POLYANIONS OF THE HEAVY
GROUP 13, 14 AND 16 ELEMENTS
IN BASIC MEDIA

BY

© MAR BJÖRGVINSSON, B.Sc.

A Thesis
Submitted to the School of Graduate Studies
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for the Degree
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POLYANIONS OF THE HEAVY
GROUP 13, 14 AND 16 ELEMENTS
IN BASIC MEDIA
TO MY MOTHER

AND

IN THE MEMORY OF MY FATHER
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AUTHOR:  Már Björgvinsson, B.Sc.  (University of Iceland)  

SUPERVISOR:  Professor G. J. Schrobilgen  

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ABSTRACT

This Thesis describes the preparation and characterization of some classical and cluster main-group polyanions in solution by multinuclear magnetic resonance spectroscopy (multi-NMR) and in the solid state by X-ray crystallography.

A novel series of classical anions, Pb$_2$Ch$_3^{2-}$ (Ch = Se, Te) and M$_2$Se$_3^{2-}$ (M = Sn, Pb), have been characterized in solution and the detailed geometry of Pb$_2$Se$_3^{2-}$ and Pb$_2$Te$_3^{2-}$ obtained from the crystal structures of (2,2,2-crypt-$k^+$)$_2$ Pb$_2$Ch$_3^{2-}$ (Ch = Se or Te) as determined by X-ray crystallography. The anions were found to have a trigonal bipyramidal structure with the Pb and/or Sn atoms in the axial positions and the chalcogen atoms in the equatorial plane.

The Se$_n^{2-}$ and Te$_n^{2-}$ ($n = 1 - 4$) anions and the new chain-like heteropolychalcogenide anions, Te$_k$Se$_{2-k}^{2-}$ and Te$_p$Se$_4-p^{2-}$ and ($k = 1, 2$ and $p = 2, 3$) have been characterized in solution and their chemical exchange behavior directly observed by NMR spectroscopy. The structures of these anions can be rationalized on the principle that the more electronegative atom is positioned at the sites of highest electron density. Furthermore, the
large one-bond coupling constants observed for $\text{Ch}^\text{e}-\text{Ch}^\text{b}$ bonds indicate that the nature of these bonds are significantly different from those of $\text{Ch}^\text{b}-\text{Ch}^\text{b}$ bonds. The detailed geometry of the V-shaped TeSe$_2^{2-}$ ($C_{2v}$) and the pyramidal TeSe$_3^{2-}$ ($C_{3v}$) anions have been determined from the X-ray crystal structures of $(2,2,2\text{-crypt-K}^+)_2\text{TeSe}_n^{2-}\cdot\text{en}$ ($n = 2$, 3). In addition, the TeS$_m$Se$_3\cdot m^{2-}$ anions ($m = 0 - 3$), have been characterized in solution. A significant involvement of $\pi(d-p)$ bonds is evident in these species.

A new series of three-coordinated Sn(IV) telluride anions have been identified in solution by multi-NMR. The NMR data indicated the presence of polyanions consisting of linked trigonal planar SnTe$_3$-units in which each SnTe$_3$-unit is undergoing fast intramolecular "spinning" on the NMR time scale.

The extraction of K/Sn/Tl and K/Pb/Tl alloys in ethylenediamine and/or liquid ammonia gave rise to new polyatomic Tl-Sn and Tl-Pb cluster anions. The formation of the anions were found to be strongly dependent on the solvent used for the extraction and the presence of 2,2,2-crypt, as well as the alloy preparation method. The multi-NMR study indicated that the new Tl-Sn cluster anions were nonfluxional. The structures of two of the anions have been proposed, i.e., a bicapped square antiprism for Tl$_2$Sn$_8^{4-}$ and a coupled TlSn$_3$-tetrahedra for (Sn$_3$TlTlSn$_3$)$_4^{4-}$.
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CHAPTER 1
INTRODUCTION

(A) HISTORICAL BACKGROUND

In 1891 Joannis\(^1\) reported that certain main-group heavy metals reacted with alkali metal/liquid ammonia. Many of the species so formed were highly colored and soluble in liquid ammonia, but insoluble intermetallic phases precipitated out if excess alkali metal was used. Among the phases Joannis isolated and identified were Na\(_3\)Sb, NaPb and NaBi. Franklin and Kraus\(^2\) were the first to study the nature of the species formed in the liquid ammonia solutions when they measured the conductivity of the solutions at different temperatures. The conductivity-temperature curves they obtained were found to be similar to ordinary solutions of electrolytes suggesting the presence of ions in the ammonia solutions. Later, Kraus\(^3\) electrolyzed the green liquid ammonia solution of the sodium-lead alloy by passing an electric current between two lead electrodes immersed in the solution. He found that the amount of lead metal plated out on the anode equaled the amount that dissolved at the cathode, indicating the existence of a lead anion in solution. Furthermore, from the electrolysis Kraus found
that there was one equivalent of electricity per two atoms of lead and he therefore suggested that the ions Na\(^+\) and Pb\(_2\)\(^{2-}\) existed in solution. The early work of Kraus is significant in that it provided one of the first pieces of evidence for the formation of anions of relatively electropositive metals in a very basic environment, i.e., an alkali metal/liquid ammonia solution. In the following years Smyth,\(^4\) Peck,\(^5\) Kraus and Chiu\(^6\) and Bergstrom\(^7\) determined the ratio of the heavy metal to alkali metal more accurately for these species by electrolysis and/or solubility measurements of the heavy metals in alkali metal-ammonia solutions. The species which could be identified by these workers were Na\(_4\)Pb\(_9\), Na\(_3\)Sb\(_7\), Na\(_2\)Te\(_2\), Na\(_2\)Te\(_4\) and K\(_2\)Se\(_n\) (n = 1 - 5). The solutions of these species are therefore mainly electrolytes with the alkali metal element present as the cation and the more electronegative heavy metal element as a complex anion. The precise structures of these metal anions were not known, but Kraus\(^8\) suggested that they were complexes of the heavy metal atoms with the corresponding heavy metal anion of filled valence octet, i.e., the anions Pb\(^{4-}\), Sb\(^{3-}\) and Te\(^{2-}\) formed the complexes Pb\(^{4-}\)·Pb\(_8\), Sb\(^{3-}\)·Sb\(_6\), Te\(^{2-}\)·Te and Te\(^{2-}\)·Te\(_3\).

Among the major experimental difficulties associated with identifying these species were long alloy extraction times and, in some cases, unavoidable exposure of the solutions to atmospheric oxygen and moisture. For example,
the reaction between antimony and sodium metal in liquid ammonia took from several months to an entire year before the deep red colored solution of Na₃Sb₇ was obtained. The long reaction time led to the unavoidable reaction of the sodium metal with ammonia to form amide, thus making the determination of the M/Na ratio (M = heavy metal) difficult. In the course of their extensive studies on the polyanions of the heavy post-transition metals in the 1930's, Zintl and co-workers⁹ used mainly potentiometric titrations and conductivity measurements to identify the polyanions formed in liquid ammonia solution.

The apparatus Zintl and co-workers employed for their titrations is shown in Figure 1.1. A solution of sodium metal in liquid ammonia was titrated with the iodide or sulfide salts of the metals dissolved in liquid ammonia. If the sulfide or iodide was insoluble in ammonia then the sodium metal/liquid ammonia solution was used to titrate a suspension of metal sulfide or iodide in NaI-ammonia solution. At the beginning of each titration a small amount of the solution was drawn into the salt bridge, an evacuated cavity connected to the solution to be titrated by means of a capillary tube (Figure 1.1). The solution in the cavity thus served as a reference solution throughout the titration experiment. After adding a known amount of titrant to the test bulk solution, its stable potential was measured against
the reference electrode. A sudden change in the solution potential was taken as evidence for formation of a polyanion. From the inflection points in the potentiometric curve, the M/Na ratio could be determined considerably more accurately. Some of the species Zintl and co-workers managed to identify are listed in Table 1.1. Only insoluble intermetallic phases were obtained when the salts of Cd, Hg, Au and Tl were allowed to react with sodium/liquid/ammonia solution.

When Zintl and Harder\textsuperscript{10} attempted to isolate the \((\text{Na(NH}_3)_n\text{)}^{n+}_4 \text{Pb}_9^{4-}\) salt by evaporating the solvent, only an amorphous compound was obtained as was evident from X-ray crystallography. Further evaporation of ammonia resulted in decomposition of the salt to the corresponding Na-Pb intermetallic phases. Similar results were obtained for the salts of other polyanions,\textsuperscript{11} e.g.,

\begin{equation}
3 \text{Na(NH}_3)_n^{+} + \text{Sb}_7^{3-} \longrightarrow 3 \text{NaSb} + 4 \text{Sb} + n \text{NH}_3 \quad (1.1)
\end{equation}

Owing to the instability of the solvated polyanion salts, no structural information could be obtained on the anions by X-ray crystallography. However, in the ensuing years Zintl and co-workers\textsuperscript{12} pioneered an X-ray crystallographic study of these types of intermetallic phases, obtaining, for the first time, the structures of the anion networks in these phases.
Table 1.1  
Composition of some Sodium Metal Compounds Prepared and  
Identified by Zintl and Co-workers\textsuperscript{9} in Liquid Ammonia

<table>
<thead>
<tr>
<th>Insoluble in NH\textsubscript{3}(l)</th>
<th>Soluble in NH\textsubscript{3}(l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>Ca</td>
<td>Na-Zn</td>
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<td></td>
<td></td>
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</table>

Figure 1.1 Apparatus used by Zintl and co-workers\textsuperscript{9} for potentiometric and conductometric titrations in NH\textsubscript{3}(l); (A) reaction vessel, (B) burette (a) Pt-electrode, (b) cavity for reference solution, (k) capillary tube (salt bridge).
(B) **Zintl Phases**

Zintl noted early on in his crystallographic study of a number of alkali and alkaline earth intermetallic phases of main-group metals and metalloids that the maximum number of electropositive metal atoms in the alloys corresponded to a salt-like stoichiometry where the more electronegative main-group metal atom had a filled valence shell such as in $\text{Ba}_2\text{Ge}$, $\text{Na}_3\text{As}$ and $\text{Na}_2\text{Te}^{12}$. In addition, the phases corresponded to a salt lattice in which the next nearest neighbors of the metalloid atoms were the alkali or alkaline earth metal atoms. Zintl and co-workers$^{12}$ isolated and structurally characterized many other intermetallic phases of well-defined stoichiometry but richer in metalloid. An interesting trend was observed in NaTl-type phases for alkali metal-Group 13 element structures.$^{13}$ It was evident that the radii of the alkali metal atoms in a series were significantly shorter than the metal radius whereas the corresponding radius of the metalloid element did not change. In order to rationalize the structures of the NaTl-type phases, Zintl proposed covalent bonding between the metalloid atoms and ionic or heteropolar bonding interactions between the alkali metal and the metalloid elements. Thus, in the NaTl phase the thallium atoms formed a diamond-type lattice similar to the ones found for the Group 14 elements. Consequently, each thallium atom with three valence electrons
appeared to have accepted the single valence electron from the alkali metal atom, forming the lattice expected for a main-group element with four valence electrons.

The concept of transferring the valence electron(s) from the active metal to the metalloid originally postulated by Zintl was later generalized by Klemm et al.\textsuperscript{14} in order to rationalize the structures of other Zintl phases. The latter workers demonstrated that the anionic partial lattice formed by the main-group metal is isosteric with the corresponding isovalent element according to the $(8-N)$ rule for a completed noble-gas configuration. Thus, the tetrahedral M\textsubscript{4}\textsuperscript{4-} units formed by the Group 14 elements, as in NaPb,\textsuperscript{15} are isostructural with P\textsubscript{4} in white phosphorus whereas the silicon atoms in CaSi\textsubscript{2}\textsuperscript{16} form a two-dimensional network as in elemental arsenic ($\alpha$-form). The antimony atoms in NaSb\textsuperscript{17} form spiral chains as in selenium metal but planar zig-zag chains of silicon atoms are formed in CaSi.\textsuperscript{18} The latter chains are not isosteric with the elemental lattice but the expected two-coordination for a noble-gas configuration is retained. In the compounds above, the main-group elements have integer formal negative charges. However, the Zintl-Klemm concept can still be used for rationalizing the anionic lattice of phases where the metalloids have a formal fractional charge. For example in Li\textsubscript{7}Si\textsubscript{2}\textsuperscript{19} there are isolated Si\textsuperscript{4-} anions and Si\textsubscript{2}\textsuperscript{6-} dumbbells
and a four-atom chain is formed by the $\text{As}_4^{6-}$ anion in $\text{Sr}_3\text{As}_4$.$^{20}$

Today, a large number of alkali and alkaline earth metal alloys of main-group metals have been prepared and structurally characterized by X-ray crystallography. For excellent reviews of this topic, see references (21) and (22) by Schäfer et al. Furthermore, von Schnering and Hönle$^{23a}$ and Baudler$^{23b}$ have recently reviewed the structures and properties of the polyphosphide anions.

As a result of Zintl's extensive study of heavy-metal polyanions in liquid ammonia and his crystallographic work on the corresponding intermetallic phases, the post-transition element polyanions and their alkali and alkaline earth intermetallic phases have been dubbed "Zintl anions" and "Zintl phases", respectively, by subsequent workers in the field.

(C) MODERN DEVELOPMENTS

(i) Zintl Anions: Clusters and Cages

It was not until 1970 that Kummer and Diehl$^{24}$ managed to isolate stable, solvated salts of Zintl anions. By using the less volatile solvent ethylenediamine (en), the salts were obtained by extracting the intermetallic alloys $\text{NaM}_x$ (M = Sn, Ge, Sb) with en. An incomplete crystal structure of the salt $(\text{Na}^+)_4 \text{Sn}_9^{4-} \cdot 7\text{en}$ was thus obtained which was shown to
contain the Sn$_9^{4-}$ anion and whose structure appeared to be that of a tricapped trigonal prismatic cluster.$^{25}$ Owing to the short contact distances between the Na$^+$ cations and the Sn$_9^{4-}$ anion and the large thermal ellipsoids for the anion, it was evident that the anion was highly disordered. At about the same time Corbett and Edwards$^{26}$ reported that stable salts of Zintl anions could be obtained from NH$_3$ or en by strongly complexing the alkali metal cations with the specific bicyclic ligand 4, 7, 13, 16, 21, 24-hexaoxa 1, 10 diaza bicyclo (8, 8, 8) hexacosane or 2,2,2-crypt (hereafter also referred to as "crypt"). The crypt ligand contains a three dimensional cavity which the cations Na$^+$, K$^+$ and Rb$^+$ fit into, thereby forming a very stable inclusion complex such as 2,2,2-Rb$^+$ $^{27b}$

![Diagram](image)

Reversion of the alkali metal salts of the polyanions to intermetallic phases was thus prevented upon evaporation of the solvent (solv) as shown in equations (1.2) and (1.3)
\[ m \text{Na(solv)}^+ + M_k^{m-} \longrightarrow \text{Intermetallic phases} \quad (1.2) \]

\[ (\text{crypt-Na}^+)_m M_k^{m-} \longrightarrow \text{Intermetallic phases} \quad (1.3) \]

Furthermore, it was evident from crystal structures of the crypt salts that the alkali metal cations were no longer coordinated to the metal polyanion as was found in the \((\text{Na}^+)_4 \text{Sn}_9^{4-} \cdot 7\text{en salt.}\)

In the succeeding years Corbett and co-workers\textsuperscript{28-34} isolated a number of stable crypt salts of Zintl anions and determined their structures by X-ray crystallography. Examples of some of the anions so characterized by X-ray crystallography are the homopolyatomic anions \(\text{Sn}_9^{4-},\text{Ge}_9^{2-},\text{Sb}_7^{3-},\text{Sb}_4^{4-},\text{Sn}_5^{2-},\text{Pb}_5^{2-}\) and the heteropolyatomic anions \(\text{TlSn}_8^{3-},\text{TlSn}_9^{3-},\text{Tl}_2\text{Te}_2^{2-}\) and \(\text{Sn}_2\text{Bi}_2^{2-}\) (Figure 1.2). Many of the cluster polyanions are electron-deficient in the sense that each atom in the cluster has more atomic orbitals than valence electrons and are found to be isostructural with borane and carborane compounds.\textsuperscript{35} The clusters have the same number of skeletal electron pairs as the corresponding borane and carborane clusters if each atom in the polyanion is allocated one exo-skeletal electron lone pair or an inert ns\textsuperscript{2} electron pair. The geometry of the polyhedron associated with each cluster can thus be predicted from a knowledge of the number of skeletal electrons and
Figure 1.2 Structures of some Zintl anions characterized by Corbett and co-workers (see text): (a) Sn$_9^{4-}$, (b) Sn$_5^{2-}$ and Pb$_5^{2-}$, (c) TlSn$_8^{3-}$, (d) TlSn$_9^{3-}$, (e) Sb$_7^{3-}$, (f) Tl$_2$Te$_2^{2-}$.
application of Wade's rules.\textsuperscript{35} Thus, each n-atom cluster
has a closo-structure for \( n + 1 \) electron pairs, a nido-
structure for \( n + 2 \) electron pairs, an arachno-structure for
\( n + 3 \) electron pairs, such as \( \text{Ge}_9^{2-} \), \( \text{Sn}_9^{4-} \) and \( \text{Sb}_4^{2-} \),
respectively.

The polyanion clusters not only resemble boranes and
carboranes structurally and electronically, but also
chemically as the species \((K^+)_4(\text{PPh}_3)_2\text{PtSn}_9^{4-}\) and
\((K^+)_4(\text{PPh}_3)_2\text{PtPb}_9^{4-}\) have been proposed from NMR studies of
the reactions of \( \text{Pt}(\text{PPh}_3)_4 \) with \( \text{Sn}_9^{4-} \) and \( \text{Pb}_9^{4-}. \textsuperscript{36}
Haushalter \textit{et al.} \textsuperscript{37} have recently structurally characterized
the \( \text{Sn}_9\text{Cr(CO)}_3^{4-} \) anion. Undoubtedly, the reaction of
transition-metal compounds with naked metal polyanion
clusters will be explored in greater detail in the future.

Rudolph and co-workers\textsuperscript{38,39} were the first to study
Zintl anions in solution by multinuclear magnetic resonance
spectroscopy. The solutions studied were obtained by
extracting the alkali metal alloys of the heavy metals in \textit{en}
or \( \text{NH}_3 \) in the absence of cryptating agents. The anion,
\( \text{Sn}_9^{4-} \), showed only a single tin environment in the \( ^{119}\text{Sn} \) NMR
spectrum, even at -40 °C in liquid ammonia. It was evident
that the three tin environments of the \( \text{Sn}_9^{4-} \) anion were
undergoing rapid chemical exchange on the NMR time scale.
Moreover, a set of satellites symmetrically disposed about
the central \( ^{119}\text{Sn} \) peak was also observed arising from spin-
spin coupling to the magnetically equivalent spin-½ $^{117}\text{Sn}$ isotope of low natural abundance (7.6%). The satellite intensities corresponded to a nine-atom tin cluster (for details of calculations see reference (40)). As the $^{119}\text{Sn}-^{117}\text{Sn}$ coupling constant could be observed, it could be concluded that exchange between the tin environments was intramolecular. The alkali metal alloys of the binary mixtures Sn/Pb and Sn/Ge were also extracted and studied by $^{207}\text{Pb}$ and $^{119}\text{Sn}$ NMR spectroscopy. All the mixed metal clusters formed were found to be fluxional on the NMR time scale by virtue of the fact that only one chemical environment was observed and the $^{119}\text{Sn}-^{117}\text{Sn}$ spin-spin coupling was preserved. From the intensities of the corresponding $^{207}\text{Pb}$ and $^{117,119}\text{Sn}$ satellites and trends in chemical shifts, the peaks observed were assigned to the mixed metal clusters $\text{Sn}_9-n\text{Pb}_n^{4-}$ and $\text{Sn}_9-m\text{Ge}_m^{4-}$ ($n = 0-9$, $m = 0-8$). Corbett and Edwards\textsuperscript{28} estimated that the energy difference between closo and nido nine-atom polyhedral geometries to be very small as they noted that, unlike the isovalent tricapped prismatic $\text{Bi}_9^{5+}$ cation, the $\text{Sn}_9^{4-}$ anion had a unicapped antiprismatic configuration. Consequently, they proposed the nonrigidity of the $\text{Sn}_9^{4-}$ nido clusters could be attributed to the low energy barrier between the $C_{4v}$ and $D_{3h}$ nine-atom clusters.
The proposed intramolecular exchange mechanism can account for the scrambling of the atoms in the homo and hetero nine-atom clusters.

Extraction of the alloy NaSnTl_{1.5} in en gave evidence for the formation of a new fluxional cluster, TlSn_8^{5-}, which was identified by elemental analysis and $^{119}$Sn and $^{205}$Tl NMR spectroscopy. From the NMR studies, Rudolph et al. also characterized further species which were attributed to the Sn_4^{2-} and SnTe_4^{4-} anions. The Sn_4^{2-} anion is believed to be a compressed tetrahedron from theoretical calculations, which also accounts for the observed fluxional behavior of Sn_4^{2-}.

It is of interest that the novel Sn_4^{2-} anion could only be observed in solution when the alloy Na_{1-2}Sn^{39,40} was maintained in contact with the solution, indicating an equilibrium between the Sn_4^{2-} anion and the alloy. This type of equilibrium between the metal anions in solution and the alloy is not unexpected. Haushalter et al. reported
that ethylenediamine solutions of K₄Sn₉ and K₄Pb₉ form metal films on solid surfaces such as graphite, polyimides and even Pt and Au metals. In order to rationalize the surface metallization Haushalter proposed a mechanism whereby the polyanions deposit on a metal nucleation site, reducing the substrate and forming a metal film. The alkali metal cations then intercalate into the substrate to balance the negative charge. Zintl and Harder¹⁰ reported that negatively charged colloid particles of lead could be observed in an ammonia solution of the Pb₉⁴⁻ anion through a microscope. In view of these facts it would not be unusual for a particular anion to exist only in the presence of bulk alloy and, possibly, colloidal particles suspended in solution.

In recent years, a extensive solution ³¹P NMR study of polyphosphide anions has allowed the identification and structural characterization of a relatively large number of polyanions.²³ Several of the more complex polyanions that have also been characterized in solution are, e.g., P₁₆³⁻, P₂₁³⁻ and P₂₆⁴⁻.

(ii) **Classically Bonded Anions**

From Corbett,⁴⁵ Rudolph,⁴⁹ and Belin's⁴⁶ work it became apparent that extraction of Zintl alloys of mixtures of a electropositive element, such as Hg, Sn or As, and electronegative elements, such as Se and/or Te, produced
classical anions. The anions are classical in the sense that the chalcogen atoms are bonded to a central electropositive element and when terminal, the chalcogen atom (Ch) acts as a pseudohalogen if a negative charge is assigned to it, i.e., Ch$^-$. Thioanions of many main-group elements such as HgS$_2^{2-}$, SnS$_4^{4-}$, AsS$_3^{2-}$ and SbS$_4^{3-}$ have been known for some time and have served as a basis for a metal separation scheme in qualitative analysis (for a general separation scheme see reference (47)). The thioanions were prepared by allowing the metal sulfides, such as HgS, As$_2$S$_3$, Sb$_2$S$_5$ and SnS$_2$, to react with sodium sulfide or ammonium sulfide in aqueous solution, whereas sulfides such as PbS, Bi$_2$S$_3$ and CdS do not dissolve. Since 1970 Krebs and co-workers$^{48}$ have prepared and characterized a large number of thio- and selenoanions of many main-group elements. The anions were prepared by the conventional nucleophilic degradation of the metal sulfides or selenides with aqueous alkaline sulfide or selenide solutions. In most of the systems, mixtures of anions were formed in solution, but by careful control of the pH of the solution, systematic condensation reactions of thioanions took place, allowing the isolation of hydrated salts of the anions. For example, the condensation of the GeS$_4^{4-}$ anion to the Ge$_2$S$_7^{6-}$ anion would be given by
\[ 2 \text{GeS}_4^{4-} \rightarrow \text{Ge}_2\text{S}_7^{6-} + \text{S}^{2-} \] (1.4)

Krebs et al.\textsuperscript{48} characterized a number of thiogerma nates and determined the pH ranges over which the anions were stable. Their finding suggested that the acidity of the solvent medium strongly effects the existence and chemistry of the anions. From the pH range dependence, the effect of medium acidity upon the condensation reaction of the anions becomes apparent, i.e., at higher solution acidities the degree of condensation is higher. Presumably increasing the acidity of the solvent leads to stronger solvation of the $\text{S}^{2-}$ anion and, eventually, to its protonation to form $\text{HS}^{-}$

\[ \text{S}^{2-} + \text{H}_3\text{O}^+ \rightleftharpoons \text{HS}^{-} + \text{H}_2\text{O} \] (1.5)

To extend the classical anion series Schrobilgen et al.\textsuperscript{49} initially carried out a series of solution studies by extracting alkali metal chalcogenide phases of some main-group elements in en or NH\textsubscript{3}(1) in the presence of crypt and used multinuclear magnetic resonance (multi-NMR) spectroscopy to characterize the resulting anions. The NMR-active nuclides $^{203,205}\text{TI}$, $^{199}\text{Hg}$, $^{119}\text{Sn}$, $^{77}\text{Se}$ and $^{125}\text{Te}$ served as the structural probes in these studies. The Se/Te anions so identified were $\text{HgSe}_n\text{Te}_2-n^{2-}$, $\text{SnSe}_n\text{Te}_4-n^{4-}$ and $\text{Tl}_2\text{Se}_n\text{Te}_2-n^{2-}$ as well as the entirely new series of mixed classical polyanions $\text{CdSe}_n\text{Te}_2-n^{2-}$, $\text{SnSe}_n\text{Te}_3-n^{2-}$ and $\text{TlSe}_n\text{Te}_3-n^{3-}$. The
assignment of the charge on the tin species was based on $^{119}$Sn Mössbauer studies and the charge on the thallium species was assigned by analogy to the tin species.\textsuperscript{50} The new tin and thallium anions are believed to have trigonal planar structures with the Sn and Tl atoms in the trigonally coordinated positions by analogy with the isovalent $\text{CO}_3^{2-}$ anion. Interestingly, the dimers of $\text{SnSe}_3^{2-}$ and $\text{SnTe}_3^{2-}$, i.e., the $\text{Sn}_2\text{Se}_6^{4-}$,\textsuperscript{51} and $\text{Sn}_2\text{Te}_6^{4-}$,\textsuperscript{52} anions, have recently been structurally characterized in solid state by a X-ray crystallography whereas only the monomers were found to exist in en solution. However, the $\text{Sn}_2\text{Se}_6^{4-}$ anion has been identified in ethylenediamine solution by Devereux \textit{et al.}\textsuperscript{53}

A large number of ternary alkali metal chalcogenide phases of main-group elements have been prepared by the conventional high-temperature melts, crystalline phases isolated and characterized by X-ray crystallography and elemental analysis. This method is particular useful as many phases are unstable in polar solvents and solvolysis takes place. As before, the structures of the anions in these phases are found to be isostructural with the classical heteropolyanions with the bridging and terminal chalcogen atoms bonded to the central metalloid element. In recent years Schäfer and co-workers have prepared and structurally characterized a large number of alkali and earth alkali metal pnictide (Group 15) alloys of main-group metals by a similar
method. Interestingly, the anions in the lattices are found to be isostructural with corresponding metal chalcogenide anions. Thus, a 2-coordinate pnicogen atom, Pn, acts like a pseudochalcogen of negative charge, Pn\(^-\), as is found for the \([\text{SiP}_2^{2-}]_\infty\) anion in the \(\text{K}_2\text{SiP}_2\)\(^{54}\) phase (isoelectronic with SiS\(_2\)). When in a terminal position, the pnicogen behave like a pseudohalogen having a -2 charge (Pn\(^2-\)) as has been found, for example, for antimony in the \(\text{Al}_2\text{Sb}_6\)\(^{12-}\),\(^{55}\) anion. The bulk of this work has been summarized in a recent review by Schäfer\(^{56}\) (also see reference (22)).

For some systems of main-group metal chalcogenide anions, a chain of chalcogen atoms is found to be bridging two metalloid elements as, for example, the As\(_2\)Se\(_6\)\(^2-\) anion.\(^{46}\) In particular, these types of chain bridges are common in many metal-tellurium anions, for example, Sn\(_2\)Te\(_7\)\(^4-\),\(^{57}\) and Hg\(_4\)Te\(_{12}\)\(^4-\).\(^{58}\) Furthermore, in some structures of metal telluride anions, the metal atoms are found to be directly bonded to each other as is found for the germanium atoms in both isomers of the Ge\(_4\)Te\(_{10}\)\(^8-\),\(^{59,60}\) anion. Although most main-group chalcogenide anions are chalcogen-rich, two new arsenic-rich tellurium anions, As\(_{10}\)Te\(_3\)\(^2-\),\(^{61}\) and As\(_{11}\)Te\(_3\)\(^3-\),\(^{62}\) have recently been isolated and structurally characterized.
MULTINUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

As a Structural Probe for Polyanion Chemistry in Basic Media

All of the post-transition elements possess at least one natural abundance NMR-active isotope (Table 1.2). Because many of the NMR-active nuclei have a nuclear spin quantum number $I = \frac{1}{2}$, multinuclear magnetic resonance spectroscopy is a powerful technique for the study of Zintl anions in solution. Corbett et al. have noted that a large number of polyanion crypt salts isolated and structurally characterized by X-ray crystallography are the least soluble and most easily crystallized species. The polyanions so characterized therefore may not be the major species in solution. For example, the trigonal planar thallium anions, TlCh$_3$$^{3-}$ (Ch = Se/Te), could be identified in solution by NMR even though the Tl$_2$Te$_2$$^{2-}$ anion crystallized from solution and was subsequently characterized in solid state by X-ray crystallography.

For most ternary and quaternary Zintl phases, the phase diagrams are generally unknown. Therefore, the alloys extracted in en or NH$_3$ in the presence of a cryptating agent are often times a mixture of phases, and in the majority of cases there remains an insoluble alloy residue. The anion compositions and structures in solution must therefore be determined entirely by multi-NMR spectroscopy. In order to
Table 1.2

NMR Active Isotopes of Post-Transition Elements of Group 12, 14, 15 and 16

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Spin</th>
<th>Magnetogyric Ratio</th>
<th>NMR Frequency</th>
<th>Natural Abundance</th>
<th>Receptivity</th>
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<td>29.5</td>
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<td>769</td>
<td>-</td>
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<tr>
<td>207Pb</td>
<td>1/2</td>
<td>+5.5968</td>
<td>20.921</td>
<td>22.6</td>
<td>11.8</td>
<td>-</td>
</tr>
<tr>
<td>77Se</td>
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<td>19.091</td>
<td>7.58</td>
<td>2.98</td>
<td>-</td>
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<tr>
<td>123Te</td>
<td>1/2</td>
<td>-7.011</td>
<td>26.167</td>
<td>0.87</td>
<td>0.89</td>
<td>-</td>
</tr>
<tr>
<td>125Te</td>
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<td>31.549</td>
<td>6.99</td>
<td>12.5</td>
<td>-</td>
</tr>
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<td>24.0</td>
<td>60.4</td>
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<tr>
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<td>21.867</td>
<td>4.28</td>
<td>83.8</td>
<td>1.1</td>
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<tr>
<td>115In</td>
<td>9/2</td>
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<td>1.2</td>
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<tr>
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<td>3.488</td>
<td>7.76</td>
<td>0.617</td>
<td>-0.2</td>
</tr>
<tr>
<td>75As</td>
<td>3/2</td>
<td>+4.5816</td>
<td>17.127</td>
<td>100</td>
<td>143</td>
<td>+0.3</td>
</tr>
<tr>
<td>121Sb</td>
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<td>6.4016</td>
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<td>57.3</td>
<td>520</td>
<td>-0.5</td>
</tr>
<tr>
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<td>3.4668</td>
<td>12.959</td>
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<td>-0.7</td>
</tr>
<tr>
<td>209Bi</td>
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<td>4.2988</td>
<td>16.070</td>
<td>100</td>
<td>777</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

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a Reference (63).
achieve this, the chemical shift of each nuclear environment must be observed and at least one coupling to another NMR-active nucleus in the anion must also be observable. For coupled nuclei having the same coupling constants, the number of equivalent nuclei each environment is coupled to can be determined from the satellite intensities relative to the central peak. A general computational technique is given in Chapter 3. In the case of the mixed Se/Te metal chalcogenide anion series, the observed number of environments helps to account for the gross structures of the anions in the series. For example, the series $\text{SnSe}_n\text{Te}_3-n^2- \ (n = 0-3)$ yields four tin, three selenium and three tellurium environments as expected for a homologous series of trigonal planar structures. Furthermore, the empirical direct additivity and/or pair-wise additivity relationships for the chemical shifts and coupling constants in each series supports the view that the observed anions are members of the same series and are isostructural.

As all post-transition element nuclei having a nuclear spin $I > 1/2$ often times have large quadrupole moments (Table 1.2) they are generally "decoupled" from other nuclei by means of quadrupolar relaxation. Their linewidths, $\Delta \nu_1$, tend to be large unless their ligand environments give rise to an electric field gradient of zero or near zero at the observed nucleus such as for the cubic symmetries $T_d$ and
$O_h$. Therefore, the number of species identifiable by NMR may be limited (Table 1.2).

Corbett and co-workers$^{26}$ originally used 2,2,2-crypt to isolate stable salts of Zintl anions (for an excellent recent review see reference (65)). Although generally anions were studied in solution during the course of this work, Zintl phases were also extracted in the presence of cryptating agents. Many Zintl phases have low solubilities in en or NH$_3$ but in the presence of a cryptating agent they are much more soluble. As most spin-$\frac{1}{2}$ nuclei studied in the course of this work by NMR are of low natural abundance (Table 1.2), solutions of maximal concentration are desirable for good quality spectra. In addition, it became apparent that for many anions broad NMR lines were observed in the absence of any cryptating agent. This presumably arises from strong ion-pair effects such that the energy barrier for chemical exchange is lowered. In the presence of a cryptating agent, ion-pair effects are presumably minimized by complexation of the alkali metal cation to give a large non-polarizing cation and, correspondingly, slower chemical exchange and enhanced signal sharpness. Corbett$^{65}$ has noted the effect of cation complexation upon the stability of ion pairs in solution possibly allows the crystallization and isolation of anions such as Pb$_5^{2-}$,$^{26}$ and Ge$_9^{2-}$,$^{29}$ not evident in Zintl's solution study. Further indications of
the effect of ion pairs on the stability of anions in solution is evident from the marked color changes often observed when crypt is added to a solution extract of a Zintl phase (this work and reference (63)).

Other large non-polarizing cations, such as the tetraalkylammonium cation, can be used,\textsuperscript{66} to precipitate polyanions from non-amine solvents by the addition of tetraalkylammonium halides to the solutions.

