resultant colourless solution was allowed to warm to room temperature and stirred for a further 24h under N₂. Solvent removal in vacuo afforded a white solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 2h. (Yield 15.46g, 65%; based on SnCl₄.SbCl₃.5MeCN). (Found: Sb, 17.5; Cl, 35.61%; C₁₀H₁₅N₃Cl₇SnSb requires Sb, 17.55; Cl, 35.77%); νₘₐₓ 2304, 2276 (MeCN), 408w, 392w, 360m, 334vs, br, 304m cm⁻¹ (Nujol). Recrystallization from MeCN gave colourless crystals, m.p. 92-94°C; (Found: Cl, 41.6%, C₄H₆N₂Cl₄Sn requires Cl, 41.40%); νₘₐₓ 2304, 2276 (MeCN); 392w, 360m, 334vs, br, 304m cm⁻¹ (Nujol). (Lit 259 νₘₐₓ 397w, 393w, 367s, 333-345vs, 305m cm⁻¹).

6.3.2.6: Reaction of SbCl₅ with SbCl₃ (XXXII)

A solution of sublimed SbCl₅ (11.72g, 51.37mmol) in MeCN (50cm³) was added dropwise to an ice-cold solution of
SbCl₅ (6.7 cm³, 51.5 mmol) in MeCN (100 cm³). The resultant pale yellow solution was allowed to warm to room temperature and stirred for a further 24 h under N₂. Solvent removal in vacuo afforded a white solid which was collected by filtration, washed with n-hexane (3 x 50 cm³) and pumped dry for 2 h. (Yield 24.85 g, 70%; based on SbCl₅·SbCl₃·4MeCN). Extremely moisture sensitive colourless crystals were obtained from MeCN, but were not of diffraction quality, m.p. 140-142°C; (Found: Cl, 40.67; Sb, 34.76%; C₈H₁₂N₄Sb₂Cl₈ requires Cl, 41.03; Sb 35.23%); ν_max 2310, 2280 (MeCN), 346 vs, br, 290 w and 260 s, br cm⁻¹ (Nujol); λ_max (MeCN) 37313 and 46082 (sh) cm⁻¹; δ(¹²¹Sb)(MeCN)-0.17 (1 Sb, s, SbCl₁₂). W₁/₂=175 Hz.

6.3.2.7: Reaction of BiCl₃ with SbCl₅ (XXXIII)

A solution of BiCl₃ (6.58 g, 20.86 mmol) in MeCN (100 cm³) was obtained by direct Soxhlet extraction. The solution was allowed to cool to RT and was chilled (0°C). To this a solution of purified SbCl₅ (4.70 g, 20.60 mmol) in MeCN (50 cm³) was added dropwise, the resulting colourless solution was allowed to warm to RT and stirred for a further 24 h under N₂. Solvent removal in vacuo afforded a white solid, which was collected by filtration, washed with n-hexane (3 x 50 cm³) and pumped dry for 2 h. (Yield 9.88 g, 60%; based on BiCl₃·SbCl₅·6MeCN) m.p. 67-69°C. This product could not be obtained as crystalline material. (Found: Cl, 26.5; Sb, 14.91; Bi, 26.32%; C₁₂H₁₈N₆Cl₆BiSb requires Cl, 26.94; Sb, 15.4; Bi, 26.47%); ν_max 2300, 2260 (MeCN), 385 m, sh, 350 m, sh, 310 s, br, 280 s, br and 240 s, br; λ_max (MeCN) 45045 (sh), 24965 and 31847 (sh) cm⁻¹.
6.4.1. Experimental Section for Chapter 5.

6.4.1.1. TiCl₄ as a Lewis Acid.

Reaction of TiCl₄ with MgCl₂ in MeCN (XXXIV).

A solution of MgCl₂ (4.1g, 43.1mmol) in MeCN (150 cm³) was obtained by direct Soxhlet extraction under N₂, this was added dropwise to a chilled (0°C) stirred solution of TiCl₄ (4.8cm³, 43.7mmol) in MeCN. Immediate precipitation of a bright yellow solid occurred. The solution was allowed to warm to room temperature and stirred for a further 3h. Solvent removal in vacuo gave more yellow solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 2h. Recrystallisation from MeCN gave a mass of air-moisture sensitive bright yellow needle crystals (structural determination pending). (Yield 16g, 70%). m.p. 145-146°C. (Found: C, 28.79; H, 3.85; N, 15.93; Ti, 9.21%; C₁₂H₁₈N₆Cl₆TiMg requires C, 27.13; H, 3.42; N, 15.82; Ti, 9.02%). Flame test and Titan yellow test provide evidence for the presence of Mg. vₘₐₓ = 2304, 2276 (MeCN), 412 m, sh, 402 w and 330 vs, br cm⁻¹ (Nujol); λₘₐₓ (MeCN) 43 668 and 38 461 (sh) cm⁻¹. ηₐₘ = 73 Scm²mol⁻¹ at 10⁻²M at 25.0 ± 0.1°C (A₀=110.76 Scm²mol⁻¹).