(ii) \textbf{Chemical Shift Trends}

Quantum mechanical models of the nuclear shielding are usually presented in the formalism first introduced by Ramsey.\textsuperscript{67} The nuclear shielding constant is given as a sum of a diamagnetic component, $\sigma^d$, and a paramagnetic component, $\sigma^p$, as shown in equation (1.6).

$$\sigma = \sigma^d + \sigma^p$$ (1.6)

The nuclear shielding arises from induced magnetic fields felt by the nucleus arising from the interaction of nearby electrons with an external magnetic field. The diamagnetic shielding arises from a magnetic field formed by the classically induced free rotation of the electrons in an external magnetic field. The paramagnetic term has its origin in quantum mechanics and is caused by induced paramagnetic currents formed by the mixing of the ground
state of the system with excited states in an external magnetic field.

It is generally believed that the paramagnetic term makes the dominant contribution in the magnetic shielding of the heavier elements. Moreover, the electronic currents localized on the atom containing the nucleus of interest are the primary cause of shielding variations for the nucleus in different chemical environments. The major component for the shielding term for the heavier nuclei is therefore the local paramagnetic term, $\sigma^P(\text{loc})$, as given by equation (1.7) in the average excitation energy approximation

$$
\sigma^P(\text{A, loc}) = \frac{-(\mu_0 e^2 h^2)}{(24 \pi^3 m^2 \Delta E)} < r^{-3} >_{np} P_A
$$

(1.7)

where $\mu_0$ is the permeability constant, $h$ is Planck's constant, $m$ is the electron mass, $E$ is the average excitation energy, $<r^{-3}>_{np}$ is the inverse cube expectation value for the np valence electrons and $P_A$ is the p electron unbalance as given by

$$
P_A = (P_{xx} + P_{yy} + P_{zz}) - \frac{1}{4} (P_{xx}P_{zz} + P_{yy}P_{xx} + P_{yy}P_{zz}) + \frac{1}{2} (P_{xy}P_{yx} + P_{xz}P_{zx} + P_{zy}P_{yz})
$$

(1.8)

where $P_{\mu\tau}$ is defined as

$$
P_{\mu\tau} = \Sigma_j 2 C_{\mu j} C_{\tau j}^*
$$

(1.9)
and \( C_{\mu j} \) is the coefficient for the \( p_\mu \) atomic orbital of A in the \( j \)th molecular orbital.\(^{68}\)

In the previous solution NMR study of the main-group metal chalcogenide anions,\(^{49}\) i.e., \( \text{HgCH}_2^2^- \), \( \text{TlCH}_3^3^- \), \( \text{SnCH}_3^2^- \) and \( \text{SnCH}_4^4^- \) (Ch = Se, Te), the chemical shifts \( \delta \) of the electropositive metals and the chalcogen elements were found to be linear when plotted against \( n \), the number of selenium atoms (Table 1.3). The chemical shifts of the electropositive metal atoms were shifted to higher frequency as the number of the more electronegative selenium atoms increased. Although the observed trend can be rationalized by the diamagnetic term, \( \sigma^d \), as being due to decreased electron density on the nucleus, the paramagnetic term, \( \sigma^p \), must be primarily responsible for the observed trend as the chemical shift range is too large. A similar trend for the chemical shifts has been observed in other mercury and tin compounds.\(^{69}\)

The \(^{125}\text{Te} \) and \(^{77}\text{Se} \) chemical shifts of the anions were found to decrease linearly with the number of selenium atoms (Table 1.3). This appears to contradict what is expected on the basis of simple inductive effects. In general, it is observed for a number of organoselenium and tellurium compounds that the chemical shielding decreases as the electronegativity of the group bonded to the chalcogen atom increases.\(^{70,71}\) Consequently, one would expect the chemical
Table 1.3

$^{77}$Se, $^{125}$Te and Central Metal Chemical Shifts

for Some Metal Chalcogenide Anions, $\text{MSe}_n\text{Te}_{m-n}^\text{k-}$ ($n = 0$–$m$) $^a$

<table>
<thead>
<tr>
<th>Series</th>
<th>Isotope</th>
<th>Chemical shifts (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MSe}<em>n\text{Te}</em>{m-n}^\text{k-}$</td>
<td>M</td>
<td>$\delta$(M)</td>
</tr>
<tr>
<td>$\text{HgSe}<em>n\text{Te}</em>{2-n}^2-$</td>
<td>$^{199}\text{Hg}$</td>
<td>$-2178 + 686n$</td>
</tr>
<tr>
<td>$\text{TlSe}<em>n\text{Te}</em>{3-n}^3-$</td>
<td>$^{205}\text{Tl}$</td>
<td>$389 + 802n$</td>
</tr>
<tr>
<td>$\text{SnSe}<em>n\text{Te}</em>{3-n}^2-$</td>
<td>$^{119}\text{Sn}$</td>
<td>$-1162 + 302n$</td>
</tr>
<tr>
<td>$\text{SnSe}_{n-1}\text{Te}_4-n^4-$</td>
<td>$^{119}\text{Sn}$</td>
<td>$-1813 + 337n$</td>
</tr>
</tbody>
</table>

$^a$ Reference (49).
shielding of the selenium atom to decrease as the effective electronegativity of the central metal it is bonded to increases. Interestingly, a similar type of trend for the $^{77}\text{Se}$ chemical shifts has been observed in organophosphorus selenide compounds, $\text{R}_3\text{PSe}$.\textsuperscript{72} The canonical forms I and II,

$$\text{R}_3\text{P}^+ - \text{Se}^- \quad \text{I}$$
$$\text{R}_3\text{P} = \text{Se} \quad \text{II}$$

have been suggested for these compounds of which I is believed to make the major contribution based on the high shielding of the selenium nucleus. Although the shielding of the selenium atom decreased initially when an alkyl group was replaced by a electronegative group such as $-\text{N(CH}_3)_2$ or $-\text{OCH}_3$, the shielding increased again as more groups were substituted. This was taken as evidence for canonical form II and that $\pi$(p-d) bonding makes a significant contribution to the selenium chemical shift. The contribution is decreased when $\pi$-donating groups, such as $-\text{N(CH}_3)_2$ and $-\text{OCH}_3$, compete with the selenium atom for the 3d orbitals on the phosphorus atom. This type of resonance is not unreasonable if one considers the paramagnetic shifts of 2000 ppm observed for some selenoketones.\textsuperscript{73} Canonical form II would therefore be expected to have a large effect upon the chalcogen chemical shift even though its overall electronic contribution is small.
Similar structures may be responsible for the observed trends in the $^{77}\text{Se}$ and $^{125}\text{Te}$ chemical shifts in the metal chalcogenide anions owing to contributions of canonical forms with $\pi(p-p)$ bonds in the $\text{HgCH}_2^2-$, $\text{SnCH}_3^2-$ and $\text{TlCH}_3^3-$ anions and $\pi(p-d)$ bonds in the $\text{SnCH}_4^4-$ anions. Thus, as the weaker $\pi$-back bonding tellurium atom is substituted for the stronger $\pi$-donating selenium atom, the remaining tellurium atoms make a smaller contribution to a canonical form of type II, giving a smaller $\sigma^p$ term, i.e., increased shielding for the tellurium nucleus (Table 1.3). The trends observed in the selenium chemical shifts can also be rationalized in terms of the two canonical forms equivalent to I and II, however, substitution of a Te by Se will make the overall $\pi$-back bonding contribution of the selenium atoms in the anion smaller owing to increased competition. The $\sigma^p$ term arising from $\pi$-back bonding will therefore be smaller resulting in a shift of the selenium chemical shift to lower frequency as the number of selenium atoms increases. Although the electron imbalance for Se and Te would be expected to increase upon Se substitution as a result of the increased effective electronegativity of the central atom, M, contribution of the $\pi$-back bonding term is evidently larger for $\sigma^p$.

The trend discussed above, i.e., the higher $\pi$-back bonding ability of the more electronegative and smaller
selenium atom compared with the tellurium atom has been observed for other chalcogen systems as discussed by Kent, Gillespie and Sawyer\textsuperscript{74} for the thiofluorosulfate anion, $S_2O_2F^-$. Furthermore, it was evident from a study of the $^{18,16}_O$, $^{36,34}_S$ and $^{36,32}_S$ isotope effects on the $^{31}_P$ chemical shifts for some phosphorothioates that the oxygen atom had a greater $\pi$-back bonding ability to phosphorus than to the sulfur atom.\textsuperscript{75}

(iii) **Scalar Coupling Constants**

The nuclear spin-spin coupling constant or scalar coupling constant, $^nJ(A-B)$, results from the correlation of nuclear spins arising out of their interaction with the surrounding electrons. The coupling constant, therefore, contains information about the electronic environment between nuclei in molecules. In particular, the coupling constant between directly bonded nuclei is dependent upon the nature of the bond between the atoms, giving the chemist invaluable information about the species he is studying. The coupling constant is dependent on both electronic and nuclear properties but the latter dependence can be removed by defining the reduced coupling constant, $^nK(A-B)$, in equation (1.10)

$$^nK(A-B) = \frac{4 \pi^2}{(\hbar \gamma_A \gamma_B)} ^nJ(A-B) \quad (1.10)$$
where \( n \) is the number of bonds between nuclei A and B, \( h \) is Planck's constant and \( \gamma_A \) and \( \gamma_B \) are the gyromagnetic ratios of nuclei A and B.\(^76\)

The scalar coupling results from the interaction of the nuclear spins with the electrons orbital motions; the spin-orbit interaction, and the electron spins; the dipole-dipole and the Fermi contact interaction. It is generally believed that the dominant mechanism for a one-bond nuclear spin-spin coupling constant is the Fermi contact mechanism for most systems.\(^76\) As this mechanism results from the interaction of an electron at the nucleus, this mechanism is only dependent upon the s-electrons as only they have a finite probability of being at the nucleus. In a molecular orbital formalism developed by Pople and Santry,\(^77\) the Fermi contact term is given by equation (1.11)

\[
^1K(A-B) = \frac{4}{9} \mu^2_0 \mu^2_B |\psi_{ns,A(0)}|^2 |\psi_{ns,B(0)}|^2 \pi_{AB} \quad (1.11)
\]

where \( \mu_B \) is the Bohr magneton, \( |\psi_{ns,A(0)}|^2 \) and \( |\psi_{ns,B(0)}|^2 \) are the ns-electron densities at nuclei A and B and \( \pi_{AB} \) is the mutual polarizability of the valence ns orbitals on atoms A and B as given by equation (1.12)

\[
\pi_{AB} = 4 \sum_i \sum_j \frac{C_{is,A}C_{is,B}C_{is,A}C_{is,B}}{(E_j - E_i)} \quad (1.12)
\]

Here \( C_{n,A} \) and \( C_{n,B} \) are the LCAO coefficients of the s-type
atomic orbitals centered on A and B. Consequently, according to this mechanism, the coupling constant is dependent upon the s character of the bonds, increasing with the latter. It has been found empirically that there is a direct proportionality constant between the reduced coupling constant and the percentage s character, $\%s_A$ and $\%s_B$, of the atomic hybrids of atoms A and B used in the $\sigma$ bond joining them.\textsuperscript{76} However, as can be seen from equation (1.11), the reduced coupling constant also depends on the valence ns-electron densities at the nuclei, $|\Psi_{ns,A}(0)|^2$ and $|\Psi_{ns,B}(0)|^2$. Consequently, care has to be taken when comparing coupling constants between atoms far away in the periodic table. This becomes extremely important for the spin-spin coupling constants of the heavier elements owing to significant contribution of relativistic effects to the ns-electron density.\textsuperscript{78} Relativistic effects are very large for the heavy metal elements like Hg, Tl and Pb as they are near the gold maximum for relativistic effects. In order to be able to compare the reduced coupling constants of these metal nuclei with other main-group nuclei one would like to be able to correct for relativistic effects. One attempt to accomplish this involves multiplying the reduced coupling constant from the ratio of the calculated relativistic s-electron density, $|\Psi(0)|^2_{\text{rel}}$, and nonrelativistic s-electron density, $|\Psi(0)|^2_{\text{nonrel}}$,\textsuperscript{49} according to equation (1.13)
\[ 1_{K(A-B)}^{RC} = \frac{|\psi_A(0)|^2_{\text{nonrel}}}{|\psi_A(0)|^2_{\text{rel}}} \frac{|\psi_B(0)|^2_{\text{nonrel}}}{|\psi_B(0)|^2_{\text{rel}}} 1_{K(A-B)} \] (1.13)

Values for the relativistic and non-relativistic electron densities can be taken from the work of Pyykkö and Wiesenfeld.78

The reduced and relativistically corrected coupling constants for the classically bonded chalcogenide anions \( \text{HgCh}_2^{2-}, \text{TlCh}_3^{3-}, \text{SnCh}_3^{2-} \) and \( \text{SnCh}_4^{4-} \) (Ch = Se,Te), i.e. \( K(M-\text{Se}) \) and \( K(M-\text{Te}) \), are given in Table 1.4 as a linear function of number of selenium atoms. From the values in Table 1.4 one notes that, in general, \( 1_{K(M-\text{Ch})} \) decreases in the order \( \text{HgCh}_2^{2-} > \text{TlCh}_3^{3-} > \text{SnCh}_3^{2-} > \text{SnCh}_4^{4-} \) as expected from the \( \%s \) character of the atomic hybrid orbital of the central atom, i.e., \( \text{sp} (\text{Hg}) > \text{sp}^2 (\text{Tl},\text{Sn}) > \text{sp}^3 (\text{Sn}) \). However, the values for the heavier \( \text{Tl} \) and \( \text{Hg} \) metals are much larger than for \( \text{Sn} \). This is presumably caused by the large relativistic effect on the s-electron densities of the heavier elements with the dependency of the atomic hybrid \( \%s \) character made more evident in \( 1_{K(A-B)}^{RC} \) as can be seen from Table 1.4. In particular, it is of interest to note the similar values determined for the two trigonal planar anion series \( \text{SnCh}_3^{2-} \) and \( \text{TlCh}_3^{3-} \).
Table 1.4

One-Bond M-Se and M-Te Reduced Coupling Constants, $^{1}K$, and the Relativistically Reduced Coupling Constants, $^{1}K_{RC}$, of Some Metal Chalcogenide Anions: $\text{MSe}_{n}\text{Te}_{m-n}\text{K}^{-}$ ($\text{M} = \text{Hg, Tl, or Sn})$  \(^a\)

<table>
<thead>
<tr>
<th>Series</th>
<th>M-Se Bond</th>
<th>M-Te Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{1}K$</td>
<td>$^{1}K_{RC}$</td>
</tr>
<tr>
<td>$\text{HgSe}<em>{n}\text{Te}</em>{2-n}^{2-}$</td>
<td>559 - 2.9 n</td>
<td>154 - 0.8 n</td>
</tr>
<tr>
<td>$\text{TlSe}<em>{n}\text{Te}</em>{3-n}^{3-}$</td>
<td>501 + 15.7 n</td>
<td>142 + 4.5 n</td>
</tr>
<tr>
<td>$\text{SnSe}<em>{n}\text{Te}</em>{3-n}^{2-}$</td>
<td>217 + 8.0 n</td>
<td>132 + 4.8 n</td>
</tr>
<tr>
<td>$\text{SnSe}<em>{n}\text{Te}</em>{4-n}^{4-}$</td>
<td>140 + 7.7 n</td>
<td>85 + 4.7 n</td>
</tr>
</tbody>
</table>

\(^a\) Reference (49).
Interestingly, apart from the Hg\(\text{Ch}_2\)\(^2\text{--}\) series, the coupling constants increase linearly with the number of selenium atoms bonded to the central metal atom (Table 1.4). The increase in magnitudes of the coupling constants upon substitution of electronegative groups have been observed in many other systems.\(^7\)\(^6\) This trend can be rationalized by considering the s character of the atomic hybrid orbital used in the bonding. Thus, as the number of the more electronegative selenium atoms increases, the effective electronegativity of the central atom should also increase.\(^7\)\(^6\) Owing to this effect, the \(\sigma\) M-Ch bonds should polarize towards the central atom and the s character of central atom's atomic hybrid increases, giving a larger coupling constant. However, the change in s character of the chalcogen atomic hybrid in the bond has not been taken into account in this treatment.

(D) PURPOSE OF THE PRESENT WORK

The purpose of the present work was to extend the study of the chemistry of main-group metal chalcogenide anions by preparing and characterizing new lead chalcogenide anions. In particular this was of interest as it was expected that novel metal chalcogenide anions would form owing to the inert nature of the \(6s^2\) core of Pb. Furthermore, as only Sn(IV) chalcogenide anions had
previously been identified, the possibility that new Sn(II) chalcogenide anions could be prepared was also explored.

It was evident from a previous solution multi-NMR study of the mixed Se/Te metal chalcogenide anions\textsuperscript{49} that the solution chemistry of selenium and tellurium polychalcogenide anions played an important role in the chemistry of metal chalcogenide anions. Consequently, a significant part of the present work was devoted to the preparation and structural characterization in solution and in the solid state of the homopolychalcogenide anions of Se and Te as well as the relatively unknown heteropolychalcogenide anions of Se and Te.

The extraction of Zintl phases in the presence of crypt has allowed the isolation and characterization of stable salts of many novel polyatomic cluster anions. However, only the least soluble salts were isolated from solution and often times did not represent the true nature of these complex solutions.\textsuperscript{65} This was evident from numerous color changes observed during alloy extractions, suggesting that other hitherto of unknown species existed in crypt solutions.\textsuperscript{64} It was therefore of considerable interest to study the solution chemistries of these species by multi-NMR. Consequently, the present work was also dedicated to the synthesis and characterization of new Tl-Sn and Tl-Pb cluster anions in en or liquid ammonia in the presence of crypt.
CHAPTER 2

EXPERIMENTAL

(A) VACUUM TECHNIQUES

(i) General Comments

The majority of the compounds prepared during this work were air sensitive. Consequently, all manipulations were carried out under anhydrous conditions and, in the absence of oxygen, on glass vacuum lines, in a two-station nitrogen atmosphere dry box (Vacuum Atmospheres Model DLX) equipped with a Mettler AE 163 electronic balance and remote readout or in a glove bag. The dry box moisture and oxygen levels were routinely less than 0.01 ppm. The glove bag was flushed with dry nitrogen gas (moisture level less than 0.1 ppm) or argon gas (Matheson; \(O_2 < 1\) ppm), with the necessary apparatus placed inside the glove bag, for several hours prior to use. Owing to the build-up of electrostatic charge in the anhydrous environment of the dry box, any manipulations involving the handling of powders or finely divided materials inside the box were done in the vicinity of an \(\alpha\)-source consisting of a silver strip impregnated with 2.4 mCi of \(^{241}\text{Am}_2\text{O}_3\) (Amersham).
(ii) **Vacuum Line**

For manipulations of volatile compounds, the transfer of solvents or drying of reaction vessels, a general purpose grease-free glass vacuum line was constructed from Pyrex glass (Figure 2.1). Dynamic vacuum ($< 10^{-3}$ torr) was attained by using a direct drive rotary oil vacuum pump (Edwards E2M8). For monitoring pressures greater than $\sim 0.5$ torr in the vacuum line, a mercury manometer was used.

(iii) **Preparative Apparatus**

All synthetic procedures were performed in apparatus constructed from Pyrex glass or quartz. Sample preparations were carried out in vessels with attached grease-free Teflon valves manufactured by Rotaflo or J. Young. All glass vessels were thoroughly dried on a vacuum line under dynamic vacuum for a minimum of ten hours. During dynamic pumping the vessels were heated several times with a Bunsen burner flame or, when drying thin-walled precision glass NMR tubes, with a heat gun.

Vessels for sample preparation were connected through 1/4" o.d. tube ends to the vacuum line by means of 1/4" Teflon Swagelok unions and Teflon compression fittings (1/4" back and front ferrules, Hoke Controls).
Figure 2.1 General purpose glass vacuum line; (A) mercury manometer, (B) vacuum manifold (C) liquid nitrogen trap, (D) greaseless 6 mm J. Young glass/FEP valve.
(B) PREPARATION AND PURIFICATION OF STARTING MATERIALS

(i) Solvents

All solvents used in the course of this work were thoroughly dried and transferred by vacuum distillation. Ethylenediamine (Fisher Scientific Co.) was dried in two steps. The solvent was initially stored over ground CaH$_2$ (BDH Chemicals) in a 1 liter round bottom flask for at least two weeks and the flask contents periodically agitated. Hydrogen gas, which was given off for the first few days, was vented through a paraffin oil bubbler. In the final stage the ethylenediamine (en) was distilled under vacuum into another 250 ml round bottom flask containing freshly ground CaH$_2$. The solution in the flask was stored for at least one week prior to use and any gas formed was pumped off daily until there was no evidence for a major build up of H$_2$ pressure.

Ammonia gas (Canadian Liquid Air or Matheson), NH$_3$, was condensed from a gas cylinder at -78°C into an ammonia drying tube containing freshly cut sodium metal (0.3 - 0.4 g; BDH Chemicals). Liquid ammonia (100 - 200 ml) was stored at -78°C (dry ice-acetone bath) for at least one week prior to use.

Anhydrous ethanol (Consolidated Alcohols Ltd.) was stored in a round bottom flask over molecular sieves (Fisher Scientific Co., Type 4A) for at least one week prior to use.
(ii) **Alkali Metals**

The oxide layers of large pieces of potassium metal (MCB, > 99%) or sodium metal (BDH Chemicals, 99.98%) stored under paraffin oil were cut off and the paraffin oil removed by washing the freshly cut metals with petroleum ether (Fisher Scientific Co., boiling range, 50 - 100 °C). The ether was finally pumped off under vacuum before the metal pieces were taken into the dry box. Before each preparation, which required use of alkali metal, the thin oxide layer on the metal surface was shaved off inside the dry box, exposing the shiny metal surfaces.

Lithium metal (BDH Chemicals, 99.9%) was only cut and manipulated in a glove bag, previously flushed and filled with argon gas.

(iii) **Complexing Ligands**

The complexing ligand 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo(8.8.8)hexacosane; Merck, 99%, or Aldrich, 98%), was used as received and dried only in the evacuated port of the dry box for a minimum of 20 min. or in a open vial while flushing with dry nitrogen gas inside a glove bag.

12-Crown-4 (Aldrich Chemical Co.) was used as received and handled under anhydrous conditions in the dry box.
18-Crown-6 (Aldrich Chemical Co.) was recrystallized twice from freshly distilled acetonitrile (Fisher Scientific Co.) and then distilled under vacuum (< 0.1 torr) at -115 °C.

(iv) Main-Group Metals

The metals, selenium (Alfa Inorganics, 99.9%), tellurium (Alfa Inorganics, 99.5%), tin (Baker Analyzed, 99.9%) and lead (as shot, BDH Chemicals, 99.9%) were used as received and dried only under vacuum for a minimum of 20 min. in the dry box port.

The oxide layer present on thallium metal rod (Alfa Products, 99%) was cut off and the clean metal subsequently stored in the dry box.

(v) Miscellaneous Materials

Sulfur (BDH Chemicals), PbSe (Alfa Products, 99.99%), TlNO₃ (BDH Chemicals, 98%) and Tli (Alfa Products, ultrapure grade) were used as received inside the dry box.

Calcium hydride (BDH Chemicals) was ground inside a glove bag previously flushed and filled with dry nitrogen gas.

Dry nitrogen gas was obtained from the boil-off of liquid nitrogen (Canadian Liquid Air) and passed through an Lectrodryer to give a moisture level less than 0.1 ppm.
Argon gas (Matheson; $O_2 < 1$ ppm) was used directly from the gas cylinder.

(C) **PREPARATION OF ALLOYS**

The majority of the alloys were prepared by fusion of the appropriate elements in the required mole ratios in thick-walled Pyrex glass fusion vessels (Figure 2.2). The fusion of ternary and quaternary alloys was accomplished in two steps. Initially, a binary alloy was prepared by weighing the metals into a previously dried fusion vessel inside the dry box. The vessel was evacuated on a vacuum line and carefully heated in the flame of a Meeker burner until the metals had fused and reacted. The metals reacted exothermally and incandescence often occurred. This was particularly apparent when the electronegativity difference of the component metals was greatest, as in preparations involving an alkali metal and a p-block metal. Consequently, for the preparation of alkali metal ternary and quaternary alloys of p-block metals, the binary alloy of an alkali metal with the less electropositive main-group metal was prepared first. When the metals had reacted, the alloy was allowed to solidify on the walls near the bottom of the fusion tube by rotating it as the alloy solidified. This was done in order to facilitate an efficient reaction of the binary alloy with the metals to be added in the second step of the process.
Figure 2.2 Thick-walled Pyrex glass fusion vessel.
After the vessel had cooled down it was returned to the dry box and the remaining metal component(s) for the final alloy were added to the fusion vessel. The vessel was again evacuated and the fusion process repeated. However, once the metal(s) had reacted with the binary alloy, the final alloy was kept in a molten state and mixed thoroughly in order to ensure homogeneity. Finally, after the vessel had been allowed to cool, it was broken open inside the dry box and the alloy recovered, powdered and stored in a sealed glass vial inside the dry box until used.

A fusion vessel made of quartz was used for the preparation of the SnSe and SnTe alloys as the alloys do not melt below the softening point of glass (500 - 700 °C). After the initial exothermic reaction of the metals, the vessel was heated in the blue flame of a natural gas/oxygen torch in order to melt the alloy for good mixing.

The alloys prepared during this work are listed in Table 2.1 as well as the quantities of metals used in each preparation. When sodium or potassium metal were fused with lead and chalcogen metals in 1:1:1 ratios, lumps of malleable alloy, assumed to be lead metal, were recovered from the final alloy when the brittle alloy was powdered. The lead lumps were isolated and washed with water and acetone, dried and weighed. The stoichiometry of the final alloy was then corrected for amount of Pb metal found (Table 2.1).
Table 2.1

Alloy Composition

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<th>Alloy</th>
<th>Na</th>
<th>K</th>
<th>Tl</th>
<th>Sn</th>
<th>Pb</th>
<th>Se</th>
<th>Te</th>
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<tr>
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<td>(11.8)</td>
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</tbody>
</table>

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a The amount in moel is given in parenthesis.

b A lump of lead metal was isolated from the alloy and the final amount of Pb in the alloy corrected accordingly.

c The alloy was molten only in the course of the reaction and did not melt when heated further.

d Prepared in a welded molybdenum tube as given in reference (32).
The KSnTl alloy was also prepared, with the assistance of Mr. J.D. Garrett, McMaster Institute for Materials Research, by a procedure similar to that reported by Corbett and Burns\textsuperscript{32} except that a tube made of molybdenum instead of tantalum was used. One end of the molybdenum tube (50 mm long, 12.7 mm o.d., 11.2 mm i.d.) was welded and the tube then heated at 1600 °C under vacuum in order to remove all oxides from molybdenum surfaces. All three metals, K, Tl and Sn, were placed in the molybdenum tube in the dry box and a ground molybdenum lid placed on top of the tube. The tube was then taken outside the box, placed in a water-cooled holder and the lid argon-arc welded to the tube under vacuum. After the molybdenum tube had been sealed into a quartz ampule, the tube was heated to 950 °C for 12 hours. Finally, the molybdenum tube was cut open inside the dry box and the alloy recovered, powdered and stored in a vial inside the dry box until used.

(D) PREPARATION OF MAIN-GROUP POLYANIONS

(i) Preparations in Ethylenediamine and Liquid Ammonia Solvents

A general purpose reaction vessel for the preparation of main-group polyanions in en is depicted in Figure 2.3. The alloys to be extracted or the materials which are to be allowed to react were weighed inside the dry
box and then added to the glass ampule (B) of the reaction vessel. If an alkali metal cation complexing ligand was required in the reactions, it was weighed out and added, in the dry box, to the glass ampule or it was kept separated from the other material(s) by initially placing it in the NMR tube (A). The reaction vessel was then evacuated on a vacuum line and CaH₂-dried en statically distilled into the ice-cooled reaction ampule (A) from a 250 ml round bottom storage flask placed in a luke-warm water bath (Figure 2.4). After an approximately 6 cm high column of solvent (10 ml) had been distilled, the vessel was closed by means of the attached Rotaflo or J. Young valve and allowed to warm to room temperature. Alloy extraction or reaction of the component materials was soon evident from the coloration of the solvent, but complete extraction/reaction generally required from one to ten weeks. The samples were periodically agitated during the reaction period.

For many reactions involving K₂Te, the complexing ligand, 2,2,2-crypt, was kept separated from the solution in order to prevent possible oxidation (see Section D(v)). After K₂Te had all reacted the solution was cooled in an ice bath and 2,2,2-crypt, dissolved in en, decanted from the NMR tube in small portions into the main solution. If, however, the crypt was not initially present it was introduced into the vessel, inside a glove bag, in such a way that most of
Figure 2.3 General reaction vessel for alloy extraction and NMR sample preparation; (A) NMR tube (10 mm o.d.), (B) reaction glass ampule, (r, s) flame sealing points (flame sealing at point s only if \( \text{NH}_3(\text{l}) \) was used).
Figure 2.4 Apparatus for vacuum distillation of ethylenediamine (en) solvent into a reaction vessel; (A) reaction vessel in an ice-water bath, (B) a 250 ml round-bottom en storage flask in a luke warm temperature bath, (C) general purpose manifold, (D) Teflon 1/4" Swagelok union.
the crypt remained adhering to the neck of the reaction vessel. The solution was then cooled in an ice bath and the crypt dissolved in small portions.

The preparations of polyanions in liquid ammonia were conducted in a similar manner (see Figure 2.3) except that thick-walled glass reaction vessels and NMR tubes were used. After sodium-dried ammonia had been condensed at -78 °C into the reaction ampule, the reaction vessel was flame sealed below the valve at point s. The solutions were then allowed to warm slowly to room temperature in a well shielded area. If, however, one of the reagents was an alkali metal, the solution was kept at dry ice-acetone temperature (-78 °C) while it was reacting.

(ii) Preparation of $\text{Pb}_2\text{Ch}_3^{2-}$ (Ch = Se, Te)

For the extraction of the alloys $\text{K} \text{Pb}_0.65\text{Se}_0.33\text{Te}_0.77$ and $\text{K} \text{Pb}_0.54\text{Se}_0.77\text{Te}_0.33$, a stoichiometric amount of 2,2,2-crypt (150 - 200 mg; approximately 2% excess crypt relative to K) was added and thoroughly mixed with the powdered alloy in the glass ampule of the reaction vessel and the alloys extracted as described in Section D(i). For the first few days the extraction of an alloy was typified by the orange colored solution layer which formed above the alloy. After complete extraction of the alloys, which generally took place within 2 - 4 weeks, the final dark
red-brown solutions were isolated and their $^{77}\text{Se}$, $^{125}\text{Te}$ and $^{207}\text{Pb}$ NMR spectra recorded. Owing to the formation of mixtures of species from the extraction of the quaternary alloys, their concentrations necessarily varied over a wider range. However, as there was no evidence for formation of solids in the NMR tubes, the concentrations of the principal species in the NMR samples was estimated to be ca. 0.05 M. Furthermore, the approximate distributions of the anions extracted from the quaternary alloys were estimated from relative NMR signal intensities and are as follows: K$\text{Pb}_0.65\text{Se}_0.33\text{Te}_0.77$, 30% Pb$_2$Te$_3^{2-}$, 50% Pb$_2$SeTe$_2^{2-}$ and 20% Pb$_2$Se$_2$Te$_2^{2-}$; K$\text{Pb}_0.54\text{Se}_0.77\text{Te}_0.33$, 5% Pb$_2$Te$_3^{2-}$, 15% Pb$_2$SeTe$_2^{2-}$, 40% Pb$_2$Se$_2$Te$_2^{2-}$ and 40% Pb$_2$Se$_3^{2-}$ (see Chapter 4).

The alloy, K$\text{Pb}_0.49\text{Se}_1.00$ was extracted in en in the presence of 2,2,2-crypt for three weeks, forming a dark orange solution. The crystals of the (2,2,2-crypt-$K^+$)$_2$ Pb$_2$Se$_3^{2-}$ salt were grown from the dark orange solution by slow static distillation for several weeks, as described in Section E(i), and the crystals finally isolated for a single crystal X-ray crystal structure determination. It was noted that relatively large crystals had formed in the NMR sample of the solution resulting from the extraction of K$\text{Pb}_0.65\text{Te}$ in en in the presence of 2,2,2-crypt. The crystals of (2,2,2-crypt-$K^+$)$_2$ Pb$_2$Te$_3^{2-}$ were subsequently isolated from the NMR tube (Section E(i)) and used in an X-ray
crystallographic study (Chapter 4).

(iii) **Preparation of the Sn$_2$Se$_3^{2-}$ and SnPbSe$_3^{2-}$ Anions and Reactions of K$_2$Te with SnTe and/or SnSe**

In general, the preparations involved the reaction of K$_2$Ch (Ch = Se, Te) with SnSe, SnTe or a mixture of SnSe/PbSe or SnSe/SnTe in en in the presence of 2,2,2-crypt, similar to the preparations of the polychalcogenide anions described in Section D(v). For each reaction, K$_2$Se or K$_2$Te and SnSe and/or SnTe powders were thoroughly mixed together and added to the reaction ampule in the dry box. A stoichiometric amount of 2,2,2-crypt (120 - 220 mg, 0.32 - 0.58 mmol) was kept separated from the K$_2$Ch/SnSe mixture in the NMR tube. After en had been condensed onto the K$_2$Ch/SnCh mixture, the solution was allowed to stand for 1-2 days before the crypt was added. In reactions involving K$_2$Te, 2,2,2-crypt was not added to the solutions until all the K$_2$Te appeared to have reacted. Finally, the solutions were allowed to stand for additional 4 - 10 weeks before their NMR spectra were recorded.

When stoichiometric amounts of 2,2,2-crypt were added at 0 °C to a solution where K$_2$Te and/or SnTe was one of the reagents, the orange or reddish-orange solutions became brownish in color and a violet solid formed. The violet solid is attributed to the (2,2,2-crypt-K$^+$)$_2$Te$_2^{2-}$·x en anion.
(Chapter 5).

In typical preparations yielding the \( \text{Sn}_2\text{Se}_3^{2-} \) and \( \text{SnPbSe}_3^{2-} \) anions in en, the following amounts of reagents were used: \( \text{Sn}_2\text{Se}_3^{2-} \); K\(_2\)Se (44 mg, 0.28 mmol), SnSe (112 mg, 0.567 mmol) and 2,2,2-crypt (215 mg, 0.570 mmol). SnPbSe\(_3^{2-} \); K\(_2\)Se (52 mg, 0.33 mmol), SnSe (112 mg, 0.567 mmol), PbSe (96 mg, 0.335 mmol) and 2,2,2-crypt (265 mg, 0.570 mmol). For higher concentrations of SnPbSe\(_3^{2-} \), the reagents were skewed towards the lead containing species: K\(_2\)Se (113 mg, 0.716 mmol), SnSe (71 mg, 0.357 mmol), PbSe (307 mg, 1.074 mmol) and 2,2,2-crypt (569 mg, 1.511 mmol).

(iv) Preparation of Na\(_2\)Se, K\(_2\)Se and K\(_2\)Te in Liquid Ammonia

For each preparation, the appropriate amount of alkali metal was cut and weighed in the dry box. Weighed amounts of selenium or tellurium metal powder were transferred to arm B of an H-shaped thick-walled glass reaction vessel (Figure 2.5) and a weighed amount of the alkali metal was placed in arm A. In a typical preparation the following amounts of alkali and chalcogen metals were used: K\(_2\)Se; 1.5 g (38 mmol) K and 1.3 g (16 mmol) Se. Na\(_2\)Se; 1.5 g (65 mmol) Na and 1.8 g (23 mmol) Se. K\(_2\)Te; 1.6 g (41 mmol) K and 2.1 g (16 mmol) Te. The alkali metals were in large excess (15 - 30 \%) as some ammonolysis of the alkali metal always takes place. The vessel was then evacuated on a
vacuum line and ammonia previously dried over sodium was condensed into the arm containing the alkali metal at -78 °C. When the ammonia had filled approximately 2/3 of the arm height (25 - 35 ml), the reaction vessel was closed by means of the attached Rotaflo valve and carefully heat sealed below the valve at point p. The alkali metal/ammonia solution was then decanted in small portions onto the chalcogen metal powder at -78 °C, first forming soluble, highly colored polychalcogenide anions and finally a white solid. In order to minimize amide formation, the solution was maintained at -78 °C until all the chalcogen metal had reacted. When all the chalcogen metal powder appeared to have reacted, the solution was allowed to warm up to room temperature and the white solid collected into arm B of the vessel. Owing to inevitability of ammonolysis with the consequent formation of hydrogen gas in the closed reaction vessel, high pressure can develop which may lead to a violent pressure explosion. The reaction vessel was therefore kept in a well shielded area, particularly when these solutions were manipulated at or near room temperature. In order to remove amide and excess alkali metal, the solid was washed several times at room temperature by statically distilling the ammonia onto the solid at 0 °C and decanting the solution off the settled solid into arm A. Following complete washing of the solid, all of the ammonia was condensed into arm A at -78 °C and arm B, containing the
Figure 2.5 An H-shaped thick-walled glass reaction vessel for the preparation of alkali metal monochalcogenides in NH₃(l); (A, B) glass ampules, (p, q) points for flame sealing.
white alkali metal monochalcogenide, was isolated from the vessel by flame sealing at point q. A section of the 1/4" tube of arm A was scored and broken open inside a glove bag and a Teflon valve was attached by means of 1/4" compression fittings. The contents of the tube were then dried by evacuating the tube overnight and the monochalcogenide powder finally recovered in the dry box. It was evident from the dark brown color of $K_2Se$ that reduction of the selenium was incomplete. The crude solid was therefore treated again with 0.46 g of $K$ by the same procedure as described above, yielding a white powder as the final product.

(v) Preparation of $Ch_n^{2-}$ ($Ch = Se$ and/or $Te$, $n = 1 - 4$) and $TeS_mSe_{3-m}^{2-}$ ($m = 0 - 3$)

In general, the polychalcogenide anions were synthesized in en by allowing the alkali metal monochalcogenide to react with an appropriate amount of chalcogen metal. It was found necessary to have 2,2,2-crypt present in the reactions in order to complex all the alkali metal cation in solution which, in turn, served to slow down fast chemical exchange processes in the NMR spectra (see Chapter 5). The desired stoichiometric amounts of the monochalcogenide and the chalcogen metal powder were thoroughly mixed inside the dry box in glass ampule B of the reaction vessel (Figure 2.3). The amounts of reactants were
adjusted such that the final amount of 2,2,2-crypt used was approximately 200 - 300 mg. For almost all the preparations the solution became immediately colored when en was vacuum distilled onto the $K_2$Ch/Ch' (Ch = Se/Te) mixture at 0 °C. However, the reaction of $K_2$Ch with Ch' required 2 days to 3 weeks for completion. For many of the preparations, the 2,2,2-crypt was not added to the solution, as described in Section D(i), until all of the monochalcogenide had reacted, particularly when using $K_2$Te, so that possible oxidation of Te$^{2-}$ could be avoided or reduced. The solution was allowed to stand for at least one more week following crypt addition. In general, the addition of 2,2,2-crypt to the solution often resulted in precipitation of a large amount of crystalline material from the solution. The total time required for complete reaction was usually 2 - 4 weeks.

In order to compensate for a possible small amount of oxidation of polychalcogenide anions in solution, the monochalcogenide was always kept in 2 - 5 % excess relative to the chalcogen metals. Furthermore, the 2,2,2-crypt was weighed so that it was in 3 - 6 mole % excess relative to the total amount of alkali metal cation in each reaction, thus ensuring all the alkali metal cations were complexed in solution.
In a typical preparation for the homo- and heteropolychalcogenide anions in en the following amounts of reagents were used: \(\text{Se}^{2-};\) \(\text{K}_2\text{Se}\) (46.8 mg, 0.298 mmol) and 2,2,2-crypt (233 mg, 0.618 mmol). \(\text{Te}^{2-};\) \(\text{K}_2\text{Te}\) (64.0 mg, 0.311 mmol) and 2,2,2-crypt (239 mg, 0.633 mmol). \(\text{Te}_3^{2-};\) \(\text{K}_2\text{Te}\) (29.3 mg, 0.142 mmol), Te (34.1 mg, 0.267 mmol) and 2,2,2-crypt (112 mg, 0.297 mmol). \(\text{TeSe}_2^{2-};\) \(\text{K}_2\text{Te}\) (63.0 mg, 0.306 mmol), Se (50.1 mg, 0.634 mmol) and 2,2,2-crypt (252 mg, 0.669 mmol). \(\text{Te}_2\text{Se}^{2-};\) \(\text{K}_2\text{Se}\) (59.4 mg, 0.378 mmol), Te (96.4 mg, 0.755 mmol) and 2,2,2-crypt (290 mg, 0.771 mmol). \(\text{Te}_3\text{Se}^{2-};\) \(\text{K}_2\text{Se}\) (58.8 mg, 0.374 mmol), Te (143 mg, 1.121 mmol) and 2,2,2-crypt (289 mg, 0.767 mmol). \(\text{Te}_2\text{Se}_2^{2-};\) \(\text{K}_2\text{Se}\) (61.5 mg, 0.391 mmol), Se (30.8 mg, 0.390 mmol), Te (99.7 mg, 0.781 mmol) and 2,2,2-crypt (316 mg, 0.840 mmol). It should be noted that even though the stoichiometries of the reagents were adjusted for the preparation of the indicated anion, a mixture of species was often formed, in particular for the tri- and tetraheterochalcogenide anions.

The preparation of the \(\text{TeS}_n\text{Se}_{3-n}^{2-}\) \((n = 0 - 3)\) anions in en was conducted in the same way. Two NMR samples were prepared by allowing \(\text{K}_2\text{Te}\) to react with a 2S/Se mixture and a S/2Se mixture in en in the presence of 2,2,2-crypt (130 - 150 mg of crypt was used in each preparation). The resulting solutions were dark orange-red in color. In a similar way another sample was prepared by allowing \(\text{K}_2\text{Te}\) to react with
3Se in en (with crypt) and in liquid ammonia (without crypt).

For the preparation of some polyselenide and polytelluride anions, the alloys K\textsubscript{Pb}0.50Se\textsubscript{2.00}, K\textsubscript{Pb}0.50Se\textsubscript{3.00}, K\textsubscript{Pb}0.50Te\textsubscript{2.50} and K\textsubscript{Te}2.00 were extracted in en in the presence of crypt as described previously (see Section D(i)).

The polychalcogenide anions were also prepared in liquid ammonia by direct reaction of the alkali metal and the chalcogen metal at -78 °C in a thick-walled reaction vessel (Figure 2.3). For each preparation, a mixture of alkali metal and a stoichiometric amount of chalcogen metal powder were allowed to react at -78 °C until the alkali metal had all reacted. The solution was then warmed to room temperature in order to allow the polychalcogenide anions that had initially formed to react further with the remaining chalcogen metal powder. The solution was not decanted from the solid residue for NMR sample preparation for at least another 2 - 5 weeks. In a typical preparation the following amounts of alkali and chalcogen metals were used: K\textsubscript{2}Te\textsubscript{2}; 143 mg (3.7 mmol) K and 445 mg (3.5 mmol) Te. K\textsubscript{2}Te\textsubscript{3}; 99 mg (2.5 mmol) K and 456 mg (3.8 mmol) Te. K\textsubscript{2}Te\textsubscript{4}; 276 mg (7.06 mmol) K and 1799 mg (14.2 mmol) Te. Na\textsubscript{2}Se\textsubscript{4}; 51 mg (2.2 mmol) Na and 354 mg (4.5 mmol) Se.
(vi) Preparation of \(\text{HCh}^-\) (Ch = Se, Te)

Solution samples of \(\text{HSe}^-\) were prepared by dissolving \(\text{Na}^+\text{HSe}^-\) (prepared as described in ref. (79)) in dry EtOH and concentrating the final solutions in NMR tubes (10 mm o.d. for \(^{77}\text{Se}\) NMR and 5 mm o.d. for \(^1\text{H}\) NMR).

When the alloy LiPbTe\(_{0.7}\)Se\(_{0.3}\) (1.187 g, 3.65 mmol) and the 12-crown-4 (0.642 g, 3.65 mmol) were added to a reaction vessel, a violet solution immediately formed. Ethylenediamine was then condensed onto the mixture as described previously above. The resulting intense violet colored solution was isolated in a 10 mm NMR tube and was found to contain a high concentration of the \(\text{HTe}^-\) anion (Chapter 5). Its \(^{125}\text{Te}\) and \(^1\text{H}\) NMR spectra were subsequently recorded.

(vii) Preparation of Tl-Sn and Tl-Pb Cluster Anions

The alloys K/Sn/Tl (prepared both in glass and in molybdenum tubes) and K/Pb/Tl were extracted in en or liquid ammonia in the presence of 2,2,2-crypt as described previously. For each preparation, 250 – 550 mg of crypt and a stoichiometric amount of alloy were used such that crypt was in 3 – 7 % excess. The crypt was often kept separate in the NMR tube and not added to the solution until several hours after extraction commenced in order see to what extent complexation of the \(\text{K}^+\) cations affected the reaction. Small
lumps of alloy often formed after the crypt had been added to the solutions. In order to prevent possible long term decomposition of the anions, the alloy lumps were also isolated with the final solution in the NMR tube.

For the reactions of Sn\(_9^{4-}\) and Pb\(_9^{4-}\) with Tl\(^+\) described in Chapter 7, the alloys KSn\(_{2.04}\) (240 mg) and KPb\(_{2.05}\) (503 mg) were first extracted in en in a reaction vessel (Figure 2.3) and then TlNO\(_3\) (216 and 275 mg, respectively), which was kept in the NMR tube, was dissolved and decanted into the solution. Thallium iodide, TlI (160 mg), was also allowed to react with an en solution of KSn\(_{2.04}\) (533 mg) in like manner.

(E) **X-RAY CRYSTALLOGRAPHY**

(i) **Preparation and Isolation of Crystals**

Solutions of the appropriate polyanions were prepared by the method described in Section D(i). When the reaction was complete, a sample of the supernatant solution was decanted into the attached 10 mm o.d. thin-walled NMR tube. The crystals were then grown by tilting the vessel such that the NMR tube was horizontal and above the reaction tube. The reaction tube was immersed in a Dewar filled with water at room temperature. The en solvent slowly distilled statically from the NMR tube owing to gravity and temperature fluctuations in the room. The vessel was allowed to stand
for several weeks during which time a number of large crystals formed. The excess mother liquor was then decanted carefully off the crystals into the reaction ampule. In order to dry the crystals, the solution in the reaction ampule was carefully frozen at -196 °C overnight and the NMR tube flame sealed off from the vessel.

For many of the systems studied, relatively large quantities of crystals eventually formed in the sealed NMR sample tubes. In order to isolate these crystals they were collected in the 1/4" section of tubing at the top of the NMR tube and the solution then carefully decanted into the bottom of the 10 mm tube. The upper portion of the NMR tube, containing the crystals, was then scored, broken open in a glove bag, placed in a glass tube with a greased male ground glass joint and coupled to a female adaptor and J. Young valve assembly. The tube and crystals were evacuated on a vacuum line until residual solvent had been removed.

(ii) Crystal Mounting

The drying tube and crystals were transferred to a dry (<0.1 ppm), nitrogen-filled glovebox equipped with a microscope for mounting. The crystals were cleaved into smaller fragments with sharpened iridium needles and transferred into dried 0.2 - 0.3 mm Lindemann capillaries which had been thoroughly dried overnight in a glass ampule.
under dynamic vacuum at 200 - 250 °C. The capillaries were initially sealed inside the glovebox with dry Kel-F grease and permanently flame sealed outside the glovebox with a natural gas/oxygen micro torch.

(iii) **Crystal Structure Determination**

Single crystal X-ray structure determinations of the compounds: \((2,2,2\text{-crypt-K}^+)_2 \text{Pb}_2\text{Se}_3^{2-}\), \((2,2,2\text{-crypt-K}^+)_2 \text{Pb}_2\text{Te}_3^{2-}\), \((2,2,2\text{-crypt-K}^+)_2 \text{TeSe}_2^{2-}\cdot\text{en}\) and \((2,2,2\text{-crypt-K}^+)_2 \text{TeSe}_3^{2-}\cdot\text{en}\) were performed by Dr. J. F. Sawyer, Lash Miller Laboratories, University of Toronto.

(F) **NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY**

(i) **Instrumentation**

All spectra of the nuclei \(^1\text{H}, \, ^{77}\text{Se}, \, ^{117}\text{Sn}, \, ^{119}\text{Sn}, \, ^{123}\text{Te}, \, ^{125}\text{Te}\) and \(^{207}\text{Pb}\) were recorded on Bruker WM-250 and AM-500 pulse spectrometers equipped with cryomagnets (field strengths of 5.8719 and 11.745 T, respectively) and Aspect 2000 and 3000 computers, respectively. The \(^{203}\text{Tl}\) and \(^{205}\text{Tl}\) spectra were recorded on a Bruker MSL-100 spectrometer equipped with a cryomagnet (field strength 2.349 T) and an Aspect 3000 computer. Spectra were routinely obtained without locking (field drift < 0.1 Hz/hr). Deuterated (d\(_6\)) acetone was used to shim the spectrometers.
Variable temperature spectra were recorded using the variable temperature controller of the spectrometer. The sample was allowed to equilibrate for at least 5 - 10 min before beginning the spectral accumulation. Temperatures were checked by placing a copper-constantan thermocouple into the sample region of the probe.

The 10 mm probes used to record $^{77}\text{Se}$, $^{123}\text{Te}$, $^{125}\text{Te}$, $^{117}\text{Sn}$, $^{119}\text{Sn}$, $^{203}\text{Tl}$, $^{205}\text{Tl}$ and $^{207}\text{Pb}$ spectra were broad banded over the frequency ranges 23 - 103 (5.8719 T), 12-101 (5.8719 T) and 23 - 202 MHz (2.349 and 11.475 T). The $^{1}\text{H}$ NMR spectrum of the HSe$^{-}$ anion was recorded using a 5 mm $^{1}\text{H}$ probe on the AM-500 spectrometer whereas the $^{1}\text{H}$ NMR spectrum of the HTe$^{-}$ anion was recorded through the $^{1}\text{H}$-decoupling coils of the 10 mm probe of the WM-250 spectrometer.

The spectrometer frequencies were 500.138 MHz ($^{1}\text{H}$), 157.792 MHz ($^{125}\text{Te}$), 130.885 MHz ($^{123}\text{Te}$) and 95.383 MHz ($^{77}\text{Se}$) on the AM-500 spectrometer and 250.161 MHz ($^{1}\text{H}$), 93.276 MHz ($^{119}\text{Sn}$), 89.128 MHz ($^{117}\text{Sn}$), 78.917 MHz ($^{125}\text{Te}$), 52.174 MHz ($^{207}\text{Pb}$) and 47.704 MHz ($^{77}\text{Se}$) on the WM-250 spectrometer. The observing frequencies for $^{203}\text{Tl}$ and $^{205}\text{Tl}$ were 57.08 MHz and 57.708 MHz, respectively, on the MSL-100 spectrometer. The 10 mm narrow bore broad band probe (23-202 MHz) from the AM-500 spectrometer was mounted inside the MSL-100 spectrometer wide bore magnet and positioned by means of two aluminum shims placed at the top and the bottom of the
probe.

Free induction decays were typically accumulated in 16 or 32 K memories. Spectral width settings of 25 to 100 kHz were employed yielding data point resolutions of 3.0 to 6.1 Hz and acquisition times of 0.328 to 0.655 s, respectively. No relaxation delays were applied. The number of free induction decays accumulated depended upon the concentration and sensitivity of the nucleus under consideration with 10,000 to 300,000 scans being typical for most of these samples. Pulse widths for the bulk magnetization tip angles were 2 (\(^{1}\text{H}\)), 25 - 30 (\(^{77}\text{Se}\)), 40 (\(^{117}\text{Sn}\)), 25 - 28 (\(^{119}\text{Sn}\)), 25 - 30 (\(^{125}\text{Te}\)) and 25 - 33 \(\mu\)s (\(^{207}\text{Pb}\)) for the WM-250 spectrometer and 2 (\(^{1}\text{H}\)), 6 - 12 (\(^{77}\text{Se}\)), 26 (\(^{123}\text{Te}\)) and 10 - 18 \(\mu\)s (\(^{125}\text{Te}\)) for the AM-500 spectrometer. Pulse widths of 10 \(\mu\)s were used for the bulk magnetization tip angles of \(^{203}\text{Tl}\) and \(^{205}\text{Tl}\).

Line-broadening parameters used in the exponential multiplication of the free induction decays were 5 - 20 Hz for the heavier isotopes, however, values of the order 100-350 Hz were used for the broad lines. In order to enhance the resolution of some satellite peaks, the free induction decay was transformed with the use of a Gaussian fit rather than the conventional Lorentzian fit. In these instances, Gaussian broadenings of between 0.1 and 0.5 and a line-broadening greater than or equal to the negative of the data
point resolution were used.

(ii) **NMR Referencing**

The respective nuclei were referenced to neat samples of \((\text{CH}_3)_2\text{Se}\) (Alfa Products), \((\text{CH}_3)_2\text{Te}\) (Alfa Products), \((\text{CH}_3)_4\text{Sn}\) (Alfa Products) and \((\text{CH}_3)_4\text{Pb}\) and to 0.1 M aqueous TlNO\(_3\) (BDH Chemicals) solution at 24 °C sealed under vacuum in precision glass NMR tubes. The \(^1\text{H}\) spectrum of HSe\(^-\) was referenced to external neat \((\text{CH}_3)_4\text{Si}\) (MCD Isotopes). The chemical shift convention used was a positive (negative) sign signifies a chemical shift to high (low) frequency of the reference compound.\(^{82}\)

Tetramethyllead was prepared by the standard literature method.\(^{80}\) The sample was degassed and vacuum distilled into an 8 mm o.d. thick-walled NMR tube (cooled to −196 °C) and the frozen sample heat-sealed under dynamic vacuum. The 8 mm sample tube was centered, by means of Teflon shims, inside a 10 mm tube. The annular space contained tetramethyldisilane (Me\(_4\)Si) dissolved in CDCl\(_3\) solvent which served as the \(^2\text{H}\)-lock for the spectrometer. The \(^1\text{H}\) frequency of Me\(_4\)Si and the \(^{207}\text{Pb}\) frequency of \((\text{CH}_3)_4\text{Pb}\) were then measured at 24 °C. The absolute frequency, \(\Delta\), of \(^{207}\text{Pb}\) in neat \((\text{CH}_3)_4\text{Pb}\) was then calculated to be 20.920608 MHz (±10 Hz), assuming the protons in Me\(_4\)Si resonate at exactly 100 MHz. This value is in excellent agreement with
the previously reported value of 20.920597 MHz for 85% (CH₃)₄Pb in toluene.⁸¹

(iii) **NMR Sample Preparation**

Nuclear magnetic resonance (NMR) spectra were recorded in sealed, thin-wall precision Pyrex glass NMR tubes (10 mm or 5 mm o.d., Wilmad Glass Co.) or thick-walled 10 mm o.d. Pyrex glass tubes fabricated in the McMaster Glass Shop for use with liquid ammonia solvent.

Following extractions/reactions, any undissolved material remaining was allowed to settle before the clear solution was decanted into an NMR tube attached to the reaction vessel (Figure 2.3). The solution was concentrated by cooling the reaction ampule (B) in an ice bath while maintaining the NMR tube (A) in luke-warm (room temperature for liquid ammonia solutions) water, thus allowing the solvent to slowly evaporate from the NMR tube. If the solid residue in the reaction tube dissolved and the solution became colored again, the solid was again allowed to settle followed by decantation of the solution into the NMR tube. This was repeated several times until the solution in the larger glass reaction tube became colorless. Finally, the NMR tube and the reaction tube were cooled to 0 °C (-78 °C for liquid ammonia solutions) and the NMR tube flame sealed off from the vessel (point r, Figure 2.3). The solvent
column in the NMR tube was 3 - 6 cm high (2 - 3 ml for 10 mm o.d. NMR tubes) and before recording the NMR spectra of the solutions, any solid material which deposited as a result of solution concentration was collected into the 1/4" tube at the other end followed by careful decantation of the solution. This usually resulted in the residual solid clinging to the 1/4" tube and a clear solution in the NMR receiver coil region.
CHAPTER 3

METHOD FOR CALCULATION OF NMR SATELLITE INTENSITIES

ARISING FROM LOW ABUNDANCE NUCLEI AND THEIR USE

IN STRUCTURAL DETERMINATION

(A) INTRODUCTION

Nuclear magnetic resonance spectroscopy is undoubtedly one of the most powerful techniques available for structural characterization of molecules or ions in solution. This characteristic of NMR spectroscopy has its roots in the relatively simple appearance of the NMR spectrum of a molecule and the dependence of the NMR parameters, such as the chemical shift and spin-spin coupling constant, on the structure of the molecule. Thus, from the chemical shifts of peaks and their relative intensities one obtains information about the number of different chemical environments of an element in a molecule and the relative number of atoms in each environment. Further information on an environment's nearest neighbors in the molecule can become available if the peak is split into a multiplet. The multiplet arises from spin-spin coupling between two or more magnetically nonequivalent environments in the molecule causing their NMR peaks to be split into line components whose relative
intensities and number depend upon the spin quantum numbers of the individual coupled nuclei. For a spin coupling between two spin-$\frac{1}{2}$ nuclei, the number, $n$, of the neighboring equivalent nuclei in a given environment is coupled to can be determined by the $n + 1$ rule, i.e., the multiplet consists of $n + 1$ lines and their relative intensities are determined by Pascal's triangle (vide infra). However, this type of analysis can only be used if the nucleus of interest is coupled to spin-$\frac{1}{2}$ nuclei of 100% abundance such as $^1$H, $^{19}$F or $^{31}$P. In fact, many spin-$\frac{1}{2}$ isotopes, including those discussed in this Thesis, are of medium (10% - 90%) to low (<10%) natural abundance, making observation of a coupling to these nuclei dependent upon the probability of having the spin-$\frac{1}{2}$ nucleus in the molecule. Consequently, in the NMR spectrum of a nucleus coupled to a low abundance spin-$\frac{1}{2}$ nucleus a single line of intensity, $I_C$, is observed for each chemically nonequivalent site with a pair equal intensity satellites, $I_S$, symmetrically disposed about it.
Although the number of equivalent nuclei, \( n \), each environment is coupled to cannot be determined directly from the qualitative appearance of the multiplet pattern, \( n \) can be found by comparing the intensities of the satellite peaks, \( I_S \), with the central peak intensity, \( I_C \). To accomplish this one can use the same calculation method as has been reported for the thallium ethoxide tetramer, \((\text{TlOEt})_4\),\(^{83}\) to determine the abundances of different isotopomers of the group of \( n \) magnetically equivalent nuclei. Thus, the abundance of each isotopomer composition for the neighboring group is found from the individual terms in the binomial expansion

\[
(a + b)^n = \sum_{t=0}^{n} \binom{n}{t} a^t b^{n-t}
\]  

(3.1)

where

\[
\binom{n}{t} = \frac{n!}{t! (n-t)!}
\]  

(3.2)

The abundance of the spin-\( \frac{1}{2} \) isotope is given by \( a \), and \( b \) represents the abundance of the NMR-inactive isotopes. As the isotopomer \( a^t b^{n-t} \) will give a \((t + 1)\) multiplet, the resulting NMR spectrum is a superposition of singlet, doublet, triplet, ... subspectra, each weighted by its probability.

**EXAMPLE:** Let is determine the relative intensities of the \( ^{125}\text{Te} \) spin satellites in the \( ^{119}\text{Sn} \) NMR spectrum for the tetrahedral \( \text{SnTe}_4^{4-} \) anion. In Table 3.1 the contribution of
each isotopomer $^{125}\text{Te}^t(n^{127}\text{Te})^{n-t}$ to the spectrum has been calculated and all the subspectra superimposed to obtain the relative intensities of the multiplet peaks in the final $^{119}\text{Sn}$ spectrum (also see reference (49)). From the calculations we can see that apart from the first satellites, $I_{S1}$, the other satellites will be difficult to observe owing to their low relative intensities. For that reason, the remainder of this mathematical treatment of satellite intensities arising from low abundance spin-$\frac{1}{2}$ nuclei will deal only with the 1st ($I_{S1}$) and 2nd ($I_{S2}$) sets of satellites in the total spin coupling pattern.

Rudolph et al.\textsuperscript{40} have used the same method for calculating the theoretical $^{119}\text{Sn}$ and $^{207}\text{Pb}$ NMR multiplet intensities arising from $^{117}\text{Sn}$, $^{119}\text{Sn}$ and $^{207}\text{Pb}$ natural abundance couplings for hypothetical fluxional lead-tin cluster anions; $\text{Sn}_k\text{Pb}_m-k$. The abundances of the isotopomer NMR subspectra with varying numbers of $^{117}\text{Sn}$ and $^{119}\text{Sn}$ spin-$\frac{1}{2}$ isotopes can be determined from the binomial expansion of $(a_1 + a_2 + a_3)^n$ where $a_1$ and $a_2$ are the abundances of the $^{117}\text{Sn}$ and $^{119}\text{Sn}$ isotopes and $a_3$ is the abundance of the NMR-inactive isotopes of tin. For a group of $n$ chemically equivalent atoms one can extend this method of calculation to any number of different isotopes by expansion of the expression $(a_1 + a_2 + \ldots + a_m)^n$. 
Table 3.1

$^{119}$Sn NMR Multiplet for the SnTe$_4$ Anion

<table>
<thead>
<tr>
<th>Isotopomer$^a$</th>
<th>Abundance (%)</th>
<th>Multiplet Subspectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a^1 b^{(n-t)}$</td>
<td>$100 \times \frac{n!}{t!(n-t)!} a^t b^{(n-t)}$</td>
<td>Relative Intensities (%)</td>
</tr>
<tr>
<td>$b^4$</td>
<td>$\frac{4!}{0! \cdot 4!} (0.9214)^4$ = 72.076</td>
<td>72</td>
</tr>
<tr>
<td>$a^1 b^3$</td>
<td>$\frac{4!}{1! \cdot 3!} (0.0699)(0.9214)^3$ = 21.872</td>
<td>10.94 : 10.94</td>
</tr>
<tr>
<td>$a^2 b^2$</td>
<td>$\frac{4!}{2! \cdot 2!} (0.0699)^2(0.9214)^2$ = 2.489</td>
<td>0.62 : 1.24 : 0.62</td>
</tr>
<tr>
<td>$a^3 b^1$</td>
<td>$\frac{4!}{3! \cdot 1!} (0.0699)^3(0.9214)$ = 0.126</td>
<td>0.02 : 0.05 : 0.05 : 0.02</td>
</tr>
<tr>
<td>$a^4$</td>
<td>$\frac{4!}{0! \cdot 4!} (0.0699)^4$ = 2.3 x 10$^{-3}$</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

$^{119}$Sn NMR Multiplet Intensities

<table>
<thead>
<tr>
<th>$I_{s3}$ : $I_{s2}$ : $I_{s1}$ : $I_c$ : $I_{s1}$ : $I_{s2}$ : $I_{s3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 : 0.62 : 10.99 : 73.32 : 10.99 : 0.62 : 0.02</td>
</tr>
<tr>
<td>or</td>
</tr>
<tr>
<td>0.00 : 0.85 : 14.99 : 100.00 : 14.99 : 0.85 : 0.00</td>
</tr>
</tbody>
</table>

$^a a = 6.99$% for $^{125}$Te and $b = 92.14$% for the NMR-inactive Te isotopes. The low-abundance spin-4 isotope, $^{123}$Te (0.89%), has not been included.
One will soon realize, however, that the calculations can become tedious when \( n \) and/or \( m \) are large. For example, from the sample calculations given in Table 3.1 it can be seen that one must go through the entire procedure for each value of \( n \). It would therefore be desirable to be able to have a relatively simple expression for \( I_{sj}/I_C \) which would simplify the calculations. In this Chapter a relatively simple algebraic expression for the sum of the subspectra of the most important isotopomers will be given and an equation for the satellite peak/central peak intensity ratio, \( I_{sj}/I_C \) will be derived. The latter expression will be used extensively throughout this Thesis when discussing structural findings based upon multi-NMR spectroscopy.

(B) **PROBABILITIES OF ISOTOPOMERS**

In order to analyze the NMR spectrum of a molecule or ion, the probability of each isotopomer contributing to the total spectrum has to be determined. The simple case of a group of \( n \) chemically equivalent atoms of the element \( A \) is considered first. For most of the systems it can be assumed that the probability, \( P_\alpha \), of having the isotope \( ^\alpha A \) at one particular site in the group is independent of which isotopes of \( A \) are in the other sites. Therefore, if \( r, s, t, ...v \) is designated as the number of atoms \( A \) of isotope \( \alpha, \beta, \gamma, ...\varepsilon \) the probability of obtaining one particular type of
isotopomer of composition $\alpha_A r^\beta A_s \cdots \epsilon A_v$ is given by

$$P_A(...,\alpha_i,\ldots,\epsilon_j,\ldots) = (p_\alpha)^r (p_\beta)^s \cdots (p_\epsilon)^v$$  \hspace{1cm} (3.3)$$

where $\alpha_i$ denotes isotope $\alpha_A$ at site $i$. However, if all the isotopomers of the same composition are equivalent, then the probability, $P_A(r,s,\ldots,v)$, for obtaining the isotopomer is simply obtained by multiplying equation (3.3) by the number of isotope combinations

$$P_A(r,s,\ldots,v) = \frac{n!}{r! s! \cdots v!} (p_\alpha)^r (p_\beta)^s \cdots (p_\epsilon)^v$$  \hspace{1cm} (3.4)$$

$$n = r + s + \cdots + v$$  \hspace{1cm} (3.5)$$

EXAMPLE: The probability of obtaining the tetrahedral $Sn_4^{4-}$ isotopomer in Figure 3.1a with $^{119}Sn$ in sites 1 and 2, $^{117}Sn$ in site 3 and $^{na}Sn$ in site 4 is given by equation (3.6)

$$P_{Sn} = (p_{119})^2 (p_{117})^1 (p_{na})^1$$  \hspace{1cm} (3.6)$$

where na indicates all the non-active NMR isotopes of tin (including the spin-$\frac{1}{2}$ isotope $^{115}Sn$, 0.35 %). Here $n = 4$, $r = 2$, $s = 1$ and $v = 1$. By substituting $p_{119} = 0.0858$, $p_{117} = 0.0761$ and $p_{na} = 1 - p_{119} - p_{117} = 0.8381$ for the natural abundances into equation (3.6), one obtains $4.70 \times 10^{-2}$ % for the probability of this isotopomer. However, as can seen from Figure 3.1a, all $4!/(2!1!1!) = 12$ types of isotopomers having this composition are equivalent; therefore, the
Figure 3.1  (a) One specific type of isotopomer for the $\text{Sn}_4^{4-}$ anion of composition $^{119}\text{Sn}_2^{117}\text{Sn}^{\text{na}}\text{Sn}$. (b) The three different spin-spin couplings; $J$, $J'$ and $J''$ for the hypothetical cubic $\text{Sn}_8^{8-}$ anion.
probability for the $^{119}\text{Sn}_2^{117}\text{Sn}^{\text{nasa}}\text{Sn}$ isotopomer is $12 \times 4.70 \times 10^{-2} \% = 0.562 \%$.

Normally it cannot be assumed that all the isotopomers of a given composition are equivalent. This applies especially for molecules or ions of high symmetry where a isotopomer lowers the symmetry of the spin system. For example, the hypothetical $\text{Sn}_8^{8-}$ cube has three nonequivalent isotopomers of composition $^{119}\text{Sn}^{117}\text{Sn}^{\text{asa}}\text{Sn}_6$ as indicated by the three coupling constants $J$, $'J$ and $''J$ depicted in Figure 3.1b. The probability, $'P_A$, of equivalent isotopomers can, however, be found by simply multiplying the probability product for the isotopes in equation (3.3) by the total number, $k$, of equivalent types of isotopomers

$$'P_A = k \times (p_\alpha)^{\Gamma} (p_\beta)^{S} \cdots (p_\epsilon)^{V}$$

Thus, for the isotopomer $^{119}\text{Sn}^{117}\text{Sn}^{\text{asa}}\text{Sn}_6$ depicted in Figure 3.1b the value of $k$ is 24 for the edge ($J$), 24 for the face-diagonal ($'J$) and 8 for the diagonal ($''J$). However, if the cube is fluxional such that all the spin couplings become time averaged on the NMR time scale, then all isotopomers of the same composition are equivalent and $k$ is now simply the sum $24 + 24 + 8 = 56$ or $8! / 6! 1! 1! 1!$ as given by equation (3.4).

Often times, a molecule or ion consists of more than one element and, moreover, there can be chemically different environments for each element. Therefore, if the chemically
equivalent atoms in the molecule are collected into groups (A, B, C, ..., Q), then the total probability, \( P_T \), of a particular isotopomer is simply calculated as the product of the isotopomer probabilities of each group of chemically equivalent atoms as given by equation (3.8)

\[
P_T = P_A \times P_B \times P_C \times \cdots \times P_Q
\]  

(3.8)

The NMR spectrum of each isotopomer can now be calculated. As before, the final NMR spectrum of the molecular species is simply a superposition of the NMR spectra of all the possible isotopomers, each weighted by its total probability factor. One must note, however, that when there is more than one possible type of isotopomer for each isotope composition, equation (3.8) does not apply. The total probability has to be calculated by a method similar to that used in equation (3.7), i.e., take the product of the abundances of all the isotopes (for all the groups) of the isotopomer and multiply by the total number of equivalent types of nuclei giving identical NMR spectra. For most species the total number of isotopomers possible can be quite large but in practice one only has to consider the environment which gives rise to the NMR peak under study and the environments to which it is spin coupled. Furthermore, in most systems where the NMR-active isotopes are of relatively low abundance, isotopomers containing a relatively
large number of NMR-active isotopes are of very low probability.

In many of the spin systems one encounters, the environment giving rise to the NMR peak is bonded to one or more group of n chemically equivalent atoms. Therefore, in the following sections relatively simple expressions for the \( I_s / I_c \) ratios will be derived for common systems such as \( A \) bonded to a group of \( n \) equivalent atoms \( Y, A_kX_n, \) and a spin-spin coupling within a group of \( n \) chemically equivalent atoms \( A, A_n, \) where two isotopes of \( A \) have spin-\( \frac{1}{2} \). A more complex system such as \( AX_nY_m \) and \( A_kX_n \) will also be considered.