6.4.2. Ti(IV) Cations

6.4.2.1. Reaction of [TiCl₃(MeCN)₃][SbCl₆] with Me₄NCl (XXXV)

A solution of [TiCl₃(MeCN)₃][SbCl₆] m.p.95-96°C (6.14g, 10mmol) in MeCN (100cm³) was added dropwise to a chilled (0°C), stirred suspension of vacuum dried Me₄NCl (1.05g, 9.82mmol) in MeCN (100cm³). The bright yellow suspension was allowed to warm to RT and left to stir for 24h under N₂. Full dissolution of Me₄NCl had occurred to give a clear bright yellow solution. Solvent removal in vacuo gave a bright yellow
solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 2h. Recrystallization from MeCN gave bright yellow air-sensitive crystals. m.p. 158-160°C; (Found: Ti, 17.45; Cl, 52.6%; C₄H₆N₂TiCl₄ requires Ti, 17.62; Cl, 52.19%); νₚₙₙ 2310, 2300, 2290, 2285 (MeCN), 385 vs, br and 315 w cm⁻¹ ν(TiCl); λₚₖₙ (MeCN) 45 248, 38 610 and 32 679 cm⁻¹. The mother liquor from this recrystallisation has λₚₖₙ 37 313 cm⁻¹; δₕₕ (CD₃CN) -0.1123 (1Sb, s, SbCl₆⁻) W 1/2. 172 Hz.

6.4.2.2 Reaction of [TiCl₃(MeCN)]₃[SbCl₆] with PPh₃ (XXXVI)

A solution of PPh₃ (1.53g, 5.83mmol) in MeCN (100cm³) was added dropwise to a chilled (0°C) solution of [TiCl₃(MeCN)]₃[SbCl₆] (3.6g, 5.83mmol) in MeCN (70cm³). The resulting yellow solution was allowed to warm to RT and stirred for 24h under N₂. Solvent removal in vacuo gave a yellow solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 2h.

6.4.2.3 Reaction of [TiCl₃(MeCN)]₃[SbCl₆] with PPh₃ (XXXVII)

A solution of PPh₃ (3.2g, 12.19mmol) in MeCN (100cm³) was added dropwise to a chilled (0°C) solution of [TiCl₃(MeCN)]₃[SbCl₆] (3.73g, 6.1mmol) in MeCN (100cm³). An orange coloured precipitate formed within minutes of addition of the phosphine. This suspension was allowed to warm to RT and stirred for 24h under N₂. Solvent removal in vacuo gave more orange solid which was collected by filtration, washed with n-hexane (3 x 50cm³) and pumped dry for 3h. Yield 62%. This air-sensitive solid was not obtained as crystalline material, its solubility in common organic solvents (and concentrated mineral acids) was extremely low. m.p. 209-210°C. (Found: Ti, 3.9%; C₅₄H₄₃Cl₉P₃TiSb requires Ti, 3.75%) spot test positive for
Sb; $\nu_{\text{max}}$ 1440 s, 1120 s, 1060 m, 995 m, sh, 750 m, sh, 730 s, sh, 690 m, sh, 537 s, sh, 455 w, sh, 437 m, sh, 360 w, 340 s, br and 280 m, br cm$^{-1}$ (Nujol); $\lambda_{\text{max}}$ (MeCN) 45 248, 39 062 and 36 764 cm$^{-1}$; $\delta_H$ ((CD$_3$)$_2$SO) 7.75 (45H, m, Ph); $\Delta m$=171.59 Scm$^2$mol$^{-1}$ at 10$^{-3}$M in DMSO solution.