(C) **SATELLITE PEAK/CENTRAL PEAK INTENSITY RATIOS, \( I_s / I_c \)**

(i) **The \( A_kX_n \) System**

In order to analyze the multiplet pattern in the \( ^{\alpha}A \) NMR spectrum that arises from spin coupling with the spin-\( \frac{1}{2} \) \( \beta Y \) isotopes it is assumed that both the \( A \)'s and the \( Y \)'s are chemically equivalent groups and, moreover, that there is only one type of spin-spin coupling, namely \( J^{(\alpha A-\beta Y)}. \) According to equations (3.4) and (3.8), the probability of having the isotopomer \( ^{\alpha A_i}n_{A_k-i}^{\beta Y_t}n_{A_y}n_{-t} \) is

\[
P_T = \left( \frac{k_i}{p_{\alpha}} \frac{p_{\alpha}}{p_{\alpha}} \frac{k-i}{p_{\alpha}} \right) \times \left( \frac{n_t}{p_{\beta}} \frac{p_{\beta}}{p_{\beta}} \frac{n-t}{p_{\gamma}} \right) \quad (3.9)
\]

where \( p_{\alpha}, p_{\alpha}, p_{\beta} \) and \( p_{\gamma} \) are the abundances of \( ^{\alpha}A, n_{A}, ^{\beta}Y \) and
n_{\alpha Y}, respectively. However, all the isotopomers with the same number of $\beta Y$ but differing numbers of $\alpha A$ will all have identical $\alpha A$ NMR multiplet patterns. As one is comparing the relative intensities of peaks in the multiplet, one need only consider the probabilities of the isotopomers of $Y$, $\alpha Y_t n_{\alpha Y n-t}$, as given in equation (3.10).

$$p_{\gamma}(t) = n_{C_t} p_{\beta}^{t} p_{\gamma}^{n-t} \quad (3.10)$$

The $\alpha A$ NMR multiplet pattern is now simply the sum of the subspectra of a singlet, doublet, triplet, etc. resulting from isotopomers of the group $Y_n$ having zero, one, two or more of the $\beta Y$ isotopes. In Table 3.2 we can see the effect such a superposition has on the final multiplet. Thus, the central lines of a singlet, triplet, quintet, etc. all contribute to the central line of intensity $I_C$ while the central and most intense lines of a doublet, quartet, etc. give arise to the innermost satellites of intensity $I_{S1}$. In general, only lines from even number $(t + 1)$ multiplets and only odd number $(t + 1)$ multiplets can superimpose. This assumes that isotope shifts are negligible and cannot be resolved. As the relative intensities of the $(t + 1)$-line multiplet are given by Pascal's triangle, one can express the relative intensities of the individual multiplets by the formula
### Table 3.2

**Relative Intensities of \((t + 1)\) Multiplets**

<table>
<thead>
<tr>
<th>(t)</th>
<th>(I_{s5})</th>
<th>(I_{s4})</th>
<th>(I_{s3})</th>
<th>(I_{s2})</th>
<th>(I_{s1})</th>
<th>(I_{c})</th>
<th>(I_{s1})</th>
<th>(I_{s2})</th>
<th>(I_{s3})</th>
<th>(I_{s4})</th>
<th>(I_{s5})</th>
<th>(\Sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td>3</td>
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<tr>
<td>5</td>
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</tr>
<tr>
<td>(t)</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
(t/2 + j/2)! (t/2 - j/2)! \\
\text{where } j = 0, 1, 2, \ldots, t
\]

\[
\Sigma = 2^t
\]
\[ t_{M_j} = 2^{-t} \times \frac{t!}{(t/2 + j/2)! (t/2 - j/2)!} \] (3.11)

where \( j = 0, 2, 4, \ldots t \) for \( t \) even and \( j = 1, 3, 5, \ldots t \) for \( t \) odd. Note that the lines of each multiplet have been normalized by multiplying by the factor \( 2^{-t} \) in equation (3.11).

The intensity of each line of an isotopomer having \( \beta_y \) isotopes is then simply the product of the isotopomer probability and the corresponding multiplet line intensity. The final intensity of the central line, \( I_C \), and the \( j \)th satellite line, \( I_{S_j} \) (Table 3.2), is then simply obtained by summing the appropriate peaks as given by equations (3.12) and (3.13)

\[ I_C = \sum_{t=0, \text{even}}^{\leq n} \frac{n!}{t!(n-t)!} \ p_\beta^t \ p_y^{n-t} \ t_{M_0} \] (3.12)

where \( t \) is even and

\[ I_{S_j} = \sum_{t=j}^{\leq n} \frac{n!}{t!(n-t)!} \ p_\beta^t \ p_y^{n-t} \ t_{M_j} \] (3.13)

where \( t \) takes on only odd values for \( j = 1, 3, 5, \ldots \), but for \( j = 2, 4, 6, \ldots \), only even values are allowed for \( t \).

The satellite/central peak intensity ratio, \( I_{S_j}/I_C \), can now be calculated from equations (3.12) and (3.13) and compared with the measured ratio, allowing one to determine
the number of atoms, \( n \), of \( X \). For most spin dilute systems the contributions from a quintet or higher multiplets are small owing to their relatively low probabilities. The theoretical ratios \( I_{S1}/I_C \) and \( I_{S2}/I_C \) can therefore be determined to a good approximation by including only the intensities of the lines resulting from the singlet, doublet, triplet and quartet as given by formulae (3.14) and (3.15)

\[
I_{S1}/I_C = n Z \left( \frac{1 + (n-1)(n-2)Z^2/2}{1 + n(n-1)Z^2} \right) \quad (3.14)
\]

and

\[
I_{S2}/I_C = \frac{1/2 n(n-1)Z^2}{(1 + n(n-1)Z^2)} \quad (3.15)
\]

where \( Z = p_\beta/2p_y \).

The \( I_{S1}/I_C \) ratio for environments bonded to \( n \) atoms of Se, Te or Pb and the \( I_{S2}/I_C \) ratio for Pb, have been calculated using formulae (3.13) and (3.14) are listed in Table 3.3.

(ii) **The A\(_n\) System for the Spin-\( \frac{1}{2} \) Isotopes \( ^\alpha A \) and \( ^\beta A \)**

For systems in which an element has two spin-\( \frac{1}{2} \) isotopes, \( ^\alpha A \) and \( ^\beta A \), with different gyromagnetic ratios, the resulting magnetic nonequivalence allows observation of the spin-spin coupling between the two isotopes even though they belong to a group in which the atoms are all chemically
Table 3.3
Satellite Peak/Central Peak Intensity Ratios for n Mutually Bonded Se, Te and Pb Atoms

<table>
<thead>
<tr>
<th>n</th>
<th>77_{Se}^b</th>
<th>125_{Te}^c</th>
<th>123_{Te} + 125_{Te}^d</th>
<th>207_{Pb}^e (%)</th>
<th>(\frac{I_{S1}}{I_C}) (%)</th>
<th>(\frac{I_{S2}}{I_C}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.1</td>
<td>3.8</td>
<td>4.3</td>
<td>14.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.2</td>
<td>7.6</td>
<td>8.5</td>
<td>28.0</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>12.2</td>
<td>11.3</td>
<td>12.7</td>
<td>39.7</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>16.2</td>
<td>15.0</td>
<td>16.8</td>
<td>49.5</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20.0</td>
<td>18.6</td>
<td>20.8</td>
<td>57.7</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>23.8</td>
<td>22.1</td>
<td>24.7</td>
<td>64.8</td>
<td>19.5</td>
<td></td>
</tr>
</tbody>
</table>

a Calculated using equations (3.14) and (3.15).
b \(P_{77} = 0.0758\) and \(P_y = 0.9242\).
c \(P_{125} = 0.0699\) and \(P_y = 0.9214\).
d In cases when the \(125\) Te and \(123\) Te coupling constants cannot be resolved: \(P_{123}/125 = 0.0786\) and \(P_y = 0.9214\).
e \(P_{207} = 0.226\) and \(P_y = 0.774\).
equivalent. As was discussed in the introduction, these types of spin systems were considered by Rudolph and co-workers\textsuperscript{40} for fluxional naked tin clusters of nuclearity \( n = 2 - 12 \), such as the \( \text{Sn}_9^4^- \) anion, where all the tin atoms are equivalent on the NMR time scale and only \( ^{117}\text{Sn}-^{119}\text{Sn} \) spin-spin coupling was observed.

As was the case for the \( A_kY_n \) system, it would be convenient to also derive a simpler equation for the satellite peak/central peak ratios in order to be able to determine the number of chemically equivalent atoms \( n \) in \( A_n \) when only one type of spin coupling exists between two spin-\( \frac{1}{2} \) isotopes of different gyromagnetic ratios within a group of chemically equivalent nuclei. As before, equation (3.4) can be used to obtain the probability of the isotopomer \( \alpha_A^i\beta_A^j\alpha_A^{n-i-j} \)

\[
P(i,j) = n_{c_{i,j}} (p_\alpha)^i (p_\beta)^j (p_\alpha)^{n-i-j} \quad (3.16)
\]

where \( p_\alpha, p_\beta \) and \( p_\alpha \) are the abundances of isotopes \( \alpha_A, \beta_A \) and the NMR-inactive isotopes, respectively, and

\[
n_{c_{i,j}} = \frac{n!}{i!j!(n-i-j)!} \quad (3.17)
\]

For a group of \( n \) atoms which are chemically equivalent on the NMR time scale, the \( \alpha_A \) NMR spectrum will, as before, consist of a single peak and satellite doublet arising from spin
coupling to the relatively low abundance $^{13}\text{A}$ isotope. The intensity of the central line, $I_C(i,j)$, arising from the multiplet resulting from an even number of $^{13}\text{A}$ is given by

$$I_C(i,j) = P(i,j) \, i \, 2^{-j} \frac{j!}{(j/2)!(j/2)!} \tag{3.18}$$

For a given value of $j$, all the isotopomers with the same value of $j$, but varying numbers of $i$, will give the same $^{13}\text{A}$ NMR spectrum so one can consequently sum over all possible values of $i$

$$I_C(j) = \sum_{i=1}^{(n-j)} I_C(i,j) \tag{3.19}$$

where values of $j = 0, 2, 4, \ldots$ contribute to the central line intensity, $I_C$. Note that the maximum value for $j$ is $(n-1)$ and not $n$ as at least one isotope of $^{13}\text{A}$ must be present in the isotopomer in order to observe the $^{13}\text{A}$ NMR spectrum. Finally, one obtains, after algebraic manipulation, the total intensity for the central line given by

$$I_C = n \, p_\alpha \, \sum_{j=0}^{\leq(n-1)} \frac{(n-1)!}{j!((n-1)-j)!} \, p_\beta^j (1-p_\beta)^{n-j-1} \, j \, M_0 \tag{3.20}$$

where $p_\alpha = (1-p_\alpha-p_\beta)$. Equation (3.20) is, of the same form as equation (3.12) and the intensity of the first satellite
pair, $I_{S1}$, can be calculated by the same procedure as given for $I_C$ yielding

$$I_{S1} = n \sum_{j=1}^{\leq(n-1)} p_\alpha \frac{(n-1)!}{j!(n-1-j)!} p_\beta^j (1-p_\beta)^{n-1-j} J_{M_1}$$

(3.21)

where the sum is same as that given by equation (3.13). Consequently, the satellite peak/central peak ratio, $I_{S1}/I_C$, can be calculated as before, i.e., by including only contributions from the singlet, doublet, triplet and quartet giving

$$I_{S1}/I_C = (n-1) Y \left( \frac{1 + (n-2)(n-3)Y^2/2}{1 + (n-1)(n-2)Y^2} \right)$$

(3.22)

where $Y = p_\beta/2(1 - p_\beta)$.

The $^{117}$Sn ($^{119}$Sn) satellite peak/central peak ratios in the $^{119}$Sn ($^{117}$Sn) NMR spectra have been calculated for n chemically equivalent n tin atom clusters ($n = 2 - 10$) using equation (3.22) and are listed in Table 3.4 along with those calculated by Rudolph et al. for comparison.

(iii) The $AX_nY_m$ System for the Spin-1/2 Isotopes $^\alpha X$ and $^\beta Y$

The NMR spectrum of a NMR-active isotope of A will have, as before, an intense central line, but now there are two pairs of satellites owing to the spin couplings $J(\alpha X-A)$ and $J(\beta Y-A)$ arising from spin dilute spin-1/2 isotopes $^\alpha X$ and
Table 3.4

$^{119}\text{Sn}$ and $^{117}\text{Sn}$ Satellite Peak/Central Peak Ratios \(^a\)

for Fluxional Sn\(_{n}\)\(^{K-}\) and MSn\(_{n}\)\(^{F-}\) Clusters

<table>
<thead>
<tr>
<th>(n)</th>
<th>(^{119}\text{Sn} ) Spectrum</th>
<th>(^{117}\text{Sn} ) Spectrum</th>
<th>M Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>117\text{Sn} b c</td>
<td>119\text{Sn} b</td>
<td>117\text{Sn} / 119\text{Sn} d c</td>
</tr>
<tr>
<td>1</td>
<td>- -</td>
<td>-</td>
<td>4.5/5.1 4.5/5.1</td>
</tr>
<tr>
<td>2</td>
<td>4.1 4.1</td>
<td>4.7</td>
<td>9.0/10.1 9.2/10.4</td>
</tr>
<tr>
<td>3</td>
<td>8.2 8.2</td>
<td>9.3</td>
<td>13.4/15.0 13.9/15.6</td>
</tr>
<tr>
<td>4</td>
<td>12.3 12.2</td>
<td>13.9</td>
<td>17.6/19.8 18.6/20.7</td>
</tr>
<tr>
<td>5</td>
<td>16.2 16.2</td>
<td>18.4</td>
<td>21.7/24.3 22.9/25.4</td>
</tr>
<tr>
<td>6</td>
<td>20.1 20.1</td>
<td>22.8</td>
<td>25.7/28.7 26.7/29.8</td>
</tr>
<tr>
<td>7</td>
<td>23.9 23.9</td>
<td>27.0</td>
<td>29.5/33.0 30.6/33.4</td>
</tr>
<tr>
<td>8</td>
<td>27.6 27.6</td>
<td>31.1</td>
<td>33.2/37.0 34.0/37.5</td>
</tr>
<tr>
<td>9</td>
<td>31.1 31.2</td>
<td>35.0</td>
<td>36.9/41.0 37.3/41.0</td>
</tr>
<tr>
<td>10</td>
<td>34.6 34.5</td>
<td>38.7</td>
<td>40.4/44.8 40.0/44.1</td>
</tr>
</tbody>
</table>

\(a\) Natural abundances: 8.58\% (\(^{119}\text{Sn}\)), 7.61\% (\(^{117}\text{Sn}\)) and 83.81\% (\(^{123}\text{Sn}\)).

\(b\) Calculated by equation (3.22).

\(c\) Reference (40).

\(d\) Calculated by equation (3.27).
\( \beta_y \). By calculating the probabilities of the different isotopomers and summing up, as before, the intensities for the central line, \( I_C \), and the first satellite pairs arising from \( \alpha_x \) and \( \beta_y \) coupling, \( I_{XS1} \) and \( I_{YS1} \), respectively, one obtains similar expressions for the satellite peak/central peak intensity ratios as in equation (3.14), i.e.

\[
I_{XS1}/I_C = n \ Z_x \ \left( \frac{1 + (n-1)(n-2)Z_x^2/2}{1 + n(n-1)Z_x^2} \right) \quad (3.23)
\]

\[
I_{YS1}/I_C = m \ Z_y \ \left( \frac{1 + (m-1)(m-2)Z_y^2/2}{1 + m(m-1)Z_y^2} \right) \quad (3.24)
\]

However, equations (3.23) and (3.24) are only valid if the two coupling constants \( J(\alpha_x-A) \) and \( J(\beta_y-A) \) are not equal or one of the couplings is not a whole number multiple of the other.

(iiv) **The A\_XN System for the Spin\-\( \frac{1}{2} \) Isotopes \( \alpha_A, \beta_A \) and \( J_X \)**

For an \( A_X N \) system comprised of two chemically equivalent groups there are three unique coupling constants, \( J(\alpha_A-\beta_A) \), \( J(\alpha_A-\tau X) \) and \( J(\beta_A-\tau X) \). The intensities of the satellite peaks arising from \( \alpha_A-\tau X \) and \( \alpha_A-\beta_A \) couplings in the \( \alpha_A \) (or \( \beta_A \)) NMR spectrum can be calculated by methods similar to those described above. One obtains expressions for the \( I_{XS1}/I_C \) and \( I_{AS1}/I_C \) ratios that are identical to
equations (3.14) and (3.22), respectively. However, as was the case for the \( AX_nY_m \) system, the coupling constants cannot be equal nor can they be whole number multiples of one another.

To calculate the intensities of multiplets in the \(^7\text{X}\) NMR spectrum, the central peak and the satellites arising from \( \alpha_A \) and \( \beta_A \), only the probabilities of the isotopomers, \( \alpha_{A_i}\beta_{A_j}^{nA}A_k\)–\( i-j \), of \( A_k \), i.e., \( P(i,j) \), need be considered (see equation (3.16)). If the two coupling constants, \( J(\alpha_A-^7\text{X}) \) and \( J(\beta_A-^7\text{X}) \) do not overlap, the intensities of the central line, \( I_C \), and one of the satellite peaks, \( I_{\alpha\text{S}1} \), are given by

\[
I_C = \sum_{j=0}^{k-j} \sum_{i=0}^{k-j} P_A(i,j) \times M_0 \quad \text{for even } i,j \quad \text{and even } k \quad (3.25)
\]

\[
I_{\alpha\text{S}1} = \sum_{j=0}^{k} \sum_{i=1}^{k-j} P_A(i,j) \times M_1 \quad \text{for even } i, j \quad \text{and odd } k \quad (3.26)
\]

If both spin-\( \frac{1}{2} \) isotopes of A are of relatively low abundance, expressions (3.25) and (3.26) can be approximated by including only the isotope combination \( (i,j) = (0,0), (2,0) \) and \( (0,2) \) for \( I_C \); and \( (1,0), (3,0) \) and \( (1,2) \) for \( I_{\alpha\text{S}1} \). After algebraic manipulation one arrives at the following expression for the satellite peak/central peak ratio
\[ \frac{I_{\alpha S1}}{I_C} = k z_\alpha \left( \frac{1 + \frac{1}{2}(k-1)(k-2)\left( \frac{z_\alpha^2}{z_\alpha^2} + 2 \frac{z_\beta^2}{z_\beta^2} \right)}{1 + k(k-1)\left( \frac{z_\alpha^2}{z_\alpha^2} + \frac{z_\beta^2}{z_\beta^2} \right)} \right) \]  

(3.27)

where \( z_\alpha = p_\alpha^2/2p_\alpha \), \( z_\beta = p_\beta^2/2p_\alpha \) and \( p_\alpha = (1-p_\alpha-p_\beta) \).

The \(^{117}\text{Sn}\) and \(^{119}\text{Sn}\) satellite intensity ratios in the M NMR spectrum of fluxional MSn\(_n\)\(^{-}\) type clusters have been calculated using equation (3.27) and are given in Table 3.4 along with the values calculated by Rudolph et al.\(^{40}\)

**CONCLUSIONS**

Relatively simple expressions (eq. (3.14) and (3.22)) for the satellite peak/central peak ratios as a function of the number of atoms bonded to the nucleus of interest have been obtained for the more common systems \( A_kY_n \) and \( A_n \). Furthermore, the same equations can be applied to \( AX_nY_m \) NMR spectra and to the \( ^\alpha A \) (or \( ^\beta A \)) NMR spectrum of the \( A_kX_n \) system (where \( ^\alpha A \), \( ^\beta A \) and \( ^\gamma X \) are spin-\( \frac{1}{2} \) isotopes) provided the coupling constants are not whole number ratios of one another. A somewhat different expression (eq. (3.27) is obtained for the \( I_{\alpha S1}/I_C \) ratio in the \( ^\gamma X \) NMR spectrum for the \( A_kX_n \) system. As equations (3.14), (3.22) and (3.27) only include contributions from a singlet, doublet and triplet, one can expect deviations when the number of neighboring atoms increases and/or the abundance of the spin-\( \frac{1}{2} \) isotope
increases. However, the equations can be modified by including the contributions of a quartet, quintet and higher multiplets to the central and satellite peak intensities.

In general, equations (3.14), (3.22) and (3.27) only apply if isotopomers of the same isotopic composition have identical NMR spectra. Furthermore, they are only valid if all the NMR subspectra are first order and the multiplets arise from spin couplings to spin-½ isotopes. If the NMR spectra of some of the isotopomers are second order then the spectrum of each isotopomer has to be calculated individually, multiplied by its isotopomer probability and the NMR spectra of all the isotopomers superimposed in order to obtain the final NMR spectrum of the molecule or ion. Although this can be a very tedious procedure, in most cases one only has to consider the subspectra of the most probable isotopomers, i.e., isotopomers with no more than three low abundance spin-½ isotopes.

When the satellites arise from a spin coupling to quadrupolar nuclei, the equations obtained in the previous sections cannot be used as the Pascal's triangle pattern only applies for spin-½ nuclei. However, for first order spectra one can obtain a similar kind of triangular form for the multiplet pattern and derive a expression for the multiplet line intensities, similar to the $^{1}M_{J}$- factors in Pascal's triangle.84
CHAPTER 4

DILEAD(II) CHALCOGENIDE ANIONS Pb₂Ch₂⁻ (Ch = Se, Te)

INTRODUCTION

Although much of the earlier work on Zintl anions has produced cluster, cage and ring cluster species,⁶⁵ it was soon apparent that extraction of Zintl alloys of mixtures of electropositive elements such as Hg, Tl, Sn or As and electronegative elements such as Se or Te in ethylenediamine produce classical anions, e.g., HgTe₂²⁻,⁴⁵ SnTe₄⁴⁻ ³⁹,⁸⁵ and As₂Se₆²⁻ ⁴⁶ (see also ref. (48)). A similar extraction of the alloys KM(Te/Se) or NaM(Te/Se), where M = Hg, Cd, Tl, or Sn, with en or NH₃(l) in the presence of 2,2,2-crypt gave rise to solutions containing HgCh₂²⁻, SnCh₃²⁻, TlCh₃³⁻, SnCh₄⁴⁻ and Tl₂Ch₂²⁻ where Ch = Se and/or Te.⁴⁹ The cryptand served mainly to enhance the rate of solution extraction of the alkali metal alloy and the solubility of the anion species. All of the species could be structurally characterized in solution by direct NMR observation of the naturally abundant and/or enriched spin-½ isotopes ²⁰₃,²⁰₅Tl, ¹⁹⁹Hg, ¹¹⁹Sn, ⁷⁷Se and ¹²⁵Te. This solution study showed that multinuclear magnetic resonance spectroscopy was well-suited to the rapid and representative characterization
of the chemistry of solution extracts of Zintl anions. In addition, invaluable information on the nature of the metal-chalcogen bonds in these species was obtained from the hetero- and homonuclear spin-spin coupling constants.

In view of the successes which established the existence of the mixed series of classically bonded tin (IV) species SnCh$_3$$^2$- (trigonal planar) and SnCh$_4$$^4$- (tetrahedral)$^{49}$ in en solution using NMR spectroscopy, it was of interest if these studies could be extended to the lead chalcogenide anions. As all of the previously established tin chalcogenide anions contain tin in its +4 oxidation state, it might be anticipated that by virtue of lead's propensity for the +2 oxidation state it should exhibit a novel chalcogenide anion chemistry of its own.

RESULTS AND DISCUSSION

(A) NMR SPECTROSCOPY OF THE Pb$_2$Se$_n$Te$_3$-n$^2$- (n = ≤3) ANIONS

(i) Structural Characterization by NMR Spectroscopy

The experimental approach involved the syntheses of the quaternary alloys K$_{0.54}$Te$_{0.33}$Se$_{0.67}$ and K$_{0.65}$Te$_{0.67}$Se$_{0.33}$ by fusion of the elements. Subsequent extraction in en in the presence of a slight excess of 2,2,2-crypt resulted in dark-red colored solutions although the Te-rich solution produced a more brownish-red color. In all cases a residual solid remained after extraction, but
these residues were not investigated in view of the lack of data concerning the appropriate quaternary systems except to note that they were, like the initial alloy compositions, hydrolytically unstable.

Identification of the Zintl anions present in the en extracts was accomplished by direct NMR observation of the spin-½ nuclides $^{207}\text{Pb}$, $^{125}\text{Te}$ and $^{77}\text{Se}$ at their natural abundance levels. The solutions, when isolated from the alloy residues, yielded a total of four $^{207}\text{Pb}$, three $^{125}\text{Te}$ and three $^{77}\text{Se}$ environments with accompanying satellite spectra (Figures 4.1, 4.2 and 4.3). In addition, the $^{77}\text{Se}$ spectrum exhibited one intense resonance without satellites. As the chemical shift is identical to the one observed from the extraction of $\text{K}_2\text{Se}$ in en in the presence of 2,2,2-crypt, the signal is assigned to $\text{Se}^{2-}$ (Chapter 5). A comparison of the magnitudes of the satellite doublet spacings in each spectrum yielded the one-bond scalar couplings $J(^{207}\text{Pb}-^{77}\text{Se})$ and $J(^{207}\text{Pb}-^{125}\text{Te})$, and from the latter it was possible to identify the set of $^{207}\text{Pb}$, $^{125}\text{Te}$ and $^{77}\text{Se}$ chemical shifts corresponding to each new species. Comparison of the satellite peak/central peak area (integrated or peak height), ratios, $I_s/I_c$, in the $^{207}\text{Pb}$ spectra with the calculated ratios gave the total number of Se or Te atoms bonded to each Pb environment. Owing to the smaller magnetogyric ratio of $^{77}\text{Se}$ compared to that of $^{125}\text{Te}$, the former satellite lines
Figure 4.1 $^{207}\text{Pb}$ NMR spectra (52.174 MHz) of the Pb$_2$Ch$_3$$^{2-}$ series: (A) Pb$_2$Se$_3$$^{2-}$; (B) Pb$_2$Se$_2$Te$_2$$^{2-}$; (C) Pb$_2$Se$_2$Te$_2$$^{2-}$; (D) Pb$_2$Te$_3$$^{2-}$. Peaks a', b' and c' $^{77}\text{Se}$ satellites; peaks b'', c'' and d'' $^{125}\text{Te}$ satellites.
Figure 4.2 $^{125}$Te NMR spectrum (78.917 MHz) of the Pb$_2$Ch$_3^{2-}$ series. (B) Pb$_2$Se$_2$Te$_2^{2-}$; (C) Pb$_2$SeTe$_2^{2-}$; (D) Pb$_2$Te$_3^{2-}$. Peaks b'', c'' and d'' $^{207}$Pb satellites.
Figure 4.3 $^{77}\text{Se}$ NMR spectrum (47.704 MHz) of the Pb$_2$CH$_3$$^{2-}$ series. (A) Pb$_2$Se$_3$$^{2-}$; (B) Pb$_2$Se$_2$Te$_2$$^{2-}$; (C) Pb$_2$SeTe$_2$$^{2-}$. Peaks a', b' and c' 207pb satellites. Peak S corresponds to Se$^{2-}$. 
were always innermost and well separated from the $^{125}\text{Te}$ lines. The number of Se atoms, $n$, or Te atoms, $m$, bonded to each Pb atom was found to be $n = 0 - 3$ or $m = 0 - 3$ such that $n + m = 3$. Since only four lead-containing species were observed, the spectra of the species formed are assigned to the four mixed Se/Te species $\text{Pb}_x\text{Se}_n\text{Te}_{3-n}^2^-$. Additional information concerning the nature of these species is obtained from the lead satellite peak/central peak area ratios in the $^{77}\text{Se}$ NMR spectra and the corresponding ratios in the $^{125}\text{Te}$ NMR spectra, allowing the conclusion that the three chalcogen atoms were equivalently bonded to two lead atoms (Table 4.1). As the most common and stable oxidation state of lead is +2 and each chalcogen atom may be assumed to possess a formal oxidation state of $-2$, it can be inferred that the anions are dinegative, that is, they consist of the series of dinuclear lead chalcogenide anions $\text{Pb}_2\text{Se}_n\text{Te}_{3-n}^2^-$. In addition, it is found that plots of the $^{207}\text{Pb}$, $^{77}\text{Se}$ and $^{125}\text{Te}$ chemical shifts and $^{207}\text{Pb}$-$^{77}\text{Se}$ and $^{207}\text{Pb}$-$^{125}\text{Te}$ coupling constants versus the number of chalcogen atom substituents are near linear, further indicating the series is homologous and isostructural (see below). The structure, which is consistent with the NMR findings, is based upon a trigonal bipyramid with the chalcogen atoms occupying the equational positions and bonded to two Pb atoms in the apical positions (Structure I).
(ii) Chemical Shift Trends

The general trend found in this work with respect to the electropositive Pb atom nucleus is that a decrease in the total electron withdrawing ability of the ligand atoms attached to the lead atoms results in a near-additive increase in the lead shielding (Table 4.1). This behavior parallels that exhibited by central atom nuclei in other classically bonded chalcogenide anions, i.e., Cd\(\text{CH}_2\)\(^2\), Hg\(\text{CH}_2\)\(^2\), Tl\(\text{CH}_3\)\(^3\), Sn\(\text{CH}_3\)\(^2\) and Sn\(\text{CH}_4\)\(^4\).\(^{49}\) For the Pb\(_2\text{Se}_n\text{Te}_3\)\(^n\) series of anions, the \(^{125}\text{Te}\) and \(^{77}\text{Se}\) chemical shift trends, like that of \(^{207}\text{Pb}\), also show near-additive decreases in their shieldings on increasing the total ligand electronegativity (Table 4.1). Interestingly, these trends in chalcogen shieldings are opposite to those previously observed in the Cd, Hg, Tl and Sn series\(^{49}\) of chalcogenide anions. As was discussed in Chapter 1, the unexpected trend
<table>
<thead>
<tr>
<th>Anion</th>
<th>$^{207}$Pb</th>
<th>$^{77}$Se</th>
<th>$^{125}$Te</th>
<th>$^{207}$Pb-$^{77}$Se</th>
<th>$^{207}$Pb-$^{125}$Te</th>
<th>$^{1}J_{\text{Rb-Te}}^{b}$(Hz)</th>
<th>$^{1}J_{\text{Rb-Te}}^{c}$(Hz)</th>
<th>$^{1}J_{\text{Rb-Te}}^{c}$(Hz)</th>
<th>$^{1}J_{\text{Rb-Te}}^{c}$(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PbSeO}_{3}^{2-}$</td>
<td>3290</td>
<td>-99.4</td>
<td></td>
<td>149</td>
<td>(145)</td>
<td>12 ±1c</td>
<td>28d</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3353)</td>
<td>(-99.6)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\text{Rb}<em>{2}\text{SeO}</em>{2}^{2-}$</td>
<td>2894</td>
<td>-190.0</td>
<td>-699.2</td>
<td>188</td>
<td>(188)</td>
<td>3 ±1c,e</td>
<td>29 ±1d</td>
<td>29 ±3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2832)</td>
<td>(-189.7)</td>
<td>(-700.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Rb}<em>{2}\text{SeO}</em>{2}^{2-}$</td>
<td>2375</td>
<td>-279.7</td>
<td>-817.0</td>
<td>227</td>
<td>(227)</td>
<td>8 ±1c,e</td>
<td>32 ±1d</td>
<td>26 ±2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2311)</td>
<td>(-278.8)</td>
<td>(814.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Rb}<em>{2}\text{Te}</em>{2}^{2-}$</td>
<td>1727</td>
<td></td>
<td>-927.1</td>
<td></td>
<td>1070</td>
<td>12 ±1.6d</td>
<td>30 ±3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1790)</td>
<td></td>
<td>(-928.4)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>af</td>
<td>1790.3</td>
<td>-370.0</td>
<td>-928.5</td>
<td>226</td>
<td>1070</td>
<td></td>
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<td>fb</td>
<td>520.8</td>
<td>90.15</td>
<td>114.0</td>
<td>-39.0</td>
<td>-77.5</td>
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<tr>
<td>rf</td>
<td>0.993</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

---

a Calculated values in parentheses; estimated errors in $^{207}$Pb-$^{77}$Se and $^{207}$Pb-$^{125}$Te are ±2 and ±12 Hz, respectively.

b Theoretical ratio in parentheses.

c Ratio measured from the integrated peak areas.

d Ratio measured from the peak heights.

e Value given for the $^{125}$Te satellites only; the $^{77}$Se satellites overlap extensively with the central peak.

f Linear least squares regression analysis: $\delta = a + bn$ and $^{1}J_{\text{Rb-Te}} = a + bn$, where $n =$ number of Te atoms in the anion and $R$ is the correlation coefficient.
observed for the latter series of anions can be rationalized as being due to a small \( \pi \)-back bonding contribution from the terminal chalcogen atom to the central metal atom. However, a similar \( \pi \)-back bonding contribution for the two-coordinated Ch atom of the \( \text{Pb}_2\text{Ch}_3^2^- \) anions would be expected to be insignificant. The observed chalcogen chemical shift trends for the \( \text{Pb}_2\text{Ch}_3^2^- \) series are therefore as expected, where the chemical shielding increases with decreasing electron unbalance for the chalcogen atom.

For the series of \( \text{Pb}_2\text{Se}_n\text{Te}_{3-n}^2^- \) anions, each component nucleus was subjected to a linear least-squares regression analysis of its chemical shift as a function of \( n \), the number of selenium substituent atoms when \( n \leq 3 \). It was found that the calculated values for the chemical shifts were generally in excellent agreement with the observed shifts (Table 4.1). Thus, their additivity supports the assignments of these species using the criteria originally used for their identification. The additivity of chemical shifts in this series of anions is also illustrated by the correlation factors (given in Table 4.1). This agreement is helped by the fact that no significant concentration dependence of chemical shifts (or coupling constants) was noted for any of these species.
(iii) **Coupling Constants \( ^1J, ^1K \) and \( ^1K_{RC} \)**

The spin-spin coupling constants \( ^1J(^{207}\text{Pb}-^{77}\text{Se}) \) and \( ^1J(^{207}\text{Pb}-^{125}\text{Te}) \) are also directly additive and decrease with increasing total electron withdrawing ability of the ligand atoms or \( n \), the number of selenium atoms. The trend is the same as that observed previously for \( \text{HgCH}_2^{2-} \) but opposite to those trends observed for \( \text{TlCH}_3^{3-} \), \( \text{SnCH}_3^{2-} \) and \( \text{SnCH}_4^{4-} \).

The nuclear spin-spin coupling interaction results from a correlation of nuclear spins arising out of their interaction with the surrounding electrons. In high-resolution NMR spectroscopy one-bond spin-spin coupling is usually dominated by the Fermi contact mechanism.\(^{77}\) This mechanism is dependent upon the \( s \) character of the bond between the two coupled nuclei A and B as has been discussed in Section D(iii) Chapter 1. However, in order to compare coupling constants between different elements, the reduced coupling constant, \( nK(A-B) \), must be used as nuclear-dependent terms have been factored out (Chapter 1). The reduced one-bond coupling constants for the \( \text{Pb}_2\text{CH}_3^{2-} \) and \( \text{Tl}_2\text{CH}_2^{2-} \) anion series are given in Table 4.2. Although the reduced coupling constants are comparable within each chalcogen series, \( ^1K(\text{Pb-Se}) \) and \( ^1K(\text{Pb-Te}) \), there is a considerable difference between individual \( ^1K(\text{Pb-Se}) \) and \( ^1K(\text{Pb-Te}) \) values. Furthermore, the values of \( ^1K(\text{Pb-Se}) \) and \( ^1K(\text{Pb-Te}) \) for the \( \text{Pb}_2\text{CH}_3^{2-} \) anions are considerably smaller than the
corresponding values for the HgCh₂²⁻, TlCh₃³⁻, SnCh₃²⁻ and SnCh₄⁴⁻ series (Chapter 1). However, relativistic effects can be extremely important when making comparisons between Fermi contact dominated spin-spin couplings involving heavy elements such as Pb, Te and Se. In the case of Pb, in particular, the relativistic effect on s-electron density, \( |\Psi_{\text{rel}}(0)|² \), is very large as this nucleus with \( Z = 82 \) is near Au (\( Z = 79 \)), which exhibits the maximum for relativistic effects. As has been previously noted, these relativistic effects on \( ^1K \) can be factored out by multiplying \( ^1K \) with the ratio \( \left( |\Psi_{\text{rel}}(0)|² \right)_{\text{rel}} / \left( |\Psi_{\text{nonrel}}(0)|² \right)_{\text{nonrel}} \) for each element to obtain the relativistically corrected reduced coupling constant, \( ^1K_{\text{RC}} \). The relativistically corrected reduced coupling constants \( ^1K(\text{Pb-Se})_{\text{RC}} \) and \( ^1K(\text{Pb-Te})_{\text{RC}} \) are given in Table 4.2. In general, \( ^1K(\text{Pb-Se})_{\text{RC}} \) and \( ^1K(\text{Pb-Te})_{\text{RC}} \) are approximately 1/20 to 1/3, respectively, magnitudes of the corresponding \( ^1K_{\text{RC}} \) values for SnCh₄⁴⁻, SnCh₃²⁻, and TlCh₃³⁻. This indicates that the s character of the Pb-Ch bonds is very small for the Pb₂Ch₃²⁻ series.

A previous study of \((\text{CH₃})₃\text{Pb-SeCH₃}\) has yielded a \( ^1J(\text{²⁰⁷Pb-⁷⁷Se}) \) value of \(-1170 ± 100 \) Hz. The calculated absolute value of \( ^1K(\text{Pb-Se})_{\text{RC}} = 68.6 \times 10^{20} \text{ NÅ}^{-2}\text{m}^{-3} \) is consistent with the high s character anticipated for this \( \text{sp}^3 \)-hybridized lead(IV) species and, in fact, agrees reasonably well with \( ^1K(\text{Sn-Se})_{\text{RC}} = 89.9 - 104.1 \times 10^{20} \) and
Table 4.2

Reduced Coupling Constants, $^{1}K$, and Relativistically Corrected Reduced Coupling Constants, $^{1}K_{RC}$, for the Anions Pb$_2$Ch$_3^{2-}$ and Tl$_2$Ch$_2^{2-}$

<table>
<thead>
<tr>
<th>Anion</th>
<th>$^{1}K_{RC}$ (10$^{20}$ NA$^{-2}$m$^{-3}$)</th>
<th>M-Se</th>
<th>M-Te</th>
<th>$^{1}K_{RC}$ (10$^{20}$ NA$^{-2}$m$^{-3}$)</th>
<th>M-Se</th>
<th>M-Te</th>
</tr>
</thead>
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<tr>
<td>Pb$_2$Se$_3^{2-}$</td>
<td>31.1</td>
<td>8.74</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Pb$_2$Se$_3$Te$_2^{2-}$</td>
<td>39.2</td>
<td>115</td>
<td>26.0</td>
<td></td>
<td>11.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Pb$_2$SeTe$_2^{2-}$</td>
<td>47.4</td>
<td>125</td>
<td>28.3</td>
<td></td>
<td>13.3</td>
<td>28.3</td>
</tr>
<tr>
<td>Pb$_2$Te$_3^{2-}$</td>
<td></td>
<td>135</td>
<td>30.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl$_2$Se$_2^{2-}$</td>
<td>171</td>
<td></td>
<td>48.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl$_2$SeTe$_2^{2-}$</td>
<td>159</td>
<td>165</td>
<td>37.5</td>
<td></td>
<td>45.0</td>
<td>37.5</td>
</tr>
<tr>
<td>Tl$_2$Te$_2^{2-}$</td>
<td></td>
<td>366</td>
<td>83.0</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

a M = Pb or Tl.

b Linear least squares regression analyses of $^{1}K$(Pb-Ch)$_{RC}$ = $a_{Ch} + b_{Ch}n$, where n = number of Se atoms in the anion and R is the correlation coefficient: $a_{Se} = 15.6$, $b_{Se} = -2.3$, R = 1.000; $a_{Te} = 30.4$, $b_{Te} = -2.2$, R = 1.000. Values of $a_{Ch}$ and $b_{Ch}$ in units of 10$^{20}$ NA$^{-2}$m$^{-3}$. 
1K(Sn-Te)_{RC} = 98.2 - 123.0 \times 10^{20} \text{NA}^{-2}\text{m}^{-3}\) for the sp\textsuperscript{3}-hybridized series of anions SnCH\textsubscript{4}\textsuperscript{4-}.\textsuperscript{49} This value contrasts with the p-bonded lead(II) cage series Pb\textsubscript{2}CH\textsubscript{3}\textsuperscript{2-} where 1K(Pb-Se)\textsubscript{RC} and 1K(Pb-Te)\textsubscript{RC} are much smaller and in the ranges 8.74 - 13.3 \times 10^{20} and 26.0 - 30.4 \times 10^{20} \text{NA}^{-2}\text{m}^{-3}, respectively. It is therefore apparent that the s characters of the metal-chalcogen bonds are greatly diminished in the trigonal bipyramidal lead(II) anion series Pb\textsubscript{2}CH\textsubscript{3}\textsuperscript{2-} when compared to other classically bonded Zintl species and lead(IV) species. The apparent diminution of s character in the Pb-Ch bonds of Pb\textsubscript{2}CH\textsubscript{3}\textsuperscript{2-} may arise from the inherent cluster-like character of the anions which may rely more heavily upon the use of pure p orbitals for the skeletal bonding. Alternatively, the effect may be viewed as a consequence of geometrical constraints in a classically bonded system. It appears that Pb-Ch-Pb and Ch-Pb-Ch bond angles may be too small to accommodate optimal s-orbital participation in the classical bonding scheme, causing the need to invoke greater p-orbital character in the bonding (see Section B). Furthermore, due to the inert nature of the 6s\textsuperscript{2} core of lead(II), the s character of the Pb-Ch bonds is expected to be greatly diminished. Thus, the 1K_{RC} values are overall significantly smaller than in the previously cited mononuclear cases where the formal oxidation states of the electropositive central metals are high, geometrical
constraints are lacking and the valence s-electron pairs of the central metal atoms are formally involved in classical hybridization schemes possessing significant s character, i.e., sp (MCh₂²⁻), sp² (MCh₃²⁻, z = 2 or 3) and sp³ (SnCh₄⁴⁻).

The butterfly shaped Tl₂Te₂²⁻ anion³³ may be regarded as a close structural relative to the Pb₂Ch₃²⁻ series whereas one of the vertices occupied by a chalcogen atom has been left vacant in Tl₂Te₂²⁻. Again, the Te-Tl-Te bond angles (ave: 97°, c.f. Tl-Te-Tl: 75°) are, as in Pb₂Se₃²⁻ and Pb₂Te₃²⁻ (see Section B), considerably less than the ideal tetrahedral angle and are, in fact, closer to the ideal 90° angle indicative of metal pure p-valence-orbital involvement in the bonding scheme and inertness of the 6s² pair. Again, this view is supported by comparisons of ¹K(Tl-Ch)RC among the trigonal planar (formally sp²-hybridized Tl valence orbitals) TlCh₃³⁻ and the Tl₂Ch₂²⁻ series (Table 4.2) where the former series are found to possess substantially larger ¹K(Tl-Ch)RC values than the Tl₂Te₂²⁻ series. The validity of assigning an sp² hybridization scheme to TlCh₃³⁻ presumes extensive involvement of the 6s² core in bonding and is supported by the close similarity of ¹K(Sn-Ch)RC values of the SnCh₃²⁻ series (136 - 174 x 10²⁰ NA⁻²m⁻³) and those of the TlCh₃³⁻ series (146 - 184 x 10²⁰ NA⁻²m⁻³). An interesting comparison can be made between the Tl₂Ch₂²⁻ and
Pb$_2$Ch$_3^{2-}$ series in that overall, the values of $^1$K(Tl-Ch)$_{RC}$ are significantly larger than $^1$K(Pb-Ch)$_{RC}$ values, which correlates well with Ch-M-Ch bond angles in Pb$_2$Ch$_3^{2-}$ (ave Se-Pb-Se = 90°, ave Te-Pb-Te = 92°, see Section B) and Tl$_2$Te$_2^{2-}$ (ave Te-Tl-Te = 97°) and which argues for significantly higher p character for the M-Ch bonds in the Pb$_2$Ch$_3^{2-}$ series.

(B) CRYSTAL STRUCTURES AND BONDING

(i) (2,2,2-crypt-K$^+$)$_2$Pb$_2$Se$_3^{2-}$

Crystals of (2,2,2-crypt-K$^+$)$_2$Pb$_2$Se$_3^{2-}$ consist of an ordered assembly of discrete cryptated potassium ions and Pb$_2$Se$_3^{2-}$ anions. The crystal data is given in Table 4.3. The most interesting aspect of the structure is the anion; a flattened trigonal bipyramidal shape of approximately D$_{3h}$ symmetry (Figure 4.4). The atomic distances and bond angles for the Pb$_2$Se$_3^{2-}$ anion are given in Table 4.4. The Pb atoms are in apical positions and the Se atoms in equatorial positions, in agreement with the gross structure deduced from the solution NMR studies. Perhaps one of the more interesting features of the Pb$_2$Se$_3^{2-}$ structure is the short Pb(1)–Pb(2) distance of 3.184 (3) Å. While the equatorial Se⋯Se distances of 3.81, 3.89 and 3.95 Å are close to van der Waals contact distances (3.8 Å) and comply with localized valence bond Structure I, the Pb(1)–Pb(2) distance is
<table>
<thead>
<tr>
<th>Compound</th>
<th>((2,2,2-\text{K}^+)_2\text{Pb}_2\text{Se}_3^{2-})</th>
<th>((2,2,2-\text{K}^+)_2\text{Pb}_2\text{Te}_3^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(\text{C}<em>{36}\text{H}</em>{72}\text{K}_2\text{N}<em>4\text{O}</em>{12}\text{Pb}_2\text{Se}_3)</td>
<td>(\text{C}<em>{36}\text{H}</em>{72}\text{K}_2\text{N}<em>4\text{O}</em>{12}\text{Pb}_2\text{Te}_3)</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1482.5</td>
<td>1628.3</td>
</tr>
<tr>
<td>System</td>
<td>Monoclinic</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Space Group</td>
<td>(\text{P}2_1/n) (no. 14)</td>
<td>(\text{P}3\text{cl}) (no. 165)</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>10.320(4)</td>
<td>11.828(3)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>47.011(11)</td>
<td></td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>11.430(4)</td>
<td>21.889(4)</td>
</tr>
<tr>
<td>(\beta) (deg)</td>
<td>90.25(4)</td>
<td></td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>5545</td>
<td>2652</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>(F(000))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\rho_{\text{calcd}}) (g cm(^{-3}))</td>
<td>1.78</td>
<td>2.04</td>
</tr>
<tr>
<td>(\lambda) (Å)</td>
<td>0.71069</td>
<td>0.71069</td>
</tr>
<tr>
<td>(\mu) (Mo Kα), (cm(^{-1}))</td>
<td>82.6</td>
<td>114</td>
</tr>
<tr>
<td>Total no. data colld</td>
<td>10,457</td>
<td>10,717</td>
</tr>
<tr>
<td>Unique data</td>
<td>8087</td>
<td>4511</td>
</tr>
<tr>
<td>No. observed data</td>
<td>(3956) (I ≥ 3σ(I))</td>
<td>(686) (I ≥ 3σ(I))</td>
</tr>
<tr>
<td>(R_1)</td>
<td>0.1184</td>
<td>0.0683</td>
</tr>
<tr>
<td>(R_2)</td>
<td>0.1265</td>
<td>0.1032</td>
</tr>
</tbody>
</table>
Figure 4.4 ORTEP view of the Pb$_2$Se$_3^{2-}$ anion including the atomic numbering scheme with thermal ellipsoids drawn at 50% probability.
Table 4.4
Atomic Distances and Bond Angles

for the Pb$_2$Se$_3^{2-}$ Anion

<table>
<thead>
<tr>
<th>Atomic Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(1)–Se(1) 2.743 (5)</td>
</tr>
<tr>
<td>Pb(1)–Se(2) 2.768 (5)</td>
</tr>
<tr>
<td>Pb(1)–Se(3) 2.792 (8)</td>
</tr>
<tr>
<td>Pb(1)⋯⋯Pb(2) 3.184 (3)</td>
</tr>
<tr>
<td>Se(1)⋯⋯Se(2) 3.95</td>
</tr>
<tr>
<td>Se(1)⋯⋯Se(3) 3.81</td>
</tr>
<tr>
<td>Se(2)⋯⋯Se(3) 3.89</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(1)–Pb(1)–Se(2) 91.6 (1)</td>
</tr>
<tr>
<td>Se(1)–Pb(1)–Se(3) 87.1 (2)</td>
</tr>
<tr>
<td>Se(2)–Pb(1)–Se(3) 88.7 (2)</td>
</tr>
<tr>
<td>Pb(1)–Se(1)–Pb(2) 70.9(1)</td>
</tr>
<tr>
<td>Pb(1)–Se(2)–Pb(2) 70.8(1)</td>
</tr>
<tr>
<td>Pb(1)–Se(3)–Pb(2) 70.4(1)</td>
</tr>
</tbody>
</table>
significantly less than the van der Waals contact (4.0 Å) and intermediate with respect to the bonding Pb-Pb distances in the structurally related homopolyatomic anion Pb₅²⁻ (equatorial-equatorial distances, 3.24 – 3.32 Å; equatorial-axial distances, 3.00 – 3.08 Å and axial-axial distance, 4.70 Å). Moreover, the Pb-Pb distance in Ph₆Pb₂ is 2.83 (1) Å³ whereas the shortest Pb-Pb distances in the cluster cation in α-(Pb₆O(OH)₆⁴⁺) (ClO₄⁻)·H₂O⁹⁰ are ≥ 3.44 Å and the nearest-neighbor distance in metallic lead is ca. 3.49 Å.¹⁰¹ While it is tempting to consider the present Pb(1)-Pb(2) distance to be a bonding interaction, the short Pb-Pb distance may result from geometrical constraints arising within the trigonal pyramidal PbSe₃ moiety (see Section B(iii)). The Pb-Se bond lengths in Pb₂Se₃²⁻ (which vary widely from 2.726 (5) – 2.792 (8) Å (ave: 2.751 Å) due to the anisotropy in the thermal parameters of the Pb and Se atoms), are similar to the Pb-Se distances in the Pb(SePh)₃⁻ anion (2.727, 2.733 and 2.762 (1) Å)⁹² while significantly longer than the sum of the covalent radii (2.67 Å). The latter value is derived from the covalent radius of Se (1.17Å) and the tetrahedral radius of Pb (1.44 Å).⁹³ Other reported Pb(II)-Se distances for coordination numbers of six and higher at the lead atom are in the range 2.80 – 3.30 Å.⁹⁴ However, when the metallic radius of Pb(II) (1.54 Å)⁹⁵ is employed, substantially better agreement is obtained (2.71 Å)
with our findings and those of Dean et al.\textsuperscript{92} for the Pb(SePh)\textsubscript{3}\textsuperscript{-} anion, although we note that the considerably contracted Pb-Se-Pb angles (70.4 (1), 70.8 (1) and 70.9 (1)\textdegree) would imply that the Pb-Se bonds in the present anion are "bent".

(ii) \( (2,2,2\text{-crypt-}K^+)\textsubscript{2}Pb\textsubscript{2}Te\textsubscript{3}^{2-} \)

As was found for the potassium crypt salt of Pb\textsubscript{2}Se\textsubscript{3}^{2-} the crystals of \( (2,2,2\text{-crypt-}K^+)\textsubscript{2}Pb\textsubscript{2}Te\textsubscript{3}^{2-} \) consist of discrete \( (2,2,2\text{-crypt-}K^+) \) cations and Pb\textsubscript{2}Te\textsubscript{3}^{2-} anions. The crystal data for \( (2,2,2\text{-crypt-}K^+)\textsubscript{2}Pb\textsubscript{2}Te\textsubscript{3}^{2-} \) is given in Table 4.3. The atomic distances and bond angles for the Pb\textsubscript{2}Te\textsubscript{3}^{2-} anion are given in Table 4.5. As expected, the structure of the Pb\textsubscript{2}Te\textsubscript{3}^{2-} anion is a flattened trigonal-bipyramid (Figure 4.5). Furthermore, the Pb-Pb' distance of 3.247 (3) Å for Pb\textsubscript{2}Te\textsubscript{3}^{2-} is also relatively short as was found for the Pb\textsubscript{2}Se\textsubscript{3}^{2-} anion. Interestingly, if the average bond angles of the two anions are compared we note that Se-Pb-Se < Te-Pb-Te and Pb-Se-Pb > Pb-Te-Pb. This trend can be rationalized from the electronegativity difference of Se and Te as one would expect the Ch-Pb-Ch bond angle to decrease and the corresponding Pb-Ch-Pb bond angle to increase with increasing electronegativity of the chalcogen atom. By analogy with the Pb\textsubscript{2}Se\textsubscript{3}^{2-} anion, the Pb-Te bond distances (6 x 2.958 (4) Å) are significantly longer than
Figure 4.5 ORTEP view of the $\text{Pb}_2\text{Te}_3^{2-}$ anion including the atom-numbering scheme. Ellipsoids are drawn at the 50 $\%$ level.
Table 4.5
Selected Atomic Distances and Bond Angles for the Pb\textsubscript{2}Te\textsubscript{3}\textsuperscript{2-} Anion

<table>
<thead>
<tr>
<th>Atomic Distances (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb – Te</td>
<td>2.958 (4)</td>
</tr>
<tr>
<td>Pb⋯⋯Pb'</td>
<td>3.247 (2)</td>
</tr>
<tr>
<td>Te⋯⋯Te</td>
<td>4.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (deg.)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Te – Pb – Te</td>
<td>91.8 (2)</td>
</tr>
<tr>
<td>Pb – Te – Pb'</td>
<td>67.00 (5)</td>
</tr>
</tbody>
</table>
the Pb(IV)-Te single-bond distance (2.81 Å) but are reproduced (2.91 Å) when covalent radii of 1.37 and 1.54 Å is used for Te and Pb(II), respectively.95

(iii) Bonding in Pb₂Ch₂⁻ (Ch = Se and/or Te)

The proposal, discussed in the Section A dealing with the NMR spectroscopy of Pb₂Ch₂⁻ anions, that reduced s character in the Pb-Ch bonding scheme is responsible for the low values of the relativistically corrected reduced spin-spin coupling constants \(^1K_{(Pb-Ch)}\) is further supported by the structures of Pb₂Se₃⁻ and Pb₂Te₃⁻. In this vein, we note the Se-Pb-Se and Te-Pb-Te angles are close to 90°, in accord with substantial 6p-orbital involvement on lead. It is also noteworthy that the average < Pb-Ch-Pb > bond angles (71° and 67° for Ch = Se and Te, respectively) are considerably compressed from the ideal angle of 90° and may be described as bent. In the butterfly-shaped anion Tl₂Te₂⁻ 33 the average Tl-Te-Tl bond angle is again much smaller than 90° (75°) as a consequence of minimization of non-bonded interactions between the tellurium atoms and the predominance of p-orbital bonding for Tl(I). Similar arguments may be made regarding relative s- and p-orbital energies which also hold for Pb-Se and Pb-Te bonding.

The simplest way of looking at the bonding in the Pb₂Se₃⁻ anion is to note the similarity in the Pb-Se
distances and Se-Pb-Se angles between this anion and those in the Pb(SePh)$_3^-$ anion. The lead atom possesses the classical trigonal pyramidal coordination attributable to an AX$_3$E arrangement of three bond pairs and a lone pair about Pb, while the inherent trigonal bipyramidal geometry of the PbSe$_3$ moieties of Pb$_2$Se$_3^2-$ give rise to the short apex-apex Pb-Pb distance. Moreover, the close similarity of the $^{207}$Pb chemical shift of Pb$_2$Se$_3^2-$ (3290 ppm) compared to those of the structurally-related Pb(II) ions Pb(SePh)$_3^-$ (3188 ppm)$^{93,96}$ and Pb[SeP(C$_6$H$_{11}$)$_3$]$_2^{2+}$ (3011 ppm)$^{97}$ is also noteworthy and supports the view that the bonding to Pb in all three species is very similar. Unfortunately, the $^{207}$Pb-$^{77}$Se coupling constant has not been observed in either of the latter ions. On the basis of these considerations, Structure I can be drawn to represent the bonding.

Alternatively, we can use cluster/multicenter bonding arguments and isolobal relationships in drawing an analogy between the Pb$_2$Se$_3^2-$ and Pb$_2$Te$_3^2-$ anions and the structure of Bi$_2$[W(CO)$_5$]$_3$. In the first case, after allowing one exo-skeletal electron pair for each Pb and Se atom, there remains 18 electrons for skeletal bonding. This number of electrons is consistent with a hypho cluster based on an eight-vertex polyhedron with three vertices missing; in the present case, a hexagonal bipyramid with three equatorial positions missing. In the second case, we note
the isovalent relationship between Se (Te) and W(CO)$_5$ and that Bi$_2$ and Pb$_2^{2-}$ are isoelectronic. In the structure of Bi$_2$(W(CO)$_5$)$_3$ there is a Bi$_2$W$_3$ moiety of D$_{3h}$ symmetry in which the Bi-Bi distance of 2.815 (7) Å is 0.26 Å shorter than that in Bi-metal (3.071 Å) and the Bi-W-Bi angle is 54°. In Pb$_2$Se$_3^{2-}$ (Pb$_2$Te$_3^{2-}$) the Pb-Pb distance is 0.31 Å (0.24 Å) less than the nearest neighbor distance in Pb-metal (3.49 Å).\textsuperscript{91}

The two bonding schemes for Pb$_2$Se$_3^{2-}$ anion described above can be reconciled by considering only the 4p and 6p valence orbital energies of Se (-10.8 eV)\textsuperscript{99} and Pb (-6.5 eV)\textsuperscript{99} in a simplified molecular orbital description. As already shown by the NMR spin-spin coupling results, the lead 6s$^2$ core is considered to be inert. The dissociation energy of the diatomic molecule Pb$_2$ has been measured in the gas phase and found to be 1.0 eV.\textsuperscript{100} The dissociation energy of the hypothetical Pb$_2^{2-}$ ion can therefore be estimated to have a maximum of 1.5 eV if we consider the energy of each Pb-Pb bond pair to be 0.5 eV. As a consequence, the 4p atomic orbitals of Se are lower in energy than the bonding molecular orbital of Pb$_2^{2-}$ by at least 3.0 eV. At a large separation of the Se atoms, the species would be better represented as [Pb$^{2+}$]$_2$[Se$^{2-}$]$_3$ rather than as [Pb$_2^{2-}$][Se]$_3$. Therefore, in the cluster-multi-center bonding description, where two Pb/Se valence p orbitals are tangential and one is radial, the six
filled bonding molecular orbitals ($a_1'$, $a_2''$, e' and e") would result in a very small Pb-Pb bond character. The remaining six electrons would occupy the three non-bonding tangential 4p-orbitals in the equatorial plane.

An equivalent molecular orbital description, which also corresponds to the valence bond description, can be arrived at by arranging the 4p (Se) and 6p (Pb) orbitals as follows: for a Se atom two 4p orbitals are directed towards the Pb atoms while the third 4p orbital is tangential and lies in the plane of the three Se atoms and, when filled, defines a lone pair on each Se; for a Pb atom, each of the three 6p orbitals lies along the edges of a PbSe$_3$ trigonal pyramid. In this scheme we consider the interaction of two 4p (Se) and all three 6p (Pb) atomic orbitals, where the third 4p orbital of Se is in the equatorial plane and is therefore nonbonding:
As a result of the interaction of the 4p and 6p atomic orbitals, six strongly bonding molecular orbitals \( a_1', a_2'', e', \text{ and } e'' \) are formed giving a total of six bonding pairs of electrons for the \( \text{Pb}_2\text{Se}_3^{2-} \) anion in accord with simple valence bond Structure I. The same bonding description also applies to the \( \text{Pb}_2\text{Te}_3^{2-} \) anion by considering the 5p orbital of Te \((-9.5 \text{ eV})^{99} \) and the 6p orbitals of Pb. Formally, the above molecular orbital description of the bonding in \( \text{Pb}_2\text{Ch}_3^{2-} \) anions does not allow for s orbital involvement and is in qualitative agreement with the observed magnitudes of the relativistically corrected reduced coupling constants \( ^1K(\text{Pb-Ch})_{RC} \) discussed earlier.

In the above molecular orbital description, the Pb atoms utilize the 6p orbitals in bonding to the Se (Te) atoms. The use of the van der Waals distance of 4.0 Å between the Pb atoms in the \( \text{Pb}_2\text{Se}_3^{2-} \) (\( \text{Pb}_2\text{Te}_3^{2-} \)) anion is therefore not appropriate as that distance includes a contribution from 6p valence orbitals of lead (c.f. reference (33)). One should therefore use the size of the 6s\(^2\) core for lead as the "size" of the Pb core electrons (5d\(^{10}\)6s\(^2\) included). One estimate of the size would be the ionic radius of Pb\(^{2+}\) (1.20 Å).\(^{101}\) A better estimate of the size, as shown by Kammeyer and Whitman,\(^{102}\) would be the univalent radius. Although the univalent radius of Pb\(^{2+}\) has not been reported, an upper limit may be established by using the
ionic radius of Tl$^+$ (1.40 Å), which, when doubled, is considerably under the Pb-Pb distance observed in Pb$_2$Se$_3^{2-}$ (Pb$_2$Te$_3^{2-}$). Presumably there is a repulsion between the two 6s$^2$ cores in the anion but the effect is small relative to the six filled bonding molecular orbitals. Furthermore, this repulsion is diminished by the polarization of the 6s$^2$ cores away from each other due to the electron bond pairs of the Pb$_2$Se$_3^{2-}$ (Pb$_2$Te$_3^{2-}$) anion.

It would appear that the normal geometrical constraints of closest packing of chalcogen atoms in the equatorial belt and the inherent trigonal pyramidal geometry of the PbCH$_3$ moieties of Pb$_2$Se$_3^{2-}$ and Pb$_2$Te$_3^{2-}$ give rise to a surprisingly short apical Pb-Pb distance and that the main features of the Pb$_2$Se$_3^{2-}$ and Pb$_2$Te$_3^{2-}$ anion structures are dictated by the stereo chemical activity of the valence electron lone pair of the PbCH$_3$ kernel.

(C) RELATIONSHIP OF Pb$_2$CH$_3^{2-}$ TO THE Sb$_2$Se$_4^{2-}$ AND Tl$_2$CH$_2^{2-}$ ANIONS

As noted earlier in this discussion, the NMR spectra of Pb$_2$CH$_3^{2-}$ anions containing selenium show an intense peak at -438 ppm in the $^{77}$Se spectrum which is assigned to the Se$^{2-}$ anion (see Section A(ii) Chapter 5). An intense $^{77}$Se peak (-436 ppm) arising from Se$^{2-}$ has also been reported for solutions resulting from the extraction of KTL1Ch alloys in
The latter alloys give rise to both trigonal planar TlCH$_3$\textsuperscript{3-} and butterfly-shaped Tl$_2$CH$_2$\textsuperscript{2-} species in solution. The $^{77}$Se, $^{125}$Te and $^{203,205}$Tl spectra of these extracts show the Tl$_2$CH$_2$\textsuperscript{2-} resonances are all significantly exchange broadened at room temperature relative to the trigonal planar series of TlCH$_3$\textsuperscript{3-} anions. This present work on the Pb$_2$CH$_3$\textsuperscript{2-} anions, recently published observations of the exchange behavior of Tl$_2$CH$_2$\textsuperscript{2-} species and the recent X-ray structural determinations of cis- and trans-Sb$_2$Se$_4$\textsuperscript{2-} \cite{103} suggest a close structural relationship exists among this series of metal chalcogenide anions.

Although all members of the series may be regarded as being derived from a M$_2$CH$_3$-type trigonal bipyramid by formal removal or addition of CH$_2$\textsuperscript{2-} (Figure 4.6), the observation of Se$^2_-$ in en solutions of the stable Pb$_2$CH$_3$\textsuperscript{2-} and Tl$_2$CH$_2$\textsuperscript{2-} anion series does not necessarily imply both species possess selenium-rich precursors such as Pb$_2$CH$_4$\textsuperscript{4-} and Tl$_2$CH$_3$\textsuperscript{4-} which undergo elimination of CH$_2$\textsuperscript{2-} upon extraction into en. Rather, regardless of the origin of Se$^2_-$ in these solutions, it would appear that the high formal negative charges of the structurally related Pb$_2$CH$_4$\textsuperscript{4-} and Tl$_2$CH$_3$\textsuperscript{4-} anions, which have known isovalent Sb$_2$Se$_4$\textsuperscript{2-} and Pb$_2$CH$_3$\textsuperscript{2-} analogues, are not effectively stabilized in solution with respect to the dinegative species Tl$_2$CH$_2$\textsuperscript{2-}, Pb$_2$CH$_3$\textsuperscript{2-} and Se$^2_-$. It might be anticipated that the -4 charges of Pb$_2$CH$_4$\textsuperscript{4-} and Tl$_2$CH$_3$\textsuperscript{4-}
Figure 4.6 The structural relationships among the Pb$_2$Se$_3^{2-}$, Tl$_2$Se$_2^{2-}$ 49 and the cis- and trans-Sb$_2$Se$_4^{2-}$ 103 anions resulting from the addition or removal of Se$^{2-}$. Structures in square brackets are possible intermediates.
would be more effectively stabilized by the close naked cation-anion contact distances afforded in the solid state in the absence of a cryptating agent. Indeed, many examples of ternary main-group classical Zintl anions exist in the solid state in which the counter anion of the alkali or alkaline earth cation possesses a formal negative charge exceeding $-4.48,56$

In a previous discussion of KTLCh alloy extracts using 2,2,2-crypt in en,\textsuperscript{49} equilibrium (4.1) was postulated in order to account for the trigonal planar TlCh$_3$\textsuperscript{3-} and the Tl$_2$Ch$_2$\textsuperscript{2-} butterfly-shaped species

\[
2 \text{ TlCh}_3\textsuperscript{3-} \longleftrightarrow \text{ Tl}_2\text{Ch}_2\textsuperscript{2-} + 2 \text{ Ch}_2\textsuperscript{2-} \quad (4.1)
\]

However, no evidence was found for Ch$_2$\textsuperscript{2-} although Se$_2$\textsuperscript{2-} was observed when selenium-containing alloys were extracted. The presence of Se$_2$\textsuperscript{2-} instead of Se$_2$\textsuperscript{2-} was explained by the known equilibrium (4.2)\textsuperscript{104}

\[
\text{Se}_2\textsuperscript{2-} \longleftrightarrow \text{Se}^2- + \text{Se}_3\textsuperscript{2-} \quad (4.2)
\]

However, no Se$_3$\textsuperscript{2-} was observed and it was further suggested that in the mixed Se/Te systems mixed species such as TeSe$_2$\textsuperscript{-}, Te$_2$Se$_2$\textsuperscript{-} and TeSe$_2$\textsuperscript{2-} may be formed. Again, no NMR signals corresponding to any of those species could be observed in support of this postulate. The selective broadening of Tl$_2$Ch$_2$\textsuperscript{2-} resonance lines in the 77Se, 125Te
and $203^{205}_{\text{Tl}}$ spectra of these species while the Tl\text{Ch}_3$^3$- lines remained sharp, also argues against equilibrium (4.1). Rather, the observation of Se$^{2-}$ in the en extracts suggests equilibrium (4.3) is operative and that the trigonal bipyramidal Tl$_2$Ch$_3$$^4$- anion could serve as a plausible intermediate in the chemical exchange of Ch$^{2-}$

\[ \text{Tl}_2\text{Ch}_2^{2-} + \text{Ch}^{2-} \rightleftharpoons [\text{Tl}_2\text{Ch}_3^{4-}] \] (4.3)

In contrast, the $^{77}_{\text{Se}}$, $^{125}_{\text{Te}}$ and $^{207}_{\text{Pb}}$ resonances of the series of mixed Pb$_2$Ch$_3$$^{2-}$ anions show no apparent exchange broadening in the presence of Se$^{2-}$. Chemical exchange with free Se$^{2-}$ is presumed to be very slow on the NMR time scale and suggests the Pb$_2$Ch$_3$$^{2-}$ trigonal bipyramidal cage is relatively inert. The number of M-Ch bonds and the formal charges of the metal are the same in Pb$_2$Ch$_3$$^{2-}$ and the hypothetical Pb$_2$Ch$_4$$^{4-}$ (cis- and/or trans-) anion, whereas they increase in the proposed intermediate Tl$_2$Ch$_3$$^{4-}$. Furthermore, although the formal charges on the Pb atoms would not change, the formation of a species like Pb$_2$Ch$_4$$^{4-}$ from Pb$_2$Ch$_3$$^{2-}$ and Se$^{2-}$ would inevitably involve M-Ch bond breaking and bond formation in contrast to the formation of Tl$_2$Ch$_3$$^{4-}$ from Tl$_2$Ch$_2$$^{2-}$ and Ch$^{2-}$ where bond formation is entailed and each Tl atom has available a vacant p orbital. The activation barrier for the formation of Tl$_2$Ch$_3$$^{4-}$ should therefore be much smaller. However, the high formal charge
on the thallium atoms in $\text{Tl}_2\text{Ch}_3^{4-}$ ($\text{Tl}^{2-}$) presumably renders the anion thermodynamically unstable relative to $\text{Tl}_2\text{Ch}_2^{2-}$ and $\text{Ch}^{2-}$. 
CHAPTER 5

THE HOMO- AND HETEROPOLYCHALCOGENIDE ANIONS: \( \text{HCh}^- \)

\( \text{Ch}_n^{2-} \) (\( n = 1-4, \ 6, \ \text{Ch} = \text{Se}, \text{Te} \)) AND \( \text{Te}_m\text{Se}_{3-m}^{2-} \) (\( m = 0-3 \))

INTRODUCTION

In the past fifteen years a large number of homopolychalcogenide anions of selenium and tellurium have been structurally characterized in the solid state, e.g., \( \text{Se}_2^{2-}, 103 \) \( \text{Se}_3^{2-}, 105 \) \( \text{Se}_4^{2-}, 106-107 \) \( \text{Se}_5^{2-}, 107-108 \) \( \text{Se}_6^{2-}, 52 \) \( \text{Te}_2^{2-}, 109 \) \( \text{Te}_3^{2-}, 110-111 \) \( \text{Te}_4^{2-}, 112-113 \) and \( \text{Te}_5^{2-}, 52 \) all of which have unbranched chain-like structures. Interestingly, many of the crystalline homopolychalcogenide anion salts were isolated from solutions of other metal chalcogenide anions or from solutions in which the stoichiometry of the isolated anion salt did not correspond to the overall stoichiometry of the solution. For example, the \( (2,2,2\text{-crypt-}\text{Na}^+)_2 \text{Te}_4^{2-}, 113 \) salt deposited from the solution extract of the Zintl phase NaTlTe$_2$ whereas the t-butyl ammonium salt of the Te$_5^{2-}$ anion was isolated from an aqueous solution of the K$_2$Te$_3$ phase,\(^{52}\) suggesting a complex equilibria and the existence of mixtures of polytelluride anions in solution.
Solution studies of the polyselenide and polytelluride anions have been much less extensive than their solid state studies although their chemistry is often found to differ from that of their solid state chemistry. For example, the existence of $\text{Se}_3^{2-}$, $\text{Se}_4^{2-}$ and $\text{Se}_6^{2-}$ in liquid ammonia (am) was verified by Koehler and Sharp$^{104}$ but $\text{Se}_5^{2-}$ was not present in solution and $\text{Se}_2^{2-}$ was only found in low concentrations and in equilibrium with $\text{Na}_2\text{Se}{}_{(s)}$ and $\text{Se}_3^{2-}(\text{am})$. Furthermore, although Kraus and Zeitfuchs$^{114}$ had reported that the blue ammonia solution of $\text{Na}_2\text{Te}_2$ contained the $\text{Te}_2^{2-}$ anion, it has recently been shown that the anion disproportionates in the solid state into $\text{Te}^{2-}$ anion and the novel $Z$-shaped $\text{Te}_5^{4-}$ anion.$^{115a}$ In general, more complex structures have been found for many telluride phases resulting from high degrees of association of the polytelluride anions. The structures of these interesting telluride phases have recently been reviewed by Böttcher.$^{115}$

It was soon realized from the previous solution study (reference (49) and Section D, Chapter 4) of the mixed Se/Te metal chalcogenide anions that the solution chemistry of selenium and tellurium polychalcogenide anions played an important role in the chemistry of metal chalcogenide anions. In general, the chemistry of heteropolychalcogenide anions is poorly understood and apart from the structurally characterized $\text{K}_2\text{TeSe}_4$, $^{116}$ $\text{Na}_2\text{TeSe}_3$ $^{117}$ and $\text{K}_2\text{TeSe}_3$ $^{117}$ phases,
only salts of $\text{TeSe}_2^{2-}$ and $\text{TeSe}_3^{2-}$ have been reported in the literature.\textsuperscript{118}

It was evident that a better understanding of the solution chemistry of the homopolychalcogenide anions as well as the mixed Se/Te chalcogenide anions was required in order to improve our understanding of their chemistry and that of other metal chalcogen anion species.