6.4.2.4. Reaction of [TiCl$_3$(MeCN)$_3$][SbCl$_6$] with PPh$_3$ (XXXVIII)

A solution of PPh$_3$ (3.44g, 13.14mmol) in MeCN (100cm$^3$) was added dropwise to a chilled (0°C) solution of [TiCl$_3$(MeCN)$_3$][SbCl$_6$] (2.68g, 4.38mmol) in MeCN (100cm$^3$). An orange coloured precipitate formed within minutes of addition of the phosphine. This suspension was allowed to warm to RT and stirred for 24h under N$_2$. Solvent removal in vacuo gave more orange solid which was collected by filtration, washed with n-hexane (3 x 50cm$^3$) and pumped dry for 3h. (Yield 65%) m.p. 208-210°C. This air-sensitive solid was not obtained as crystalline material, its solubility in common organic solvents and concentrated acids was very low. (Found: Ti, 4.2%; C$_{54}$H$_{45}$Cl$_9$P$_3$TiSb requires Ti, 3.75%) spot test positive for Sb; $\nu_{\text{max}}$ 1435 s, 1120 s, 1050 s, 1020 m, 990 m, sh, 740 m, sh, 720 s, sh, 690 m, sh, 535 s, sh, 455 w, 435 m, sh, 360 w, 340 s, br and 280 m, br cm$^{-1}$ (Nujol); $\lambda_{\text{max}}$ (MeCN) 44 642, 38 314 and 36 764 cm$^{-1}$; $\delta_H$ ((CD$_3$)$_2$SO) 7.75 (45H, m, Ph); $^{31}$P{H} ((CD$_3$)$_2$SO) -0.4994 (3P, S P Ph$_3$); $\Delta m$=160.52 Scm$^2$mol$^{-1}$ at 10$^{-3}$M in DMSO solution.
APPENDIX 1
Appendix 1

Conductivity Measurements

Conductivity measurements were carried using a Philips PW 9527 digital conductivity meter with solutions contained in a glass apparatus having a side-arm attachment incorporating the Pt electrodes. The sample, from a previously accurately weighed ampoule, was placed into the vessel under N₂. The ampoule was then reweighed, and the accurate mass of the sample determined by difference. The whole cell was weighed. Dry MeCN was introduced from the distillation unit. In cases where DMF and DMSO were used previously purified dried solvent was placed into the vessel under N₂. The weight of solvent was determined by difference. Full dissolution of the sample was ensured, which was then thermostatted at 25.0 ± 0.1°C for 30 minutes before the conductivity was measured. Series of conductivity readings were taken at increasing concentrations by removal of the solvent in vacuo and repeating the above procedure. This allowed application of the Onsager Law.

Prior calibration of the cell was effected with aqueous 0.1 and 0.2M potassium chloride solutions. The cell constant was measured as 0.254 cm⁻¹ at 25.0 ± 0.1°C.

The most widely used expressions for comparison of electrolyte types are the equivalent and molar conductivity, \( \Lambda_e \) and \( \Lambda_m \) respectively. They are related to \( \kappa \), the specific conductivity of a solution by the following expressions:

\[
\Lambda_e = \kappa V_e \quad \text{and} \quad \Lambda_m = \kappa V_m
\]

\[
\Lambda_e = \kappa / c_e \quad \text{and} \quad \Lambda_m = \kappa / c_m
\]
\( V_e \) and \( V_m \) are the volumes (cm\(^3\)) containing one equivalent or mole of solute respectively. \( c_e \) and \( c_m \) are solute concentrations in equiv.cm\(^{-3}\) or mol.dm\(^{-3}\) respectively.

Rather than using a single value for calculation of \( \Lambda_m \) to determine the electrolyte type the Onsager Law was used by measuring the conductivity over a concentration range. For strong electrolytes the molar conductivity, \( \Lambda_m \) varies with concentration according to the Onsager equation: (This illustrates only a weak dependence on concentration)

\[
\Lambda_0 - \Lambda_m = (A + \omega B \Lambda_0) c^{1/2}
\]

The molar conductance, \( \Lambda_m \) was initially plotted against \( c^{1/2} \), the linear portion was extrapolated to zero concentration to obtain \( \Lambda_0 \) as intercept. \( (\Lambda_0 - \Lambda_m) \) was plotted against \( c^{1/2} \) to obtain a straight line of slope \( (A + \omega B \Lambda_0) \). This term necessarily directly reflects the electrolyte type of the complex as it depends upon the charges of the ions concerned, amongst other factors (for example, the dielectric constant of the solvent).

The use of equivalent concentration, \( c_e \) and equivalent conductance \( \Lambda_e \) has been common in conductivity studies. This is explained by Feltham and Hayter, \(^{331}\) who suggest that the equivalent weights of the complexes \([ML_4]X_2\) and \([M_2L_8]X_4\) are half the monomer weight. For complexes where the cations or anion does not enter into the coordination sphere of the complex the equivalent weight is independent of the molecular complexity \( z \) in solution. A single \( \Lambda_e \) determination cannot determine \( z \) in complexes \([ML_m]_z X_{y_2}\), or the charge type, but use of the Onsager Law by measurement of conductivity at
different concentrations differentiates between electrolyte types of ionized complexes.

In the complexes studied the molar weight has been used rather than the equivalent weight. Using the same example; the equivalent weight of \([ML_2]^2+(ClO_4)_2^-\) is 1/2 the formula weight, and the equivalent weight of \([M_2L_2]^{4+}(ClO_4)_4^-\) is \((2 \times \text{formula weight})/4\) or 1/2 the formula weight, assumptions are still made regarding the molecular complexity of the complexes in the use of equivalent weights. The use of the molar weight in these conductivity studies is appropriate. Further evidence for such molecular weight assumptions is based upon analytical figures obtained for the complexes, which reflects their electrolyte type.