**RESULTS AND DISCUSSION**

(A) **SOLUTION NMR STUDY OF POLYCHALCOGENIDE ANIONS, $\text{Ch}_n^{2-}$**

(i) **General Preparation of $\text{Ch}_n^{2-}$**

The general synthetic approach for a polychalcogenide anion involved the reaction of potassium monochalcogenide with an appropriate amount of chalcogen metal powder in en or liquid ammonia as shown in equation (5.1)

$$K_2\text{Ch'} + n \text{Ch} \rightarrow 2 K^+ + \text{Ch'}\text{Ch}_n^{2-} \quad (5.1)$$

where $\text{Ch} = \text{Se}/\text{Te}$. Alternatively, the polychalcogenide anions were prepared by the reaction of the alkali and chalcogen metals in liquid ammonia according to equation (5.2)

$$2 M + n \text{Ch} \rightarrow 2 M^+ + \text{Ch}_n^{2-} \quad (5.2)$$

where $M = \text{Na}$ or $\text{K}$. The resulting solutions were then examined by $^{77}\text{Se}$, $^{123}\text{Te}$ and $^{125}\text{Te}$ NMR spectroscopy. The
species could often be identified by their characteristic colors, i.e., Te$_2^{2-}$ (blue), Te$_3^{2-}$ and Te$_4^{2-}$ (deep red) and Se$_3^{2-}$ (green).

The anions were identified by direct NMR observation of the spin-$\frac{1}{2}$ nuclides at their natural-abundance levels. By comparing the magnitudes of satellite doublet spacings observed for each environment one could determine which environments were coupled together. Furthermore, the total number of equivalent Se and/or Te atoms bonded to each environment could be determined from the measured satellite/central peak intensity ratios, I$_S$/I$_C$.

During the course of this work it became clear that peaks in the $^{77}$Se and $^{125}$Te NMR of the ethylenediamine solutions were broadened considerably unless stoichiometric amounts of the complexing ligand, 2,2,2-crypt, were added to the solutions to complex the free alkali metal cations (vide infra). However, many crypt salts of the anions were found to have solubilities too low for direct observation of the natural abundance $^{77}$Se and $^{125}$Te spin satellites. In order to enhance the NMR sensitivity, the NMR spectra of the solutions were recorded at elevated temperatures, to increase the solubility of the crypt salts, and by using high-field NMR spectrometers equipped with cryomagnets operating at 5.8719 T and 11.745 T. For some of the anions the exchange could be slowed sufficiently in uncomplexed solutions by
recording their NMR spectra at suitably low temperatures in liquid ammonia. The results from solution NMR studies are summarized in Table 5.1.

The preparation of the tri- and tetrahetero-chalcogenide anions of selenium and tellurium resulted in mixtures of species. Variation of the relative stoichiometries of Se and Te used in each preparation resulted in relative peak intensity changes which further aided in the assignment of the environments to their respective anions.

(ii) Monochalcogenide Anions, Ch$^2$-, and Hydrogenchalcogenide Anions, HCh$^-$

The phase, $K_2Te$, was treated with two equivalents of crypt in en. The light yellow solution was isolated from the solid residue and its $^{125}$Te NMR spectrum recorded. A strong singlet was observed at -1430 ppm and a weak doublet at -1095 ppm having a coupling constant of 140 Hz (Figure 5.1). The $^{125}$Te environment corresponding to the singlet is assigned to the en solvated Te$^2$- anion as it is the most shielded tellurium environment presently known. The doublet, the only $^{125}$Te environment present, was also observed in the solution extract of LiPbTe$_{0.67}$Se$_{0.33}$ + 12-crown-4 in en, but in much higher concentration. When the latter sample was proton-decoupled, the doublet collapsed into a singlet. The $^1H$ NMR
Figure 5.1 $^{125}\text{Te}$ NMR spectrum (78.917 MHz) of a solution prepared by dissolving $\text{K}_2\text{Te}$ in en in the presence of 2,2,2-crypt. The doublet is assigned to $^{1}J(1^H-^{125}\text{Te})$ of $\text{HTe}^-$. 
spectrum gave a peak having a chemical shift in the hydride region of the spectrum (-12.9 ppm) with $^{125}$Te satellites separated by 138 Hz, corresponding to the doublet splitting in the $^{125}$Te spectrum. Furthermore, the satellite/central peak ratio of 4% corresponds to bonding of the proton to one tellurium atom. The spectra are therefore assigned to the HTe$^-$ anion. During the course of this work it was learned that the X-ray crystal structure of [PPh$_4^+$][HTe$^-$] had been solved.$^{119}$ Although the H–Te bond length was not available from the structure determination, the infrared spectrum of the crystal gave a band at 1975 cm$^{-1}$ which was assigned to the H–Te stretch. The source of the proton in HTe$^-$ in the ethylenediamine solution is still unclear but the simplest explanation would be an acid-base reaction between Te$^{2-}$ and the solvent and/or the deprotonation of the complexing ligands. Some evidence for oxidation of the Te$^{2-}$ anion (colorless to pale yellow) is observed when Te$^{2-}$ solutions are prepared, giving rise to blue-violet solids attributed to a ditelluride crypt salt, (2,2,2-crypt-K$^+$)$_2$ Te$_2$$^{2-}$·x en, (vide infra).

A single, sharp peak was observed at -435 ppm in the $^{77}$Se NMR spectrum of the solution resulting from the reaction of K$_2$Se with crypt in en and is assigned to the solvated Se$^{2-}$ anion. The expected doublet of HSe$^-$ was observed at -495 ppm in the $^{77}$Se NMR spectrum when Na$^+$HSe$^-$ was dissolved in
anhydrous EtOH. As only a singlet at -448 ppm was observed when Na\(^+\)HSe\(^-\) was dissolved in en, the HSe\(^-\) anion must be undergoing fast chemical exchange on the NMR time scale arising from partial or complete deprotonation of HSe\(^-\) in the more basic en solvent. It is of interest that the chemical shift of the Se\(^{2-}\) anion is very solvent dependent as it has been reported as high as -511 ppm in aqueous solution.\(^ {120}\) The chemical shifts of the monoselenide anions are, however, far from being the most shielded selenium environments observed thus far, c.f. -666 ppm for Se(SiH\(_3\))\(_2\)\(^ {121}\) and -736 ppm for Li\(^+\)(SeSiH\(_3\))\(^-\).\(^ {122}\) For the spherical Se\(^{2-}\) anion one would have expected its environment to be the most shielded \(^{77}\)Se chemical shift known owing to its high negative charge and the fact that the paramagnetic shielding term, \(\sigma_P\), (see eq. (1.6) and (1.7)) should be absent for a spherically symmetric environment. Undoubtedly, the Se\(^{2-}\) anion is solvated to a high degree through hydrogen bond formation with the solvent, breaking the spherical symmetry of the anion to a certain degree so that the paramagnetic term would make a significant contribution to the chemical shift of the anion. A similar chemical shift solvent-dependence would be expected for the Te\(^{2-}\) anion in a solvent which it is stable in.
(iii) **Dichalcogenide Anions, \( \text{CH}_2^{2-} \)**

An intense blue solution was obtained when \( \text{K}_2\text{Te} \) was allowed to react with one equivalent of \( \text{Te} \) in \( \text{en} \). A single sharp line was observed at \(-1073 \) ppm in the \( ^{125}\text{Te} \) NMR spectrum which is assigned to the \( \text{Te}_2^{2-} \) anion. However, when crypt was added to the solution a violet-blue solid, presumed to be a crypt salt of the \( \text{Te}_2^{2-} \) anion, precipitated. As it was of interest to observe the natural abundance \( ^{123}\text{Te} \) (0.87%) and \( ^{125}\text{Te} \) (6.99%) satellites in order to obtain the coupling constant \( J(123\text{Te}-125\text{Te}) \) between the two Te atoms in \( \text{Te}_2^{2-} \), a very concentrated solution of the anion was prepared in liquid ammonia (eq. (5.2)). The coupling constant was measured to be 3645 Hz in both the \( ^{123}\text{Te} \) (Figure 5.2) and \( ^{125}\text{Te} \) NMR spectra and represents the largest coupling constant presently known between two tellurium nuclei.

The reaction of \( \text{K}_2\text{Se} \) with \( \text{Te} \) gave a blue solution and a red solid in \( \text{en} \). However, unlike the case with \( \text{Te}_2^{2-} \) in \( \text{en} \) solution, the species in solution were not in high enough concentrations to obtain their NMR spectra. The species from the reaction of \( \text{K}_2\text{Te} \) with \( \text{Se} \) in liquid ammonia were found to be somewhat more soluble, particularly at lower temperatures, although it was not possible to obtain their NMR spectra.

A dark green solution and a red solid formed when \( \text{K}_2\text{Se} \) and \( \text{Se} \) were combined in a 1:1 molar ratio in \( \text{en} \) solvent. The \( ^{77}\text{Se} \) NMR spectrum of the green solution gave a broad line
Figure 5.2  $^{123}$Te NMR spectrum (130.89 MHz) of $2K^+ + Te_2^{2-}$ in liquid ammonia at -54 °C: (C) $Te_2^{2-}$. Peaks c' arise from $^1J(^{123}Te_1^{--}^{125}Te_2)$ coupling.
at 288 ppm attributable to \( \text{Se}_3^{2-} \) undergoing fast exchange as was observed for the \( \text{Te}_3^{2-} \) anion (see Section A(iv)). Sharp and Koehler\(^{104} \) had reported that the \( \text{Se}_2^{2-} \) anion produced a red color in liquid ammonia. Crypt was therefore added to the remaining solid in en. Although the solid immediately dissolved to give an intense red color, within two hours a muddy reddish-brown solid precipitated. The reaction was repeated with a different complexing ligand, 18-crown-6, and \( \text{Na}_2\text{Se} \) instead of \( \text{K}_2\text{Se} \). A dark green solution formed and a white solid (\( \text{Na}_2\text{Se} \)) remained at the bottom of the reaction vessel. The \( ^{77}\text{Se} \) NMR spectrum of the solution gave two broad peaks in a 2:1 ratio assigned to the \( \text{Se}_3^{2-} \) anion (see Section A(iv)). These results are consistent with what Koehler and Sharp found in liquid ammonia.

(iv) \( \textbf{Trichalcogenide Anions, Ch}_3^{2-} \)

When the \( ^{125}\text{Te} \) NMR spectrum of the solution resulting from the reaction of \( \text{K}_2\text{Te} \) with \( 3\text{Te} \) was recorded in en only a single, broad peak was observed as shown in Figure 5.3a. It was presumed that the two anticipated tellurium environments (Structure I), \( \text{Te}_\text{c} \) and \( \text{Te}_\text{p} \), were undergoing fast chemical exchange on the NMR time scale. The complexing ligand, 2,2,2-crypt, was therefore added to the solution in order to complex all the \( \text{K}^+ \) cations in solution. The \( ^{125}\text{Te} \) NMR spectrum of the resulting solution gave the expected two
Figure 5.3 $^{125}\text{Te}$ NMR spectrum of (a) $2\text{K}^+\text{Te}_3^{2-}$ (78.917 MHz) and (b) $2(2,2,2\text{-crypt-K}^+)\text{Te}_3^{2-}$ (157.792 MHz) in en (F) $\text{Te}_3^{2-}$ (exchange averaged); (F_t, F_b) T_{et} and T_{eb} of $\text{Te}_3^{2-}$. Satellite peaks f due to $^{1J}(^{125}\text{T}_{et}-^{125}\text{T}_{eb})$ coupling. Peak labeled * is a spurious spike.
peaks in a 2:1 ratio, consistent with the V-shaped Te$_3^{2-}$ anion (Figure 5.3b). The weighted-average chemical shift of -323 ppm for the cryptated Te$_3^{2-}$ solution is in good agreement with the chemical shift of -326 ppm observed for the non-cryptated solution. Evidently the presence of "free" K$^+$ cations in solution lowers the activation barrier for exchange of the tellurium environments by means of strong ion pair formation in solution. Further evidence for strong ion pair formation in the solutions of the polychalcogenide anions could be inferred from the fact that the intense dark colors of these solutions often became brighter when crypt was added. These results are not unexpected as it has been found that the size of the counter cation affects the geometry and therefore the electronic structure of the Te$_3^{2-}$ anion.$^{111}$ Thus, the Te-Te bond lengths decrease with increasing cation size and the more isolated the anion is in the lattice. No general trend has been observed for the bond angles although they are found to be larger when the metal cation is completely complexed and well isolated from the Te$_3^{2-}$ anion as in the case of (2,2,2-crypt-K$^+$)$^{110}$ and [Ba(en)$_4$-en-Ba(en)$_4$]$^{4+}$ $^{111}$ cations.

The triselenide anion was prepared and characterized by a method analogous to that used for the tritellururide anion discussed above. When the K$_2$PbSe$_4$ phase was allowed to react with crypt in en, the Se$_3^{2-}$ anion formed and an
Figure 5.4 $\text{^{77}Se}$ NMR spectrum (47.704 MHz) of $2(2,2,2$-crypt-K$^+)$ + Se$_3^{2-}$ in en solvent. $Se_t$ and $Se_b$ denote the terminal and bridging environments of Se$_3^{2-}$, respectively. Peaks s arise from $^{1}J(\text{^{77}Se}_t-\text{^{77}Se}_b)$ coupling.
insoluble residue remained which is presumed to be PbSe. The
$^{77}\text{Se}$ NMR spectrum showed the expected two selenium
environments for a V-shaped (Structure IV) species in a 2:1
intensity ratio along with their spin satellites (Figure 5.4).

A green solution formed when two equivalents of
selenium were allowed to react with $\text{K}_2\text{Te}$ in en. The NMR
spectra of the solution showed two new spin-coupled
environments, one in the $^{77}\text{Se}$ NMR spectrum and one in the
$^{125}\text{Te}$ NMR spectrum. The environments are therefore assigned
to the new $\text{TeSe}_2^{2-}$ anion ($C_{2v}$) having two terminal selenium
atoms and a central tellurium atom (Structure III). The
assignment was further supported by the satellite/central
peak ratios. A considerable amount of the new pyramidal
$\text{TeSe}_3^{2-}$ anion could also be found in the NMR spectra of the
solution. The origin of $\text{TeSe}_3^{2-}$ is still unclear but
presumably results from oxidation of the $\text{Te}^{2-}$ anion as was
discussed above. In order to minimize the possibility of
oxidation, the crypt was not added to the solution until a
few days later, after the white $\text{K}_2\text{Te}$ solid had all reacted.
However, some oxidation probably took place as an alloy residue remained in the reaction tube after the crypt was added to the solution.

Solutions resulting from the reaction of K₂Se with two equivalents of tellurium gave environments in the ⁷⁷Se and ¹²⁵Te NMR spectra arising from the TeSe₃²⁻, TeSe₂⁻ and Te₃²⁻ anions. In addition, two new tellurium environments and one selenium environment, all spin coupled to one another, were also observed in the ⁷⁷Se and ¹²⁵Te NMR spectra (Figure 5.5). These environments are assigned to a new V-shaped Te₂Se²⁻ anion (C₅) with a terminal selenium atom (Structure II). The assignments of the terminal selenium and tellurium environments were based on the fact that their chemical shifts and the one-bond coupling constants are very similar to those of the corresponding environments in the TeSe₂⁻ and Te₃⁻ anions. Moreover, the chemical shift of the central tellurium atom in the trichalcogenides was found to vary linearly with the number of selenium atoms bonded to it (Table 5.1). A similar type of linear trend was also found in a previous study of the central nucleus in the metal chalcogenide anions (reference (49) and Chapter 4) lending further support to the assignment of the species.

The coexistence of TeSe₂⁻, Te₂Se²⁻ and Te₃⁻ in the tellurium rich solution suggest an equilibrium among the species as shown in equation (5.3)
Figure 5.5 (a) $^{77}$Se NMR spectrum (95.383 MHz) and (b) $^{125}$Te NMR spectrum (157.792 MHz) of the en solution resulting from the reaction of $K_2$Se with 2Te in the presence of 2,2,2-crypt; (H) $\text{TeSe}_2^{2-}$; (G) $\text{Te}_2\text{Se}^2$; (G$_b$) and (G$_t$) $\text{Te}_b$ and $\text{Te}_t$, respectively, (F$_t$) $\text{Te}_t$ of $\text{Te}_3^{2-}$. Peaks g', g'' (and h') and g'''' arise from $^{125}_{\text{Te}}$-$^{125}_{\text{Te}}$, $^{77}_{\text{Se}}$-$^{125}_{\text{Te}}$ and $^{77}_{\text{Se}}$-$^{125}_{\text{Te}}$ couplings, respectively.
\[
2 \text{Te}_2\text{Se}^{2-} \rightleftharpoons \text{TeSe}_2^{2-} + \text{Te}_3^{2-} \quad (5.3)
\]

Interestingly, the total number of Te-Se and Te-Te bonds does not change so that the energy difference for the equilibrium should be small.

(v) **Tetrachalcogenide Anions, \( \text{Ch}_4^{2-} \)**

The reaction of \( \text{K}_2\text{Te} \) with three equivalents of \( \text{Se} \) in en or ammonia gave only one tellurium and one selenium environment in high intensity in their respective NMR spectra. The two environments were found to be coupled to one another and from the satellite/central peak ratios it was found that each selenium was coupled to one tellurium but that each tellurium was bonded to three equivalent selenium atoms. In the absence of crypt in liquid ammonia solution the \( ^{125}\text{Te} \) peak was not found to broaden at lower temperatures to an appreciable extent, even down to \(-70^\circ\text{C}\), indicating that the single peak was not the result of fast intramolecular exchange averaging. The selenium and tellurium environments are therefore assigned to a pyramidal shaped (C\( _{3v} \)) \( \text{TeSe}_3^{2-} \) anion with a central tellurium atom (Structure V). The pyramidal-shaped \( \text{TeSe}_3^{2-} \) anion has been further verified from the crystal structure of its (2,2,2-crypt-\( \text{K}^+ \)) salts (see Section C) as well as in the \( \text{Na}_2\text{TeSe}_3 \) and \( \text{K}_2\text{TeSe}_3 \) phases.\(^{117}\)

The \( \text{TeSe}_3^{2-} \) anion is, as expected, isostructural with the
In attempts to prepare the remaining mixed Se/Te tetrachalcogenide anions, two samples were prepared by allowing K₂Se to react with Se/2Te and with 3Te in en followed by complexation of the potassium cations with crypt. Along with sharp peaks for TeSe₃²⁻ in the ⁷⁷Se and ¹²⁵Te NMR spectra of the solutions, two new ⁷⁷Se NMR peaks and two new ¹²⁵Te NMR peaks could also be observed (Figure 5.6). The two new environments in each spectrum belonged to different species, as the relative intensities of the peaks were found to vary from sample to sample with the intensity ratios of the two Se environments being roughly the same as the intensity ratios of the two Te environments for a given sample. The ⁷⁷Se and ¹²⁵Te chemical shifts of the peaks are similar, indicating their chemical environments are also similar. Moreover, the chemical shifts of the Se environments are at only slightly higher frequencies than the Seₖ environments bonded to Teₐ in the TeSe₂²⁻ and Te₂Se²⁻ anions, suggesting similar Seₖ-Teₐ chemical environments in
Figure 5.6  (a) $^{77}$Se NMR spectrum (95.383 MHz) and (b) $^{125}$Te NMR spectrum (157.792 MHz) of the en solution at 5 °C resulting from the reaction of K$_2$Se with a 2Te/Se mixture in the presence of 2,2,2-crypt: (L) Te$_2$Se$_2^{2-}$; (K) Te$_3$Se$_2^{2-}$; (Kb) Te$_b$ ($^\text{Se}+^\text{Te}_b$+$^\text{Te}_b$+$^\text{Te}_c$). Peaks 1' and k' arise from $^1J(^{77}\text{Se}-^{125}\text{Te})$ couplings and peak 1'' is tentatively assigned to the coupling $^2J(^{77}\text{Se}-^{125}\text{Te})$. 
the two new tetrachalcogenide anions. Furthermore, the Se and Te environments were found to be spin coupled to each other with only slightly smaller coupling constants than in the $\text{Se}_t\text{-Te}_b$ environments of the trichalcogenide anions. Thus, the new environments are attributed to the $\text{Se}_t\text{-Te}_b$ units of the tetrachalcogenides $\text{SeTe}_3^{2-}$ and $\text{Se}_2\text{Te}_2^{2-}$ (Structures VII and VIII)

\[
\begin{array}{ccc}
\text{VI} & \text{VII} & \text{VIII} \\
\text{Te} & \text{Te} & \text{Te} \\
\text{Se} & \text{Te} & \text{Se} \\
\end{array}
\]

The environments at higher frequency are assigned to $\text{Se}_2\text{Te}_2^{2-}$ anion as their intensities were found to be higher in the selenium-rich sample. The remaining two Te environments of $\text{SeTe}_3^{2-}$ ($\text{Te}_t\text{-Te}_b'\text{Te}_b\text{Se}_t'$), Te$_t$ and Te$_b'$, were only found as broad peaks at -160 ppm and 180 ppm, respectively, with a poor signal to noise ratio. Evidently the two tellurium environments are undergoing slow exchange on the NMR time scale. Interestingly, the chemical shift of Te$_b$ changes by approximately 480 ppm from Te$_t$Te$_b$Ch$_2^{2-}$ to Se$_t$Te$_b$Ch$_2^{2-}$, and is not very different from the change of 450 ppm observed for the Te$_b$ in the trichalcogenide anions.
The reaction of crypt with both $K_2Te_4$ and $K_2PbTe_5$ in en gave only a single broad peak at approximately +10 ppm, indicating that the $Te_C$ and $Te_B$ environments of $Te_4^{2-}$ (Structure VI) were undergoing fast exchange on the NMR time scale. Owing to the similar chemical nature of the tellurium environments in the two anions, the exchange-averaged chemical shift of $Te_4^{2-}$ is in good agreement with the average chemical shift value of the $Te_C$-$Te_B$ unit (10 ppm) in $Te_3Se^{2-}$. The rate of chemical exchange between the tellurium environments of $Te_4^{2-}$ could not be slowed sufficiently in en at 4 °C (freezing point of 4 °C) using the highest available field strength (11.745 T) to allow observation of separate environments. Unfortunately, the solubility of the crypt salt of $Te_4^{2-}$ was found to be too low below 0 °C for observation in liquid ammonia.

Two samples were prepared by allowing $K_2Te$ to react with 3Te and with 2Te in liquid ammonia, respectively. However, only a single relatively sharp peak at -150 ppm ($\Delta\nu_1 \approx 700$ Hz) in the 125Te NMR spectrum was observed for both solutions at temperatures as low as -75 °C. This probably resulted from a fast exchange between a mixture of $Te_3^{2-}$ and $Te_4^{2-}$ in solution. Evidently the reactions have not gone to completion as was further apparent from the relatively large amount of solid material remaining, even after allowing the reactions to proceed for several weeks.
Corbett and Cisar\textsuperscript{110} reported the potassium-crypt salt of the Te\textsubscript{3}\textsuperscript{2−} anion could be isolated from the reaction of K\textsubscript{2}Te with excess tellurium. When K\textsubscript{2}Te was allowed to react with approximately 2.6 equivalents of tellurium powder in the presence of crypt, only a single broad peak was observed at +11 ppm (Δν\textsubscript{1} = 2000 Hz) in the \textsuperscript{125}Te NMR spectrum at 10 °C. As discussed earlier, the potassium-crypt salt of Te\textsubscript{3}\textsuperscript{2−} was found not to be very soluble in en at room temperature. Consequently, the broad peak at 11 ppm is presumably mainly due to the Te\textsubscript{4}\textsuperscript{2−} anion as is indicated by its \textsuperscript{125}Te chemical shift value.

(vi) **The Tetra- and Hexaselenide Anions, Se\textsubscript{4}\textsuperscript{2−} and Se\textsubscript{6}\textsuperscript{2−}**

The \textsuperscript{77}Se NMR spectrum of a dark brown solution resulting from dissolution of Na\textsubscript{2}Se\textsubscript{4} in liquid ammonia was recorded at -75 °C and gave two sharp singlets in a 1:1 ratio, consistent with a chain structure for Se\textsubscript{4}\textsuperscript{2−} (IX)

\[
\text{IX}
\]

A set of satellite shoulders separated by approximately 130 Hz for a Gaussian lineshape was associated with each peak and is assigned to a one-bond \textsuperscript{77}Se\textsubscript{t}\textsuperscript{−77}Se\textsubscript{b} coupling for the anion (Figure 5.7). The reaction of K\textsubscript{2}Se with three equivalents of
Figure 5.7 $^{77}\text{Se}$ NMR spectra (47.704 MHz) of $2\text{Na}^+ + \text{Se}_4^{2-}$ in \(\text{NH}_3(1)\) at -75 °C with (a) Lorentzian and (b) Gaussian lineshapes. \(\text{Se}_b\) and \(\text{Se}_t\) denote the bridging and terminal environments of \(\text{Se}_4^{2-}\), respectively. Peaks labeled i are assigned to the spin-spin coupling $^1J(\text{Se}_t-\text{Se}_b)$. 
Se metal in en also resulted in a dark brown solution. When 2,2,2-crypt was added, the color of the solution changed to dark green and black crystals formed. The $^{77}\text{Se}$ NMR spectrum of the resulting solution gave only two sharp peaks having a 2:1 ratio and chemical shifts essentially the same as those of the $\text{Se}_3^{2-}$ anion. Surprisingly, neither the brown color of the $\text{Se}_4^{2-}$ anion nor its $^{77}\text{Se}$ NMR spectrum could be observed in the cryptated en solution even though the cryptated $\text{Ba}^{2+}$ salt of the anion has been isolated by other workers from en solution.\textsuperscript{106a} Evidently the $\text{Se}_4^{2-}$ anion in en solution disproportionates to $\text{Se}_3^{2-}$ and $\text{Se}_5^{2-}$ or $\text{Se}_6^{2-}$ when the potassium cations are cryptated

\[ 3 \text{Se}_4^{2-} \rightarrow 2 \text{Se}_3^{2-} + \text{Se}_6^{2-} \]  

(5.4)

The number of $\text{Se}_t$-$\text{Se}_b$ and $\text{Se}_b$-$\text{Se}_b$ bonds is the same on both sides of the equation suggesting the difference in energy for the anions is small. A dark brown solution formed from the reaction of $\text{K}_2\text{Se}$ with 4Se in en which also turned dark green when 2,2,2-crypt was added to the solution. However, the existence or absence of $\text{Se}_5^{2-}$ in solution could not be ascertained as no peaks were observed in the solution $^{77}\text{Se}$ NMR spectrum.

An intense dark green solution formed when the reaction $\text{K}_2\text{Se} + 5\text{Se}$ was conducted in en. When an equivalent amount of 2,2,2-crypt was added to the solution, a large
quantity of black crystalline material precipitated; the solution, however, retained its dark green color. No sharp peaks could be observed in the $^{77}$Se NMR of the solution and only one small broad peak at 700 ppm was observed. The difficulty in observing the peaks is attributed to the relatively low solubility of the potassium cryptated salt of the Se$_6^{2-}$ anion in en and exchange broadening of the lines.

(vii) Chemical Exchange

As was noted earlier, complexation of the "free" K$^+$ cation slowed the fast exchange between the tellurium environments in the Te$_3^{2-}$ anion, indicating the exchange was intermolecular rather than intramolecular as no reasonable intermediate could be invoked which involved K$^+$ cations in the latter mechanism. For an intermolecular exchange, the existence of solvated cations in solution may simply lower the potential barrier of two anions coming in contact with each other or the cation may stabilize the formation of an intermediate by strong ion pair formation. Interestingly, for the tetrachalcogenide anions one can invoke two possible intermediates for an intramolecular exchange, i.e., a planar Ch$_4^{2-}$ species, as in the isovalent I$_4^{2+}$ cation,$^{125}$ or a pyramidal Ch$_4^{2-}$ anion, as for the TeSe$_3^{2-}$ anion. However, the exchange broadening of the Ch$_4^{2-}$ anion NMR resonances was found to be dependent on the relative concentration of
<table>
<thead>
<tr>
<th>Anion</th>
<th>$\delta$ (ppm) $^{77}$Se</th>
<th>$\delta$ (ppm) $^{125}$Te</th>
<th>$^1 J$ (A - B) (Hz)</th>
<th>Temp. ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$^{2-}$</td>
<td>-435</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Te$^{2-}$</td>
<td>-1430</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>HSe$^{-}$</td>
<td>-495</td>
<td></td>
<td></td>
<td>24 ($^1 H$-$^{77}$Se)</td>
</tr>
<tr>
<td>HTe$^{-}$</td>
<td>-1095</td>
<td></td>
<td></td>
<td>140 ($^1 H$-$^{125}$Te)</td>
</tr>
<tr>
<td>Te$_2$$^{2-}$</td>
<td>-1080</td>
<td></td>
<td></td>
<td>3645 ± 20 ($^{123}$Te-$^{125}$Te)</td>
</tr>
<tr>
<td>Te$_2$$^{2-}$</td>
<td>-1074</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Se$_3$$^{2-}$</td>
<td>304 (Se$_B$)</td>
<td>278 (Se$_B$)</td>
<td></td>
<td>262 ± 6 ($^{77}$Se$_C$-$^{77}$Se$_B$)</td>
</tr>
<tr>
<td>Te$_3$$^{2-}$</td>
<td>-286 (Te$_C$)</td>
<td>-367 (Te$_B$)</td>
<td></td>
<td>2175 ± 6 ($^{125}$Te$_C$-$^{125}$Te$_B$)</td>
</tr>
<tr>
<td>Te$_3$$^{2-}$</td>
<td>-298 (Te$_C$)</td>
<td>-372 (Te$_B$)</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>TeSe$_2$$^{2-}$</td>
<td>-92</td>
<td>536</td>
<td></td>
<td>670 ± 6 ($^{77}$Se-$^{125}$Te)</td>
</tr>
<tr>
<td>Te$_2$Se$_2$$^{2-}$</td>
<td>-134</td>
<td>-266 (Te$_C$)</td>
<td></td>
<td>621 ± 6 ($^{77}$Se-$^{125}$Te$_B$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>106 (Te$_B$)</td>
<td></td>
<td>2235 ± 20 ($^{125}$Te$_C$-$^{125}$Te$_B$)</td>
</tr>
</tbody>
</table>

continued . . .
Table 5.1 (continued)

<table>
<thead>
<tr>
<th>Anion</th>
<th>$\delta^{77}\text{Se}$</th>
<th>$(\delta^{125}\text{Te})$</th>
<th>$^{1}J (A - B)$</th>
<th>Temp. ($^\circ\text{C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}_4^{2-}$ h</td>
<td>321 (Se$_7$)</td>
<td>608 (Se$_9$)</td>
<td>$130 \pm 12$ ($^{77}\text{Se}_7$-$^{77}\text{Se}_9$)</td>
<td>-75</td>
</tr>
<tr>
<td>$\text{Te}_4^{2-}$ i</td>
<td>7 $\pm$ 4</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>$\text{Te}_4^{2-}$ i</td>
<td>19 $\pm$ 8</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>$\text{TeSe}_3^{2-}$ j</td>
<td>468</td>
<td>1087</td>
<td>$214 \pm 12$ ($^{77}\text{Se}$-$^{125}\text{Te}$)</td>
<td>24</td>
</tr>
<tr>
<td>$\text{TeSe}_3^{2-}$ j</td>
<td>1077</td>
<td></td>
<td></td>
<td>-78</td>
</tr>
<tr>
<td>$\text{Te}_2\text{Se}_2^{2-}$ k</td>
<td>-59</td>
<td>656</td>
<td>$650 \pm 30$ ($^{77}\text{Se}$-$^{125}\text{Te}$)</td>
<td>5</td>
</tr>
<tr>
<td>$\text{Te}_2\text{Se}_2^{2-}$ k</td>
<td>-55</td>
<td>666</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>$\text{Te}_3\text{Se}_2^{2-}$ l,m</td>
<td>-64</td>
<td>632 ($\text{Te}_7\text{Te}_9\text{Se}_7$)</td>
<td>$430 \pm 30$ ($^{77}\text{Se}_7$-$^{125}\text{Te}_9$)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>175 ($\text{Te}_7\text{Te}_9\text{Te}_9$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-180 ($\text{Te}_9\text{Te}_9\text{Te}_9$)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a All the NMR parameters reported for the anions were measured in ethylenediamine and with all the potassium cations complexed by 2,2,2-crypt unless otherwise indicated.

b Linear least-squares regression analysis for the Te$_D$Se$_n$Te$_2-n$$_2^2$- series gave $\delta(\text{Te}_D) = -360 + 452n$ where the correlation coefficient is $R = 1.000$.

c [Na$^+$][HSe$^-$] dissolved in EtOH, $\delta(^1\text{H}) = -5.4$ ppm.

d $\delta(^3\text{H}) = -12.9$ ppm.

e Prepared by the reaction $2\text{K} + 2\text{Te}$ in liquid ammonia.

f Prepared by the reaction $\text{K}_2\text{Te} + \text{Te}$ in the absence of 2,2,2-crypt.

g $^{2}J(^{77}\text{Se}_7$-$^{125}\text{Te}_9) = 419 \pm 6$ Hz.

h Na$_2\text{Se}_4$ dissolved in liquid ammonia.

i Linewidths were usually, $\Delta \nu_1$, 2000 - 4000 Hz, see text.

j Prepared by the reaction $\text{K}_2\text{Te} + 3\text{Se}$ in liquid ammonia.

k $^{2}J(^{77}\text{Se}_7$-$^{125}\text{Te}_9) = 350 \pm 40$ Hz, tentative estimate.

l The assigned tellurium chemical shift value is for the underlined tellurium environment.

m Linewidths, $\Delta \nu_1$, were 1000 and 200 Hz for Te$_D$ and Te$_D'$, respectively.
the species in solution, therefore, strongly indicating an intermolecular exchange.

In general, the observed trends in chemical exchange behavior in this study are such that the exchange rate increases, in particular for the tellurium environments, with increasing chalcogen anion chain length and as the number of tellurium atoms in a chain increases. As discussed in the introduction, a high degree of association of polytelluride anions has been found in the solid state by Böttcher et al.\textsuperscript{115} where the negatively charged terminal atoms coordinate to a two-coordinated atom in the chain. In general, a higher degree of association is found for the longer chain-length polytelluride anions, presumably reflecting the high polarizability of the tellurium atom. It is likely that similar types of association are responsible for the increase in exchange rate resulting as the number of tellurium atoms increases and the chain length increases, although the exact type of mechanism for the intermolecular exchange cannot be determined from this study. Furthermore, an exchange mechanism through the association of the terminal atoms cannot be excluded as is evident from the Te\textsubscript{5}\textsuperscript{4-} anion in NaTe\textsuperscript{115a} and in the polymeric (Te\textsubscript{6}\textsuperscript{2-})\textsubscript{∞} anion of LiTe\textsubscript{3}.\textsuperscript{126}
(B) STRUCTURAL RELATIONSHIPS AND NMR PARAMETERS OF Chₙ²⁻

(i) Structural Correlations

The structures of the polychalcogenide anions can be rationalized by considering the electronegativity difference of Se and Te and by using the Topological Charge Stabilization Rule, TCSR.¹²⁷ The TCSR has its theoretical basis in first-order perturbation theory where the perturbation Hamiltonian arises from changes in the nuclear charge of an atom in a molecule. If we consider substituting a tellurium atom with a more electronegative selenium atom having a greater effective nuclear charge, the latter goes to the position with the highest electron density. Therefore, if we start with Te₃²⁻ and successively substitute a Te atom with a Se atom we obtain the species shown in Scheme I

![Scheme I]

The structures are identical with those observed in solution. The same pattern is obtained after two successive substitutions of Te₄²⁻ (Scheme II), the selenium atoms go to the positions with the highest negative charges, i.e., the
terminal positions. However, the structure expected from the TCSR for the TeSe$_3^{2-}$ anion is not the observed structure but the pyramidal shaped (C$_{3v}$) species. Evidently higher-order terms become important for the perturbation Hamiltonian, with the chain structure becoming less stable than the pyramidal structure as indicated in Scheme II.

![Scheme II](image)

The three Se-Te bonds of the pyramid evidently outweigh the Set-Teb, Seb-Teb and Set-Seb bonds of the alternative chain structure. Furthermore, the Set-Te bonds of the pyramid have a higher bond order resulting from π back-bonding, and are therefore stronger than single bonds.
(ii) Correlation of Se and Te Chemical Shifts

As was discussed in Chapter 1, it is generally believed from the theory of chemical shifts that the paramagnetic term, $\sigma^p$, makes the dominant contribution to the observed chemical shift ranges of the heavy nuclei. In the average energy approximation $\sigma^p$ is given (in SI units) by

$$\sigma^p(A) = - \left( \frac{\mu_0 e^2 h^2 <r^{-3}>_{np}}{24 \pi^3 m^2 \Delta E} \right) \ P_u(A) \quad (5.5)$$

where all symbols have their usual meanings (also see eq. (1.7)). Previous NMR investigations of organoselenium and organotellurium compounds have shown that a linear correlation exists between the $^{125}$Te and $^{77}$Se chemical shifts for the elements in isostructural environments. A similar linear relationship was found for the corresponding isostructural environments of selenium and tellurium in the polychalcogenide anions (Figure 5.8). The parameters for the best line fit were obtained by least squares analysis and are given by equation (5.6)

$$\delta(^{125}\text{Te})_{\text{ppm}} = 2.10 \ \delta(^{77}\text{Se})_{\text{ppm}} - 47 \ \text{ppm} \quad (5.6)$$

Although only five points were used to determine the line, the high value of the correlation coefficient, $R = 0.999$, and the large range of the $^{77}$Se and $^{125}$Te chemical shifts fitted, 750 ppm and 1650 ppm, respectively, increases one's
Figure 5.8  Correlation of the $^{125}_{\text{Te}}$ and $^{77}_{\text{Se}}$ chemical shifts for isostructural environments of the polychalcogenide anions (Ch = Se/Te).
confidence in the validity of the relationship. Interestingly, the slope (2.10) is significantly larger than the slopes of 1.6 - 1.8 reported for the organochalcogenides.\textsuperscript{128-131} McFarlane \textit{et al.}\textsuperscript{128} rationalized the value of the slope of the linear relationship by considering the paramagnetic shielding ratio of selenium and tellurium (equation (5.7))

\[
\frac{\delta(^{125}\text{Te})}{\delta(^{77}\text{Se})} = \frac{\Delta\varepsilon(\text{Se})}{\Delta\varepsilon(\text{Te})} \frac{<r^{-3}>_{4p}(\text{Te})}{<r^{-3}>_{3p}(\text{Se})} \frac{P_u(\text{Te})}{P_u(\text{Se})} \tag{5.7}
\]

They estimated the slope to be 1.56 when the ratio $P_u(\text{Te})/P_u(\text{Se})$ was taken as unity. However, a value of 1.96 is obtained for the slope if one uses the $<r^{-3}>_{np}$ ratio estimated by Bawir \textit{et al.}\textsuperscript{131} The high value found for the polychalcogenide anions can be attributed to the higher negative charge of Se relative to Te for isostructural environments. The $P_u(\text{Te})/P_u(\text{Se})$ ratio will be higher than unity because the value of $P_u(\text{Se})$ should be smaller than that of $P_u(\text{Te})$ owing to the higher negative charge on Se. Moreover, the $<r^{-3}>_{np}$ values decrease with higher negative charge owing to increased screening of the nuclear charge by the valence electrons. The values for the $<r^{-3}>_{np}$ ratio should therefore be greater than estimated from the neutral atoms\textsuperscript{128,131} and should also apply to the organochalcogenides. However the charge difference of Se and Te in
isostructural environments is expected to be greater in the polychalcogenide anions because homochalcogen and heterochalcogen bonds are being compared.

(iii) **Coupling Constants** \((^1J, ^1K\) and \(^1K_{RC}\))

The most significant findings resulting from the present solution NMR study of the polychalcogenide anions are the large one-bond spin-spin coupling constants found for the \(\text{Ch}_t-\text{Ch}_t\) and \(\text{Ch}_t-\text{Ch}_b\) units (Table 5.1). In order to be able to compare coupling constants of \(\text{Ch}_n^{2-}\) with other systems the reduced coupling constants, \(^1K\), have been calculated and are listed in Table 5.2.

The one-bond \(^{77}\text{Se}-^{77}\text{Se}\) coupling constants reported for a large number of diselenides,\(^{132}-^{133}\) organopolyselenides\(^{134}\) and \(\text{Se}_n\text{S}_8-\text{n}\) species\(^{135}\) are, in general, small, i.e., 4 - 55 \(\text{Hz} (1 - 13 \times 10^{20}\text{ N.m}^{-3}).\) Similar small values for the coupling constants are observed in diaryl ditellurides,\(^{136}\) 213 - 269 \(\text{Hz} (21 - 27 \times 10^{20}\text{ N.m}^{-3})\) and 170 - 207 \(\text{Hz} (14 - 17 \times 10^{20}\text{ N.m}^{-3})\) for \(^1J(\text{^{123}Te-^{125}Te})\) and \(^1J(\text{^{125}Te-^{125}Te}),\) respectively, and \(\text{MeSeTeMe},^{137}\) 169 \(\text{Hz} (23 \times 10^{20}\text{ N.m}^{-3}).\) This has been rationalized by McFarlane as being due to approximately equal but opposite contributions of different excitations in the Fermi contact interaction, i.e., mainly the transitions \(\sigma \rightarrow \sigma^*\) and \(\text{\tilde{n}} \rightarrow \sigma^*\) (where \(\text{\tilde{n}}\) is a lone pair) for a Ch-Ch bond.\(^{132}\)
Table 5.2

Reduced Coupling Constants, $^{1}K$, and Relativistically Corrected Reduced Coupling Constants, $^{1}K_{RC}$, for the Polychalcogenide Anions\(^a\)

<table>
<thead>
<tr>
<th>Anion</th>
<th>Se-Se</th>
<th>Te-Se</th>
<th>Te-Te</th>
<th>$^{1}K$ (10(^{20}) NA(^{-2}) m(^{-3}))</th>
<th>Se-Se</th>
<th>Te-Se</th>
<th>Te-Te</th>
<th>$^{1}K_{RC}$ (10(^{20}) NA(^{-2}) m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Te}_{2}^{2-}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>366</td>
</tr>
<tr>
<td>$\text{Se}_{3}^{2-}$</td>
<td>61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{TeSe}_{2}^{2-}$</td>
<td></td>
<td>92.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>55.7</td>
</tr>
<tr>
<td>$\text{Te}_{2}\text{Se}^{2-}$</td>
<td></td>
<td>86.9</td>
<td>187</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>52.3</td>
</tr>
<tr>
<td>$\text{Te}_{3}^{2-}$</td>
<td></td>
<td></td>
<td>181</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Se}_{4}^{2-}$</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Te}<em>{2}\text{Se}</em>{2}^{2-}$</td>
<td></td>
<td>87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Te}_{3}\text{Se}^{2-}$</td>
<td></td>
<td>59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{TeSe}_{3}^{2-}$</td>
<td></td>
<td>29.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The one-bond coupling constants are between the $\text{Ch}_{t}-\text{Ch}_{t}$ and $\text{Ch}_{t}-\text{Ch}_{b}$ environments of the anions as measured in en and liquid ammonia (see Table 5.1).
As the latter contribution is negative and dominates if the Ch-Ch bond has a small s character, McFarlane suggested the Ch-Ch bond has a moderately high s character as the reduced coupling constant is positive for organodiselenides\(^{132}\) and MeSeTeMe.\(^{137}\) Large couplings for directly bonded selenium atoms, 300 - 400 Hz (70 - 90 x 10\(^{20}\) \text{NAm}^{-2}\text{m}^{-3}\) have been observed for neutral species in small ring systems. This has been attributed to a forced p-orbital interaction between the adjacent atoms.\(^{134}\) For the open chain structures of the polychalcogenide anions it is unlikely that a similar type of mechanism is responsible for their observed large Ch\(_t\)-Ch\(_b\) one-bond coupling constants. Evidently, the nature of the Ch\(_t\)-Ch\(_b\) bonds is significantly different than the Ch\(_b\)-Ch\(_b\) bonds in the neutral species.

In general it has been found for the polychalcogen cations that there is a certain degree of delocalization of the positive charge from the three-coordinate atoms to the neighboring atoms\(^{138}\) for which large one-bond coupling constants are often observed.\(^{139}-140\) This suggests the large coupling constants observed for the trichalcogenide anions might be attributed to some type of delocalization of the negative charge from the terminal atom, Ch\(_t\), to the adjacent bridging chalcogen atom, Ch\(_b\). One possible mechanism for charge delocalization would be \(\pi\) back-donation of a lone pair on Ch\(_t\) to the bridging chalcogen atom as shown in Scheme III.
Scheme III

This type of delocalization could introduce a higher s character in the $\text{Ch}_t$-$\text{Ch}_b$ bond as the terminal atom could be regarded as being $sp^2$-hybridized, resulting in a larger coupling constant. However, the $\text{Ch}_t$-$\text{Ch}_b$ bond lengths for the $\text{TeSe}_2^{2-}$ (2.50 Å, see Section C) and $\text{Te}_3^{2-}$ (2.69 and 2.72 Å)$^{110}$ anions are only slightly shorter than their expected single bond lengths (2.53 Å for Se-Te and 2.74 Å for Te-Te as given by Pauling$^{141}$), indicating a relatively small degree of $\pi$ back-bonding. Furthermore, the one-bond reduced coupling constant for the $\text{TeSe}_3^{2-}$ anion is, in fact, much smaller than in the $\text{TeSe}_2^{2-}$ anion, contrary to what one would have expected as $\pi$ back-bonding is quite significant in the former anion (see Section C).

Another alternative is that the atomic hybrid of $\text{Ch}_b$ used in the $\text{Ch}_t$-$\text{Ch}_b$ bond has a high s character relative to the corresponding hybrid of $\text{Ch}_t$, as shown in Scheme IV.
The $\text{Ch}_b$ atomic hybrid would now be more electronegative than that of $\text{Ch}_t$ owing to its higher $s$ character, therefore, polarizing the $\sigma$ bond, to a certain extent, towards the $\text{Ch}_b$ atom. As a result, the bridging atom can now bear some of the negative charge of the anion although most of the negative charge is presumably concentrated mainly on the terminal atom according to TSCR. Interestingly, the bond angles observed for $\text{Te}_3^{2-}$ (113$'$)\textsuperscript{110} and $\text{TeSe}_2^{2-}$ (110$'$, see Section C) are larger than the ideal tetrahedral value for four electron pairs apparently violating the VSEPR rules for two lone pairs and two bond pairs around an atom.\textsuperscript{142} This indicates that the two bond pairs are very diffuse in the valence shell of the central chalcogen atom, consistent with a high $s$ character for its bonding atomic hybrids. In fact, the $\text{Te}_b$ atoms are close to being sp$^3$-hybridized as is evident from the bond angles. The similar values of the one-bond reduced coupling constants for $\text{Te}_3^{2-}$ and $\text{SnTe}_4^{4-}$ (Table 5.3) further suggest that the $\text{Te}_b$ atom is, like the tin atom,
sp³-hybridized, assuming hybridization of the Te₇ atoms is similar in the two anions.

An unexpected type of trend was observed for the chemical shifts of the Se₃²⁻ and Te₃²⁻ anions in that the Ch₇ atoms are more shielded than the Ch₅ atoms. This is opposite to what one would expect as the lower electron unbalance, Pᵤ, and the negative charge (smaller <r⁻³>np) of Ch₇ relative to Ch₇ should make the former more shielded according to equation (5.5). However, owing to the average energy approximation, equation (5.5) only takes filled molecular orbitals into account, whereas, in general, σP results from an interaction between p orbitals in the occupied and unoccupied molecular orbitals.⁶⁸ As a consequence of Scheme IV the σ* orbitals, which are the LUMOs, are polarized towards the Ch₅ atoms. The paramagnetic contribution to shielding, σP(Ch₇), can then become greater than σP(Ch₇) as the coefficients of the atomic p orbitals of Ch₇ in σ* increase whereas the corresponding coefficients of the p orbital of Ch₇ decrease, accounting for the chemical shift trends observed for Se₃²⁻ and Te₃²⁻.

A similar type of bonding also appears to exist for the Ch₅-Ch₇ units of the tetrachalcogenide anions, albeit to a somewhat smaller extent judging from their smaller reduced coupling constants. The Ch₇-Ch₇ bonds, however, presumably represent similar types of bonding as in the neutral
polychalcogenides, consequently, causing the chemical shift of the bridging atom environment to be more deshielded than the terminal one. The large reduced coupling constants, $^{1}K(Te_{t}-Te_{t})$, observed for $Te_{2}^{2-}$ fit the classical bonding scheme for diatomic species. However, the $s$ character of the atomic hybrids used in the $\sigma$ bond must be smaller than for $sp$-hybrid as $^{1}K(Te_{t}-Te_{t})$ is only twice the value of $^{1}K(Te_{b}-Te_{t})$ for the $Te_{3}^{2-}$ anion.

From the discussion above it became evident that the trichalcogenide anion series, $TeCh_{2}^{2-}$, resembled the metal chalcogenide anions studied previously. For further comparison, the values of $^{1}K(M-Se)$, $^{1}K(M-Te)$, $^{1}K_{RC}(M-Se)$ and $^{1}K_{RC}(M-Te)$ for the $TeCh_{2}^{2-}$ anions and those of the metal chalcogen anions are expressed as a function of $n$, the number of substituted selenium atoms, in Table 5.3. Furthermore, the formal hybridizations of the central atoms of the metal chalcogen anions are also given in Table 5.3 for comparison as, in general, the one-bond coupling constants have been found to be greater the higher the $s$ character of the atomic hybrids (see Section D(iii) Chapter 1). From Table 5.3 we note that $^{1}K(Te_{b}-Se_{t})$ and $^{1}K(Te_{b}-Te_{t})$ for the $TeCh_{2}^{2-}$ anions are roughly midway between the corresponding values for the $SnCh_{4}^{4-}$ and $Pb_{2}Ch_{3}^{2-}$ series. A similar correlation is also evident for $^{1}K_{RC}(M-Se_{t})$ and $^{1}K_{RC}(M-Te_{t})$ except the $^{1}K_{RC}(M-Te_{t})$ values for the $SnCh_{4}^{4-}$ and $TeCh_{2}^{2-}$ series are very
Table 5.1  
Linear Relationship Between the One-Bond $M$-Se and $M$-Te Reduced Coupling Constants, $^{1}K$, and the Relativistically Corrected Reduced Coupling Constants, $^{1}K_{RC}$, of $M_{2}Se_{n}Te_{m-n}^{-}$ and the Number of Se Atoms, $n$

<table>
<thead>
<tr>
<th>Series</th>
<th>$M$-Se Bond</th>
<th>$M$-Te Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{x}Se_{n}Te_{m-n}^{-}$</td>
<td>$^{1}K$</td>
<td>$^{1}K_{RC}$</td>
</tr>
<tr>
<td>HgSe$<em>{n}$Te$</em>{2-n}^{-}$</td>
<td>559 - 2.9n</td>
<td>154 - 0.8n</td>
</tr>
<tr>
<td>TlSe$<em>{n}$Te$</em>{3-n}^{-}$</td>
<td>501 + 15.7n</td>
<td>142 + 4.5n</td>
</tr>
<tr>
<td>SnSe$<em>{n}$Te$</em>{3-n}^{-}$</td>
<td>217 + 8.0n</td>
<td>132 + 4.8n</td>
</tr>
<tr>
<td>SnSe$<em>{n}$Te$</em>{4-n}^{-}$</td>
<td>140 + 7.7n</td>
<td>85 + 4.7n</td>
</tr>
<tr>
<td>TeSe$<em>{n}$Te$</em>{2-n}^{-}$</td>
<td>83 + 4.8n</td>
<td>50 + 2.9n</td>
</tr>
<tr>
<td>Pb$<em>{2}Se</em>{n}$Te$_{3-n}^{-}$</td>
<td>56 - 8.1n</td>
<td>16 - 2.3n</td>
</tr>
</tbody>
</table>

a Values in $10^{20}$ x NA$^{-2}$m$^{-3}$.

b Reference (49).

c Line defined by any two points.

d The correlation factor, $R$, is 1.000 for both $^{1}K$(Pb-Se) and $^{1}K$(Pb-Te).
similar whereas the $^{1}K_{RC}(TeB-Se_t)$ values for the $TeCh_2^{2-}$ anions are midway between the $^{1}K_{RC}(M-Se)$ values for the $SnCh_4^{4-}$ and the $Pb_2Ch_3^{2-}$ anions. As discussed previously, the former trend suggests that the atomic hybrids $TeB$ in the $TeB-Te_t$ bonds of the $TeCh_2^{2-}$ anions are similar to those of Sn in the $SnCh_4^{4-}$ anions. However, the smaller value of $^{1}K_{RC}(TeB-Se_t)$ for $TeCh_2^{2-}$ indicates that the $s$ character of the $TeB$ atomic hybrids in the $TeB-Se_t$ bonds are much smaller. This can be rationalized by the bonding scheme depicted in Scheme IV as there should be less $\sigma$ bond polarization of the negative charge to the $TeB$ atom when Te is bonded to the more electronegative selenium atom, thus, lowering the $s$ character in the atomic hybrid of $TeB$ used in the $\sigma$ bonding.

The most interesting aspect of the simple bonding depicted in Scheme IV for the $Ch_t-Ch_b$ bonds is the fact that one can rationalize the large spin coupling constants, the relatively large bond angles observed for the trichalcogenide anions and the reversed chemical shifts of the $Ch_t$ and $Ch_b$ atoms in the $Se_3^{2-}$ and $Te_3^{2-}$ anions. Interestingly, a similar bonding model for the related iodine cations, $I_3^+$, $I_2Cl^+$ and $ICl_2^+$, was used in order to estimate their charge distributions from nuclear quadrupole resonance studies. Thus, two bonding orbitals on the central iodine atom, generated from $s$, $p_x$ and $p_y$ orbitals, interact with pure $p$ orbitals on the terminal halogen atoms. However, other types
of bonding schemes cannot be excluded. The relatively large bond angles could simply arise from the repulsion of the negatively charged terminal atoms. Furthermore, one can argue that the reversed chemical shift trend for the homotrichalcogenide anions is the result of π back-bonding shown in Scheme III as a large paramagnetic chemical shift has been found for selenium π-bonded to a carbon in selenoketones. Therefore, only a small π-bonding contribution for the C₇ atom could cause it to have a higher paramagnetic chemical shift than the C₈ atom. Although the factors causing the large coupling constants would be unknown, an interesting trend can be noted for reduced coupling constants in organoditelluride, tritelluride and ditelluride anions in that there is approximately a constant linear increase of 180 x 10²⁰ NA⁻²m⁻³ per additional lone pair on the atoms directly bonded to each other. This type of trend can, for example, be rationalized in terms of increasing numbers of lone pair to σ* orbital excitations, ñ → σ*, in the Fermi contact term, and is similar to the type of mechanism discussed by Pyykkö and Wiesenfeld. It must be noted, however, that this type of additivity trend is not observed for MeSe⁻, Me₂Se and Me₃Se⁺ where the coupling constant ¹J(C-77Se) are -58, -62 and -50 Hz, respectively.
(C) CRYSTAL STRUCTURES OF THE TeSe$_2^{2-}$ AND TeSe$_3^{2-}$ ANIONS

Crystals of (2,2,2-K$^+$)$_2$ TeSe$_3^{2-}$·en were obtained by slow evaporation of solutions resulting from reactions of K$_2$Te with 3Se in en in the presence of 2,2,2-crypt. Crystals of (2,2,2-K$^+$)$_2$TeSe$_2^{2-}$·en were isolated from an NMR sample prepared by the reaction of K$_2$Te with 2Se. The X-ray crystal structures were determined by Dr. J. F. Sawyer, University of Toronto and the crystal data is given in Table 5.4. The crystal structures consisted of discrete 2,2,2-crypt-K$^+$ cations, ethylenediamine molecules and TeSe$_2^{2-}$ and TeSe$_3^{2-}$ anions.

The most interesting aspects of the crystal structures are the telluroselenide anions, the new V-shaped TeSe$_2^{2-}$ anion and the trigonal pyramidal shaped TeSe$_3^{2-}$ anion (Figure 5.9). The bond distances and bond angles for TeSe$_2^{2-}$ and TeSe$_3^{2-}$ are given in Table 5.5 as well as their average values.

The average Te-Se distance of 2.46 Å in the pyramidal TeSe$_3^{2-}$ anion is 0.07 Å shorter than the single Te-Se bond length of 2.53 Å given by Pauling.$^{141}$ This is to be expected from the resonance of the valence bond structures for the anion according to Scheme V giving a bond order of 1 1/3 for the Te-Se bond. Moreover, the Te-Se distance of 2.46 Å calculated from Paulings equation$^{144}$ for multiple bond distances is in good agreement with the measured Te-Se bond
### Table 5.4
Crystal Data for $(2,2,2-K^+)_2TeSe_2^{2-}\cdot en$ and $(2,2,2-K^+)_2TeSe_3^{2-}\cdot en$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$(2,2,2-K^+)_2TeSe_2^{2-}\cdot en$</th>
<th>$(2,2,2-K^+)_2TeSe_3^{2-}\cdot en$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>$C_{38}H_{80}O_{12}N_{6}K_{2}Se_{2}Te$</td>
<td>$C_{38}H_{80}O_{12}N_{6}K_{2}Se_{3}Te$</td>
</tr>
<tr>
<td><strong>Formula Weight</strong></td>
<td>1176.7</td>
<td>1255.7</td>
</tr>
<tr>
<td><strong>System</strong></td>
<td>Triclinic</td>
<td>Trigonal</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>P1 (No 1)</td>
<td>P3$_2$ (No 145)</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>10.9725(8)</td>
<td>12.386(5)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>12.1940(9)</td>
<td>12.386(5)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>12.3242(10)</td>
<td>30.669(15)</td>
</tr>
<tr>
<td><strong>α (deg)</strong></td>
<td>59.182(7)</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (deg)</strong></td>
<td>73.781(7)</td>
<td>90</td>
</tr>
<tr>
<td><strong>γ (deg)</strong></td>
<td>67.718(6)</td>
<td>120</td>
</tr>
<tr>
<td><strong>V (Å$^3$)</strong></td>
<td>1303</td>
<td>4076</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>603.47 (604)</td>
<td>637.32 (638)</td>
</tr>
<tr>
<td><strong>ρ_{calc} (g cm$^{-3}$)</strong></td>
<td>1.50</td>
<td>1.54</td>
</tr>
<tr>
<td><strong>λ (Å)</strong></td>
<td>0.71069</td>
<td>0.71069</td>
</tr>
<tr>
<td><strong>μ (Mo Kα), (cm$^{-1}$)</strong></td>
<td>21.7</td>
<td>27.5</td>
</tr>
<tr>
<td><strong>Total no. data colld.</strong></td>
<td>7095</td>
<td>8362</td>
</tr>
<tr>
<td><strong>Unique data</strong></td>
<td>6394</td>
<td>2304</td>
</tr>
<tr>
<td><strong>No. observed data</strong></td>
<td>4459 (I ≥ 3σ(I))</td>
<td>1810 (I ≥ 2.5σ(I))</td>
</tr>
<tr>
<td><strong>R$_1$</strong></td>
<td>0.0382</td>
<td>0.0685</td>
</tr>
<tr>
<td><strong>R$_2$</strong></td>
<td>0.0465</td>
<td>0.0711</td>
</tr>
</tbody>
</table>
Figure 5.9 ORTEP diagrams of the (a) TeSe$_2^{2-}$ and (b) TeSe$_3^{2-}$ anions including the atomic numbering schemes.
Table 5.5

Selected Bond Lengths (Å) and Bond Angles (deg) for the TeSe$_2^{2-}$ and TeSe$_3^{2-}$ Anions

**TeSe$_2^{2-}$**

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te-Se(1)</td>
<td>Se(1)-Te-Se(2) 111.3</td>
</tr>
<tr>
<td>Te-Se(2)</td>
<td></td>
</tr>
<tr>
<td>ave. Te-Se</td>
<td></td>
</tr>
</tbody>
</table>

2.501(1) 2.504(1) 2.50

**TeSe$_3^{2-}$**

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te-Se(1)</td>
<td>Se-(1)-Te-Se(2) 108.9(1)</td>
</tr>
<tr>
<td>Te-Se(2)</td>
<td>Se-(1)-Te-Se(3) 104.8(2)</td>
</tr>
<tr>
<td>Te-Se(3)</td>
<td>Se-(2)-Te-Se(3) 107.4(1)</td>
</tr>
<tr>
<td>ave. Te-Se</td>
<td>ave. Se-Te-Se 107</td>
</tr>
</tbody>
</table>

2.454(4) 2.465(4) 2.460(4) 2.46
Scheme V

length (equation (5.8)). However, the average Te-Se bond lengths of the TeSe$_3^{2-}$ anion in the Na$_2$TeSe$_3$ and K$_2$TeSe$_3$ phases (2.49 and 2.50 Å, respectively)$^{117}$ are longer than in the 2,2,2-crypt-K$^+$ salt.

$$r_n(A-B) = r_1(A-B) - 0.60 \log n \quad (5.8)$$

As discussed previously, the TeSe$_3^{2-}$ anion is isostructural with the thiotellurite anion TeS$_3^{2-}$, although the average Se-Te-Se bond angles of 102° (Na$_2$TeSe$_3$)$^{117}$ 103° (K$_2$TeSe$_3$)$^{117}$ and 107° ((2,2,2-crypt-K$^+$)$_2$TeSe$_3^{2-}$·en) for the selenotellurite anion are somewhat larger than those found for the TeS$_3^{2-}$ anions; 101° (BaTeS$_3$)$^{145}$ 103° (Ba$_2^+$TeS$_3^{2-}$·2H$_2$O)$^{123}$ 106° ((NH$_4^+$)$_2$TeS$_3^{2-}$)$^{123}$ and 102.4° (K$^+$$_3$(SH$^-$)TeS$_3^{2-}$)$^{124}$ According to the VSEPR rules this might signify that sulfur is more electronegative than selenium in these systems. However, such a comparison of these small differences in the bond angles of TeSe$_3^{2-}$ and TeS$_3^{2-}$ may not be valid as the Se-Te-Se and S-Te-S bond angles vary widely depending on the crystal environments of the anions.
Pyramidal TeSe$_3$ moieties are also found in the Te$_2$Se$_6^{2+}$ and Te$_2$Se$_8^{2+}$ cations. In general, the average Te-Se bond lengths of the cations are larger (Te-Se = 2.60 and 2.57 Å, respectively) than the single bond distance and the average bond angles (Se-Te-Se = 96° and 100°, respectively) are smaller than for the TeSe$_3^{2-}$ anion. Interestingly, the one-bond spin-spin coupling constant, $^{1}J(^{125}Te-^{77}Se)$, of Te$_2$Se$_6^{2+}$ (355 Hz) is larger than for TeSe$_3^{2-}$. From a simple consideration of the geometry of the pyramidal units one would have expected the Te-Se bond of TeSe$_3^{2-}$ to have a higher s character, and therefore a larger $^{1}J(^{125}Te-^{77}Se)$ than Te$_2$Se$_6^{2+}$. However, the coupling constants are, in general, inversely proportional to the energy difference, ΔE, of the σ and σ* orbitals. It is conceivable that ΔE is smaller for the longer and presumably weaker Te-Se bonds of Te$_2$Se$_6^{2+}$, consequently resulting in a larger value for $^{1}J(^{125}Te-^{77}Se)$.

The Te-Se bond length of the V-shaped TeSe$_2^{2-}$ anion is 0.03 Å shorter than the single bond distance. Although this could be taken as evidence for multiple bonding in the TeSe$_2^{2-}$ anion, a shortening of only 0.03 Å does not indicate a high degree of π character (bond order = 1.1 - 1.2) relative to the TeSe$_3^{2-}$ anion. As was discussed in Section C, the large bond angles of TeSe$_2^{2-}$ (111°) and Te$_3^{2-}$ (113°) could be rationalized from Scheme IV in terms of
the relatively high s character of the atomic hybrid of $\text{Ch}_b$ in the $\text{Ch}_t$-$\text{Ch}_b$ bond. In general, it has been observed for a large number of molecules that the bond distances become shorter the higher the s-character of the bonds,\textsuperscript{147} and the same rationale may account for shortening of the $\text{Ch}_t$-$\text{Ch}_b$ bonds.

It is evident from the interatomic distances that ethylenediamine solvent molecules in the crystal lattice interact only weakly with the TeSe$_2^{2-}$ and TeSe$_3^{2-}$ anions in $(2,2,2-K^+)_2\text{TeSe}_2^{2-}\cdot\text{en}$ and $(2,2,2-K^+)\text{TeSe}_3^{2-}\cdot\text{en}$. Thus, the Se$\cdots$N contact distances (3.63, 3.67 and 3.83 Å) between the TeSe$_3^{2-}$ anion and en are all longer than the sum of their van der Waals radii (3.5 Å)\textsuperscript{148} and, therefore, indicate only weak hydrogen bonding.\textsuperscript{149} However, the relatively short Se$\cdots$N contact distance (3.49 Å) between TeSe$_2^{2-}$ and en indicate a somewhat stronger hydrogen bonding interaction in $(2,2,2-K^+)\text{TeSe}_2^{2-}\cdot\text{en}$.

(D) SELENOTHIOTTELLURITE ANIONS, $\text{TeSe}_{m}\text{Se}_{3-m}^{2-}$

The existence of the isovalent and isostructural anions TeSe$_3^{2-}$ and TeS$_3^{2-}$ indicated that the corresponding mixed S/Se species could be prepared and characterized in solution by $^{77}$Se and $^{125}$Te NMR spectroscopy. The relative electronegativities of S and Se are reversed in the two most widely used electronegativity scales; Pauling\textsuperscript{150} $\chi_S = 2.5$, \[ \begin{align*}
\text{TeSe}_{m}\text{Se}_{3-m}^{2-} &
\end{align*} \]
$\chi_{Se} = 2.4$) and Allred-Rochow\textsuperscript{151} ($\chi_S = 2.4$, $\chi_{Se} = 2.5$). It was therefore of interest to study the extent to which the two elements effect the electronic structures, and consequently the NMR parameters, of the anions.