Tabulated Data for Conductivity Measurements

Table A.1.1. \([Me(MeCN)_6][SbCl_4]_2\) (I)

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<th>(c \text{ (moldm}^{-3})</th>
<th>(c^{1/2} \text{ (moldm}^{-3})</th>
<th>(\kappa \text{ (mS cm}^{-1})</th>
<th>(A_m \text{ (Scm}^2\text{mol}^{-1})</th>
<th>(A_o-A_m \text{ (Scm}^2\text{mol}^{-1})</th>
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Table A.1.2. [Sn(MeCN)_6][ShCl_4]_2 (II)

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Table A.1.3. [SnCl_3(MeCN)_3][ShCl_4] (III)

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<th>A_0 - A_m (S cm^2 mol^{-1})</th>
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<td>$A_o-A_m$ (Scm$^2$mol$^{-1}$)</td>
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<td>------------------</td>
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Table A.I.6. [In(MeCN)$_6$][ShCl$_4$]$_3$ (VI)

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<th>$\lambda_0-\lambda_m$ (S cm$^2$ mol$^{-1}$)</th>
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Table A.I.7. [BiCl$_3$(MeCN)$_6$][ShCl$_4$] (XIV)

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<th>$\lambda_m$ (S cm$^2$ mol$^{-1}$)</th>
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### Table A.1.8. [BI(MeCN)₆][ShCl₆]₃ (XY)

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<th>A₀⁻Aₘ (S cm² mol⁻¹)</th>
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### Table A.1.9. [Mg(MeCN)₆]₃[Bi₄Cl₁₈] (XIII)

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<th>c (moldm⁻³)</th>
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<th>Aₘ (S cm² mol⁻¹)</th>
<th>A₀⁻Aₘ (S cm² mol⁻¹)</th>
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### Table A.1.10. SbCl₃,SbCl₅,4MeCN (XXXII)

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<th>Λ₀⁻Λ_m (S cm⁻² mol⁻¹)</th>
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### Table A.1.11. TiCl₄,MgCl₂,6MeCN (XXXIV)

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Appendix 2

Crystal Structure Determination of $\text{[Mg(MeCN)}_6\text{Bi}_2\text{Cl}_6\text{]}$ (XII)

The crystals were prepared as described previously. A crystal of approximate size $0.35 \times 0.25 \times 0.20\text{mm}$ was set up to rotate about the $\alpha$ axis on a Stoe Stadi2 diffractometer and data were collected via variable width $\omega$ scan. Background counts were for 20s and a scan rate of $0.0333^\circ\text{s}^{-1}$ was applied to a width of $(1.5 + \sin\theta/\tan\theta)$. 5200 independent reflections were measured of which 1635 with $I > 3\sigma(I)$ were used in subsequent refinement. No deterioration in the crystal was observed during the data collection. An empirical absorption correction was made. The structure was determined by direct methods. Hydrogen atoms on the methyl groups of several of the MeCN ligands could not be located either from a difference Fourier map or via refinement as a rigid group, and were therefore not included in the refinement. The Bi, Cl and Mg atoms were refined anisotropically and the N, C atoms isotropically. Data was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003 F^2]$. The final $R$ value was 0.067 ($R_w = 0.065$). Calculations were carried out using Shelx76 and some programs on the Amdahl 5870 at the University of Reading. In the final cycles of refinement, no shift/error ratio was greater than $0.1\sigma$. In the final difference Fourier maps, the maximum and minimum peaks were $1.65e\text{Å}^{-1}$ (located close to bismuth atoms), and $-1.35e\text{Å}^3$.

Crystal data and refinement details are given in Table A.2.1. Positional parameters are given in Table A.2.2, bond lengths and angles in Tables A.2.3 and A.2.4.
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Table A.2.3. Dimensions in the Anion Coordination Sphere
(Distances, Å; angles, degrees)

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REFERENCES


31) R.J.Gillespie and R.S.Nyholm, Quarterly Rev., 1957, 11, 368.
1987, 26, 2730.
84) J. Brunvoll, A. A. Ishchenko, I. N. Miakshin, G. V. Romanov, V. P. Spiridonov,
21, 423 and references cited therein.
171.


120)


133) H. Schmidbaur, R. Nowak, B. Huber and G. Muller, Organometallics, 1987, 6, 2266.


167) A.J. Edwards, personal communication.


313) P. Sobota, T. Plusinski and T. Lis, Polyhedron., 1984, 3, 45.


333) SHELX76 Package for Crystal Structure Determination, G.M. Sheldrick.

University of Cambridge, 1976.
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Author: Helen Collins

Institution and Date: University of Warwick, 1991

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