The $\text{TeS}_m\text{Se}_{3-m}^2-$ anions where prepared in en, using both sulfur- and selenium-rich reaction mixture, according to reactions (5.9) and (5.10)

$$\text{Te}^{2-} + 2 \text{S} + \text{Se} \xrightarrow{\text{crypt}_{\text{en}}} \text{TeS}_m\text{Se}_{3-m}^2- \quad (5.9)$$

$$\text{Te}^{2-} + \text{S} + 2 \text{Se} \xrightarrow{\text{crypt}_{\text{en}}} \text{TeS}_m\text{Se}_{3-m}^2- \quad (5.10)$$

in the presence of 2,2,2-crypt. The corresponding $^{125}\text{Te}$ and $^{77}\text{Se}$ NMR spectra of both the sulfur- and selenium-rich solutions were recorded (Figures 5.10 and 5.11). As expected for a mixture of $\text{TeS}_m\text{Se}_{3-m}^2-$ anions in solution, a total of four $^{125}\text{Te}$ and three $^{77}\text{Se}$ environments were observed. The $^{77}\text{Se}$ and $^{125}\text{Te}$ environment of each could be identified by comparison of the magnitude of the satellite doublet spacing arising from the one-bond scalar couplings $^1J(77\text{Se}-125\text{Te})$. The number of selenium and tellurium atoms in each anion could be determined by comparing the measured satellite peak/central peak area ratio for each environment with the theoretical ratio. The assignment of the $^{125}\text{Te}$ environment of $\text{TeS}_3^2-$ was based on the absence of satellites associated with it and the fact that there is a linear increase in the
Figure 5.10  $^{125}\text{Te}$ NMR spectra (78.917 MHz) of the $\text{TeS}_m\text{Se}_{3-m}^{2-}$ ($m = 0 - 3$) in en solvent: (Q) $\text{TeS}_3^{2-}$; (P) $\text{TeS}_2\text{Se}^{2-}$; (O) $\text{TeSe}_2^{2-}$; (N) $\text{TeSe}_3^{2-}$.
Peaks p', o' and n' denote $^{77}\text{Se}$ satellites.
Figure 5.11  $^{77}$Se NMR spectrum (47.704 MHz) of the
$\text{TeS}_m\text{Se}_{3-m}{^2-}$ ($n = 0 - 3$) in a solvent at 50 °C
for the Se rich solution: (N) $\text{TeSe}_3{^2-}$; (O)
$\text{TeSe}_2{^2-}$; (P) $\text{TeS}_2\text{Se}_2{^2-}$. Peaks $p'$, $o'$ and $n'$
denote $^{125}\text{Te}$ satellites.
Table 5.6

$^{77}\text{Se}$ and $^{125}\text{Te}$ NMR Parameters for the $\text{TeS}_m\text{Se}_3-^m$ Anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>$^{77}\text{Se}$ (ppm)</th>
<th>$^{125}\text{Te}$ (ppm)</th>
<th>$^{1}J(\text{125Te}-^{77}\text{Se})$ (Hz)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TeSe}_3^{2-}$</td>
<td>480</td>
<td>1087</td>
<td>210 (29.0, 17.4)</td>
<td>24 50</td>
</tr>
<tr>
<td>$\text{TeS}_2\text{Se}_2^{2-}$</td>
<td>466</td>
<td>1255</td>
<td>244 (33.7, 20.3)</td>
<td>24 50</td>
</tr>
<tr>
<td>$\text{TeS}_2\text{Se}^{2-}$</td>
<td>452</td>
<td>1396</td>
<td>288 (39.8, 23.9)</td>
<td>24 50</td>
</tr>
<tr>
<td>$\text{TeS}_3^{2-}$</td>
<td>1514</td>
<td></td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>

*Estimated experimental error in $^{1}J(77\text{Se}-125\text{Te}) \pm 6$ Hz. $^{1}K(\text{Te-Se})$ and $^{1}K_{RC}(\text{Te-Se})$ are given in parentheses in units of $10^{20}$ NA$^{-2}$m$^{-3}$, respectively.*
\(^{125}\)Te chemical shifts for the anions as a function of \(m\), the number of sulfur atoms, for the \(\text{TeS}_m\text{Se}_3\text{m}^2\) anions, and is also indicative of a homologous series of anions. Similarly, the \(^{77}\)Se chemical shifts and the one-bond coupling constant, \(^{1}J(^{125}\text{Te}^{77}\text{Se})\), vary almost linearly with the number of sulfur atoms in the series. The NMR data are summarized in Table 5.6.

The \(^{77}\)Se chemical shifts of the \(\text{TeS}_m\text{Se}_3\text{m}^2\) anions are found to be at much higher frequency than the corresponding selenium environments of the \(\text{Se}_n\text{Te}_b\) units of the open chain tri- and tetrachalcogenide anions at -55 to -130 ppm (Section A). This could be caused by an increase in the electron unbalance term, \(P_u\), of the selenium atoms which serves to increase the paramagnetic chemical shift, as the selenium atoms are now bonded to a more electronegative tellurium atom. However, such a large paramagnetic contribution to the \(^{77}\)Se chemical shift for the \(\text{TeS}_m\text{Se}_3\text{m}^2\) series cannot be attributed entirely to this factor and, in fact, indicates that there is considerable \(\pi(p-d)\) character in the Se-Te bonds. This type of \(\pi\)-bonding is to be expected in the \(\text{TeS}_m\text{Se}_3\text{m}^2\) anions based on the valence bond structures depicted in Scheme V. Interestingly, the \(^{77}\)Se chemical shifts become more shielded as the number of sulfur atoms increases in the \(\text{TeS}_m\text{Se}_3\text{m}^2\) series. Although this could be interpreted to indicate that \(\chi_{\text{Se}} > \chi_{\text{S}}\), a similar
increase in the shielding was observed for a number of mixed Se/Te metal chalcogenide anions (see Section D(ii) Chapter 1). The observed trend in the $^{77}$Se chemical shift may simply arise from a decrease in $\pi$ back-bonding of Se with increasing number of stronger $\pi$-donating sulfur atoms in the anions.

From Table 5.6 we note that the $^{125}$Te chemical shift becomes more deshielded with increasing numbers of sulfur atoms. However, the change is relatively large per substitution of Se with S if one considers, for example, the correspondingly small changes in the $^{77}$Se chemical shifts. This suggests that there is an increase in participation of the tellurium 5d orbitals in the $\pi$-bonding providing an additional factor in the paramagnetic chemical shift, $\sigma^p$, for tellurium as given by equation (5.11)

$$\sigma^p = \frac{\mu_0 e^2 h^2}{24 \pi^3 m^2 \Delta E} \langle r^{-3} \rangle_{5d} D_u$$ (5.11)

where all the symbols have their usual meaning and $D_u$ is the d electron unbalance of tellurium. Thus, as the number of the stronger Te-S $\pi$-bonds increases for the TeS$_m$Se$_3$-$m^2$-anions, the 5d electron unbalance of tellurium correspondingly increases owing to increasing participation of the 5d orbitals in the bonding.

The one-bond scalar coupling constants $^{1}J(^{125}$Te-$^{77}$Se), $^{1}K$(Te-Se), and $^{1}K_{RC}$(Te-Se) for the TeS$_m$Se$_3$-$m^2$- series
are given in Table 5.6. Their values are found to increase with the number of S atoms similar to many mixed Se/Te metal chalcogenide anions when Te is substituted by the more electronegative Se atom. This would be consistent with the mechanism discussed in Section D(iii), Chapter 1, in which the s character of tellurium atomic hybrid orbital used in the Te-Se σ-bond increases as the effective electronegativity of Te is increased by increasing m, the number of S atoms. Although this would also indicate that S was more electronegative than Se, one has to consider that the values of the coupling constants are relatively small. It is therefore possible that the observed trend arises from approximately equal, but opposite contributions of different excitations in the Fermi contact interaction, similar to what was observed for the small coupling constant of the Pb₂Ch₃²⁻ series (Chapter 4).

Interestingly, even though one cannot determine with certainty the relative electronegativity order of sulfur and selenium from the trends in a single NMR parameter, most of the trends, as well as the bond angles of TeSe₃²⁻ and TeS₃²⁻, indicate that sulfur is more electronegative than selenium in this series of mixed TeₐSe₃₋ₐ²⁻ anions.
CHAPTER 6

REACTIONS OF SnCh WITH K2Ch (Ch = Se, Te):

PREPARATION OF Sn2Se3²⁻ AND SnPbSe3²⁻

INTRODUCTION

In recent years a number of tin selenide and tin telluride anions have been prepared and structurally characterized in the solid state by X-ray crystallography. Among the anions which have been characterized are the tetrahedral SnCh₄⁴⁻ (Ch = Se, Te)⁸⁵,¹⁵² anions and the Sn₂Ch₆⁴⁻ ⁵²,¹⁵³ anions. The structures of the Sn₂Ch₆⁴⁻ anions are based on two edge sharing SnCh₄ tetrahedra and are therefore isostructural with B₂H₆ (D₂h). More complex structures have been found for some tin telluride anions such as the five-membered ring Sn₂Te₇⁴⁻ in Cs₄Sn₂Te₇ and the polymeric [SnTe₅²⁻]ₘ anion in the Rb₂SnTe₅ phase.¹⁵⁴

However, for all the anions there are four chalcogen atoms tetrahedrally bonded to the Sn(IV) atoms. In their extensive multinuclear magnetic resonance solution study of the main-group metal chalcogenide anions, Schrobilgen et al.⁴⁹ characterized the mixed Se/Te SnCh₄⁴⁻ anions as well as the new series of tin chalcogenide anions, SnCh₃ᵏ⁻, in which the Sn atoms were found to be bonded to only three chalcogen
atoms. Two structures were postulated for the new anion series, SnCH₃⁻⁻; a trigonal planar Structure I for SnCH₃ Zw- (D₃h) and a trigonal pyramidal Structure II for SnCH₃₂⁻⁻ (C₃v) with a lone pair on the Sn atom

![Chemical Structures](image)

As the oxidation states of the tin atoms in the two structures are different, i.e., Sn(IV) and Sn(II) for the SnCH₃₂⁻⁻ and SnCH₃₄⁻⁻, respectively, the new anions could be assigned to the former series on the basis of their ¹¹⁹Sn Mössbauer isomer shifts.⁵⁰ Although the SnCH₃₂⁻⁻ anions could be identified as having three coordinated Sn(IV) atoms, it was unusual that they existed as monomers in solution as only the dimers, Sn₂Ch₆₄⁻⁻, were found in the solid state. The Sn₂Se₆₄⁻⁻ anion has, however, since been identified in en solutions.⁵³

From these studies it was apparent that only tin chalcogenide anions in which the tin atom was in its principal oxidation state +4 could be prepared from alkali metal tin chalcogen alloys, either directly or by extraction of the alloy in en. In fact, the formation of the SnCH₄⁺⁻ anions and the SnCH₃²⁻⁻ anions in en from the NaSnCh and
KSnCh₂ alloys, respectively, could be rationalized on the basis that only Sn(0) and Sn(IV) species existed in the alloys. It was therefore evident that Sn(II) chalcogenide anions could only be prepared by allowing Sn(II) compounds and polychalcogenide anions, Chₙ²⁻, to react directly in solution. Devereux⁵³ obtained a reddish-orange solution when anhydrous SnCl₂ was allowed to react with the ditelluride anion, Te₂²⁻, in en. As more Te₂²⁻ was added the solution became deep red and finally red-brown after three equivalents of Te₂²⁻ had been added to the solution. The ¹²⁵Te NMR spectrum of the solution showed that only the Te₃²⁻ anion was present. However, when the reaction was halted and the reddish-orange solution isolated, a number of new environments as well as the SnTe₃²⁻ anion could be identified in the ¹²⁵Te and ¹¹⁹Sn NMR spectra after a stoichiometric amount of 2,2,2-crypt had been added to the solution. Evidently the Sn(II) compound had been oxidized by the Te₂²⁻ anion to form the SnTe₃²⁻ anion. The formation of SnTe₃²⁻ and Te₃²⁻ anions in the solutions can be rationalized by reaction (6.1)

\[
\text{SnCl}_2 + 3\text{Te}_2^{2-} \xrightarrow{\text{en}} \text{SnTe}_3^{2-} + \text{Te}_3^{2-} + 2\text{Cl}^- \quad (6.1)
\]

The new species could not be characterized any further as their peaks were broad or spin satellites were lacking.
From these results it was apparent that in order to avoid complications arising from oxidation of Sn(II) compounds to Sn(IV) species when, the tin(II) chalcogenide, SnCh, must be allowed to react directly with the monochalcogenide anion, Ch^2-. This appeared to offer a relatively convenient synthetic route for tin(II) chalcogenide anions as SnCh can be prepared by the direct fusion of the elements and was, consequently, the route taken in this study.

RESULTS AND DISCUSSION

(A) REACTIONS OF K₂Se WITH SnSe AND SnSe/PbSe

(i) Preparation and Characterization of Sn₃Se³⁻

In the attempt to prepare new lead chalcogenide anions which were other than the trigonal bipyramidal Pb₂Ch₃²⁻ (Ch = Se, Te) anions (Chapter 4) it was discovered that the Pb₂Se₃²⁻ anion could be prepared in en by the direct reaction of K₂Se with PbSe in the presence of 2,2,2-crypt (Crypt). This suggested a similar approach could be used to prepare the corresponding and hitherto unknown Sn₂Se₃²⁻ anion according to reaction (6.2)

\[
K₂Se + 2 \text{SnSe} \xrightarrow{\text{Crypt, en}} 2 \text{Crypt-K}^+ + 2 \text{Sn₂Se₃}²⁻ \quad (6.2)
\]

Consequently, a K₂Se/SnSe mixture in the ratio 1:2 was
allowed to react in en in the presence of 2,2,2-crypt. From the $^{77}\text{Se}$ NMR spectrum of the yellow solution it was evident that unreacted $\text{Se}^{2-}$ anion was the major species in solution. This was not surprising as relatively large amounts of alloy residue remained in the glass ampule of the reaction vessel when the solution was isolated. However, a large number of new selenium and tin environments were observed, some of which had satellites (Table 6.1). Comparison of the satellite spacings of two new environments, one selenium and one tin, showed that they were spin coupled to one another (Figure 6.1). The satellite peak/central peak height ratios, $I_5/I_C$, indicated that the Se environment was bonded to two equivalent Sn atoms but that the Sn environment was bonded to three selenium atoms. In addition, a second pair of satellite doublet lines having a larger splitting was also observed for the Sn environment in both the $^{117}\text{Sn}$ and $^{119}\text{Sn}$ NMR spectra, and could be attributed to $^{119}\text{Sn}$ and $^{117}\text{Sn}$ spin-spin coupling, respectively. The satellite peak/central peak height intensity ratios for these satellites showed that they resulted from coupling to one Sn atom. Consequently, the new Se and Sn environments are assigned to the new trigonal bipyramidal $\text{Sn}_2\text{Se}_3^{2-}$ anion ($D_{3h}$) with the Se atoms in the equatorial plane and the Sn atoms in the apical positions (Figure 6.2 a).
Figure 6.1  (a) $^{117}\text{Sn}$ NMR spectrum (89.128 MHz) and (b) $^{77}\text{Se}$ NMR spectrum (47.704 MHz) of the trigonal bipyramidal $\text{Sn}_2\text{Se}_3^{2-}$ anion (A) in en solvent. Peaks labeled $a_1$, $a_1'$, and $a_2$ arise from $^1J(^{77}\text{Se}-^{117}\text{Sn})$, $^1J(^{77}\text{Se}-^{117}/^{119}\text{Sn})$ ($^{117}\text{Sn}$ and $^{119}\text{Sn}$ satellites are not resolved) and $^2J(^{117}\text{Sn}-^{119}\text{Sn})$ coupling, respectively.
<table>
<thead>
<tr>
<th>Anion</th>
<th>$\delta$ (ppm)</th>
<th>$\eta$ ($^{77}$Se - $\delta$) (Hz)</th>
<th>1/$\omega$/c (X)</th>
<th>$\delta$ (ppm)</th>
<th>$\eta$ ($^{119}$Sn - $\delta$) (Hz)</th>
<th>1/$\omega$/c (X)</th>
<th>$\delta$ (ppm)</th>
<th>$\eta$ ($^{117}$Sn - $\delta$) (Hz)</th>
<th>1/$\omega$/c (X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SnSe}^{2-}$</td>
<td>12</td>
<td>391 ($^{117,119}$Sn)</td>
<td>14-16</td>
<td>422</td>
<td>397 ($^{77}$Se)</td>
<td>12-14</td>
<td>421</td>
<td>378 ($^{75}$Se)</td>
<td>13-14</td>
</tr>
<tr>
<td>$\text{SnSe}^{2-}$</td>
<td>-69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Se}^{2-}$</td>
<td>-43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>-152</td>
<td>1842 ($^{119}$Sn)</td>
<td>4-6</td>
<td>-279</td>
<td>2002 ($^{75}$Se)</td>
<td>12-16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>-154</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>278</td>
<td></td>
<td>278</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Smaller peaks observed at -106, -186 and -189 ppm in the $^{77}$Se NMR spectra.
b Smaller peaks observed at 395, 310, 308 and 306 ppm in the $^{119}$Sn and $^{117}$Sn NMR spectra.
c The $^{117}$Sn and $^{119}$Sn satellites could not be resolved. The usual error limit was ±6 Hz for the coupling constants.
(ii) Preparation and Characterization of \( \text{SnPbSe}_3^{2-} \)

As a result of the successful preparations of the \( \text{Pb}_2\text{Se}_3^{2-} \) and \( \text{Sn}_2\text{Se}_3^{2-} \) anions, it was likely that the mixed tin-lead trigonal bipyramidal anion, \( \text{SnPbSe}_3^{2-} \), could be prepared by the reaction of \( \text{K}_2\text{Se} \) with a \( \text{SnSe/PbSe} \) mixture according to reaction (6.3)

\[
\text{K}_2\text{Se} + \text{SnSe} + \text{PbSe} \xrightarrow{\text{Crypt} \text{ en}} 2 \text{Crypt-K}^+ + \text{SnPbSe}_3^{2-} \quad (6.3)
\]

The \( \text{K}_2\text{Se/SnSe/PbSe} \) mixture was allowed to react in \text{en} with 2,2,2-crypt and the and \( \text{77Se}_1 \), \( \text{119Sn} \) and \( \text{207Pb} \) NMR spectra of the isolated orange solution were recorded.

The \( \text{77Se} \) NMR spectrum showed that a large amount of unreacted \( \text{Se}^{2-} \) was still present in solution. Furthermore, the same species which had formed in the \( \text{K}_2\text{Se/SnSe} \) system were also present in solution as well as the \( \text{Pb}_2\text{Se}_3^{2-} \) anion (Table 6.2). However, a new tin environment with two pairs of satellite doublets was observed at 528 ppm in the \( \text{119Sn} \) NMR spectrum (Figure 6.3). The satellite doublets are assigned to \( ^1J(\text{Sn-77Se}) \) and \( ^2J(\text{Sn-207Pb}) \) for the new trigonal bipyramidal \( \text{SnPbSe}_3^{2-} \) anion as the satellite peak/central peak height intensity ratios correspond to spin-spin coupling of the tin environment with three equivalent Se atoms and one Pb atom (Figure 6.2 b and Table 6.2). A new Pb environment, assigned to the \( \text{SnPbSe}_3^{2-} \) anion, was also
Figure 6.2 The structures of the (a) $\text{Sn}_2\text{Se}_3^{2-}$ and (b) $\text{SnPbSe}_3^{2-}$ anions.
Figure 6.3  $^{119}\text{Sn}$ NMR spectrum (93.276 MHz) of the $M_2\text{Se}_3^{2-}$ series: (A) $\text{Sn}_2\text{Se}_3^{2-}$; (B) $\text{SnPbSe}_3^{2-}$. Peaks labeled $a_1$ and $b_2$ arise from the $^1J(^{77}\text{Se}-^{119}\text{Sn})$ spin coupling. Peaks labeled $a_2$ and $b_3$ arise from $^2J(^{117}\text{Sn}-^{119}\text{Sn})$ and $^2J(^{119}\text{Sn}-^{207}\text{Pb})$ spin coupling, respectively.
observed in the $^{207}\text{Pb}$ NMR spectrum. The $^{117/119}\text{Sn}$ satellites were not resolved and the $^{77}\text{Se}$ satellites were only observed as shoulders on the peak. A new peak at $-42$ ppm was observed in the $^{77}\text{Se}$ NMR spectrum which can be assigned to the $\text{SnPbSe}_3^{2-}$ anion as the $^{77}\text{Se}$ chemical shift is midway between that of $\text{Sn}_2\text{Se}_3^{2-}$ and $\text{Pb}_2\text{Se}_3^{2-}$, as expected for a homologous and isostructural series. However, the expected spin satellite doublets could not be measured as it was evident from the $^{77}\text{Se}$ NMR spectrum that the $\text{SnPbSe}_3^{2-}$ anion was only a minor species in solution. Consequently, a more concentrated solution for the $\text{SnPbSe}_3^{2-}$ anion was required. As relatively large amounts of the $\text{Sn}_2\text{Se}_3^{2-}$ anion had formed in reaction (6.3), a $\text{K}_2\text{Se}/0.5\text{SnSe}/1.5\text{PbSe}$ mixture was allowed to react in en in the presence of $2,2,2$-crypt for 10 weeks. The $^{77}\text{Se}$ NMR spectrum of the solution (Figure 6.4) again showed the $\text{SnPbSe}_3^{2-}$ anion was not a major species in solution. However, the expected $^{117/119}\text{Sn}$ and $^{207}\text{Pb}$ satellites could be resolved at $3\degree\text{C}$ (Figure 6.5) and the satellite peak/central peak height ratios showed that the Se environment is bonded to one Sn and one Pb atom. The results from the solution NMR study for the $\text{K}_2\text{Se}/\text{SnSe}/\text{PbSe}$ system have been summarized in Table 6.2.

Interestingly, the $^{77}\text{Se}$ NMR peaks of the $\text{M}_2\text{Se}_3^{2-}$ ($\text{M} = \text{Sn}$ and/or $\text{Pb}$) anions were relatively broad at room temperature and became broader at higher temperatures ($53\degree\text{C}$).
Figure 6.4  $^{77}$Se NMR spectrum (47.704 MHz) resulting from the reaction of 
$K_2Se$ with a 0.5SnSe/1.5PbSe mixture in en solvent in the 
presence of 2,2,2-crypt; (A) $Sn_2Se_3^{2-}$; (B) $SnPbSe_3^{2-}$; (C) 
Pb$_2$Se$_3^{2-}$; (F) SnSe$_4^{4-}$. Peaks labeled $q'$ and $q''$ are $^{119}$Sn and 
$^{117}$Sn satellites, respectively.
Figure 6.5  $^{77}\text{Se}$ NMR spectrum (47.704 MHz) from the reaction of $\text{K}_2\text{Se}$ with a 0.5$\text{SnSe}/1.5\text{PbSe}$ mixture in en in the presence of 2,2,2-crypt: (B) $\text{SnPbSe}_3^{2-}$; (C) $\text{Pb}_2\text{Se}_3^{2-}$; (F) $\text{SnSe}_4^{4-}$. Peaks labeled $f'$ and $f''$ are $^{119}\text{Sn}$ and $^{117}\text{Sn}$ satellites, respectively. Peaks labeled $b_1$ and $c$ arise from $^1J(^{77}\text{Se}-^{207}\text{Pb})$ and peaks labeled $b_2$ arise from $^1J(^{77}\text{Se-}
olimits^{117}/^{119}\text{Sn})$ ($^{117}\text{Sn}$ and $^{119}\text{Sn}$ satellites not resolved).
Table 6.5

$^{77}$Se, $^{119}$Sn and $^{207}$Pb NMR Parameters and Satellite Peak/Central Peak Height Intensity Ratios for the $\text{SeSe/SnSe/PbSe/Si$_2$P}_2$-type System in Ethanol/Dimethoxyethane Solvent

<table>
<thead>
<tr>
<th>Anion</th>
<th>$\delta$ (ppm)</th>
<th>$\eta_{119}$Se = $\eta_{117}$Se = $\eta_{121}$Se (Hz)</th>
<th>$\iota_{119}$Se/1 (Hz)</th>
<th>$\eta_{119}$Sn = $\eta_{117}$Sn (Hz)</th>
<th>$\iota_{119}$Sn/1 (Hz)</th>
<th>$\eta_{207}$Pb = $\eta_{209}$Pb (Hz)</th>
<th>$\iota_{207}$Pb/1 (Hz)</th>
<th>Temp. $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$_2$Sn$_2$</td>
<td>-14</td>
<td>378224 ($^{119/117}$Sn)$^a$</td>
<td>421</td>
<td>397 ($^{77}$Se)</td>
<td>12-14</td>
<td>1514 ($^{117}$Sn)</td>
<td>3-5</td>
<td>24</td>
</tr>
<tr>
<td>Pb$_2$Sn$_2$</td>
<td>-42</td>
<td>403224 ($^{119/117}$Sn)</td>
<td>528</td>
<td>415 ($^{77}$Se)</td>
<td>11-13</td>
<td>1144 ($^{119}$Pb)</td>
<td>13-16</td>
<td>24</td>
</tr>
<tr>
<td>Pb$_2$Sn$_2$</td>
<td>-47</td>
<td>153 ($^{207}$Pb)</td>
<td>421 ($^{119/117}$Sn)</td>
<td>14-17</td>
<td>7-11</td>
<td>3439</td>
<td>160 ± 24 ($^{77}$Se)</td>
<td>24</td>
</tr>
<tr>
<td>Pb$_2$Sn$_2$</td>
<td>-103</td>
<td>153 ($^{207}$Pb)</td>
<td>26-27</td>
<td>3247</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn$_2$Se$_2$</td>
<td>-47</td>
<td>1355 ($^{117}$Sn)</td>
<td>3-6</td>
<td>1410 ($^{119}$Sn)</td>
<td>3-6</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se$_2$</td>
<td>-434</td>
<td>156</td>
<td>1953 ($^{77}$Se)</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>-15</td>
<td>1835 ($^{117}$Sn)</td>
<td>3-6</td>
<td>1941 ($^{119}$Sn)</td>
<td>3-6</td>
<td>276</td>
<td>1953 ($^{77}$Se)</td>
<td>24</td>
</tr>
<tr>
<td>R</td>
<td>-152</td>
<td>1835 ($^{117}$Sn)</td>
<td>4-6</td>
<td>1941 ($^{119}$Sn)</td>
<td>4-6</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>-152</td>
<td>1835 ($^{117}$Sn)</td>
<td>4-6</td>
<td>1941 ($^{119}$Sn)</td>
<td>4-6</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Small peaks were observed at -31, -124, -157, -194 and -196 ppm in the $^{77}$Se NMR spectra at 3 $^\circ$C and at 577, 579, 590, 310, 307 and 303 ppm in the $^{119}$Sn NMR spectra at 24 $^\circ$C.
b The $^{119}$Sn and $^{117}$Sn satellites could not be resolved. Usual error limits were ± 6 Hz for the coupling constants.
This broadening of the peaks is possibly caused by an exchange of \( \text{Se}^{2-} \) with the trigonal bipyramidal anions. Presumably intermediates similar to those already postulated in Chapter 4 to account for the structural relationship among \( \text{Se}^{2-} \), \( \text{Pb}_2\text{Se}_3^{2-} \) and \( \text{Sb}_2\text{Se}_4^{2-} \) anions may also be important in the present system. This is not an unlikely mechanism as a large amount of unreacted \( \text{Se}^{2-} \) was still present in solution (Table 6.2). The other species present in the solution did not appear to be directly involved in the exchange processes as their peaks remained relatively sharp at higher temperatures.

(iii) Comparison of the \( \text{M}_2\text{Se}_3^{2-} \) Anions \( (\text{M} = \text{Sn, Pb}) \)

The NMR parameters for the trigonal bipyramidal anions \( \text{Sn}_m\text{Pb}_{2-m}\text{Se}_3^{2-} \) \( (m = 0 - 2) \) are summarized in Table 6.3. and those for the related pyramidal shaped \( \text{Sn(SePh)}_3^{2-} \) \( 155 \) and \( \text{Pb(SePh)}_3^{2-} \) \( 92 \) anions are also included for comparison. For the series \( \text{Sn}_2\text{Se}_3^{2-} \), \( \text{SnPbSe}_3^{2-} \), \( \text{Pb}_2\text{Se}_3^{2-} \) it is noted that the \( \text{Se} \) chemical shifts become more deshielded as a \( \text{Pb} \) atom is substituted for a \( \text{Sn} \) atom. A similar constant decrease in the \( \text{Se} \) chemical shift was also observed for the \( \text{Pb}_2\text{Se}_n\text{Te}_{3-n}^{2-} \) \( (n = 0 - 3) \) anions when a \( \text{Te} \) atom was substituted for a more electronegative \( \text{Se} \) atom. It would therefore appear that the bonding in the new series of anions is, to a large degree, very similar to that of the \( \text{Pb}_2\text{CH}_3^{2-} \).
Table 6.3  
\(^{77}\)Se, \(^{119}\)Sn and \(^{207}\)Pb NMR Parameters
for the \(SnSe^{\text{2-}}\), \(SnPbSe^{\text{2-}}\), \(PbSe^{\text{2-}}\) and the \(M(SePh)_2^+\) \((M = Sn, Pb)\) Anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>(\delta^{\text{77}\text{Se}}(\text{ppm}))</th>
<th>(\delta^{\text{119}\text{Sn}}(\text{ppm}))</th>
<th>(\delta^{\text{207}\text{Pb}}(\text{ppm}))</th>
<th>(^{119}\text{Sn} -^{\text{77}\text{Se}})</th>
<th>(^{207}\text{Pb} -^{\text{77}\text{Se}})</th>
<th>(M-M)</th>
<th>(\eta_k) ((10^{20} \text{ GA}^{-\text{2m-3}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SnSe^{\text{2-}})</td>
<td>12</td>
<td>421</td>
<td></td>
<td>397</td>
<td>1514</td>
<td></td>
<td>46.5 (28.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>94.9 (46.7)</td>
</tr>
<tr>
<td>(SnPbSe^{\text{2-}})</td>
<td>-42</td>
<td>528</td>
<td>3439</td>
<td>415</td>
<td>1145</td>
<td></td>
<td>46.6 (29.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>31.9 (9.0)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>122.2 (27.8)</td>
</tr>
<tr>
<td>(PbSe^{\text{2-}})</td>
<td>-103</td>
<td>3290</td>
<td></td>
<td>153</td>
<td></td>
<td></td>
<td>31.9 (9.0)</td>
</tr>
<tr>
<td>(Sn(SePh)_2^+)</td>
<td>208</td>
<td></td>
<td></td>
<td>710</td>
<td></td>
<td></td>
<td>83.2 (50.5)</td>
</tr>
<tr>
<td>(Pb(SePh)_2^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3188</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a The relativistically corrected reduced coupling constant, \(\eta_{\text{rc}}\), given in parenthesis.

b References (96) and (155).
anions. Even though the substitution is two bonds away from the selenium atom, the change in the $^{77}\text{Se}$ chemical shift per substituted atom is much greater for the $\text{Pb}_2\text{Se}_n\text{Te}_{3-n}^2-$ anions.

As was discussed in Chapter 4, the $^{207}\text{Pb}$ chemical shifts of the $\text{Pb}_2\text{Se}_3^{2-}$ and $\text{Pb}(\text{SePh})_3^-$ anions are very similar, indicating that the bonding in the $\text{PbSe}_3$ moiety of the two anions is very similar. However, the $^{119}\text{Sn}$ chemical shifts of the corresponding $\text{Sn}_2\text{Se}_3^{2-}$ (or $\text{SnPbSe}_3^{2-}$) and $\text{Sn}(\text{SePh})_3^-$ anions are quite different (Table 6.3). Furthermore, the one-bond $^{77}\text{Se}-^{119}\text{Sn}$ spin coupling constant for the $\text{Sn}(\text{SePh})_3^-$ anion is considerably larger than that of the $\text{Sn}_2\text{Se}_3^{2-}$ and $\text{SnPbSe}_3^{2-}$ anions. This suggests that the geometries of the $\text{SnSe}_3$ moieties in the two anion types are significantly different. This is not surprising if one considers the compressed trigonal bipyramidal structure of the $\text{Pb}_2\text{Se}_3^{2-}$ anion (see Chapter 4). Any small changes in the geometry of the trigonal bipyramid will greatly affect the electronic structure of the anion. If a closest packing of the selenium atoms in the equatorial positions (van der Waals contact distance of 3.80 Å), similar to what was observed for $\text{Pb}_2\text{Se}_3^{2-}$, is assumed and the average Sn-Se bond length is set equal to 2.66 Å, as for $\text{Sn}(\text{SePh})_3^-$, one calculates 91° and 69° for the Se-Sn-Se and Sn-Se-Sn bond angles, respectively. The smaller value for the
\(^{1}J(^{77}\text{Se}-^{119}\text{Sn})\) coupling constant of \(\text{Sn}_2\text{Se}_3^{2-}\) could, therefore, simply arise from a higher \(p\) character in the Sn-Se bond relative to the \(\text{Sn}(\text{SePh})_3^-\) anion as a result of the restriction set by the geometry of the anion. Moreover, the calculated Sn-Sn distance of 3.01 Å indicates a very compressed trigonal bipyramidal structure and is only 0.20 Å longer than the single Sn-Sn bond length distance\(^{141}\) for tetravalent tin. A similar short \(\text{Pb}-\text{Pb}\) distance of 3.18 Å was found for the \(\text{Pb}_2\text{Se}_3^{2-}\) anion, although longer by 0.32 Å than the single bond length of 2.86 Å\(^{89}\) observed in \(\text{Pb}_2\text{Ph}_6\). One would therefore expect greater repulsion between the Sn atoms in \(\text{Sn}_2\text{Se}_3^{2-}\) and, consequently, greater deviation in the geometry of the SnSe\(_3\) moieties of \(\text{Sn}_2\text{Se}_3^{2-}\) and \(\text{Sn}(\text{SePh})_3^-\) which could account for differences in the NMR parameters for the two anions.

Unlike the \(\text{Pb}_2\text{CH}_3^{2-}\) anions, one can observe the spin-spin coupling between the axial atoms of the \(\text{Sn}_2\text{Se}_3^{2-}\) and \(\text{SnPbSe}_3^{2-}\) anions owing to their magnetic nonequivalence. These two-bond coupling constants are the first to be observed between Sn(II)-Sn(II) and Sn(II)-Pb(II) atoms. The \(^{2}J(^{117}\text{Sn}-^{119}\text{Sn})\) coupling constant is greater than the two-bond coupling constants between selenium bridged Sn(IV) atoms, which range from 100 - 350 Hz,\(^{156}\) but it is somewhat smaller than one-bond \(^{119}\text{Sn(IV)}-^{119}\text{Sn(IV)}\) coupling constants which range from 900 - 4000 Hz and up to 15,000 Hz.\(^{156}\) In
general, the value and sign of $^{2}J(^{119}\text{Sn}-^{119}\text{Sn})$ for the Sn-Z-Sn units are known to be dependent on the bridging atom Z and the Sn-Z-Sn bond angle as well as on the chemical environments of the spin-spin coupled tin atoms.\textsuperscript{156} However, the exact importance of each factor is far from being well understood. Owing to the lack of data for Sn(II)-Sn(II) coupling constants, it is impossible to determine if the relatively large value of $^{2}J(^{117}\text{Sn}-^{119}\text{Sn})$ for Sn$_{2}$Se$_{3}$$^{2-}$ signifies a bonding interaction between the axial metal atoms. In fact, the relatively large values for the coupling constant could be the result of through space coupling arising from the repulsion of the 5s$^{2}$-5s$^{2}$ pairs, giving rise to relatively high electron spin correlation.

(iv) \textbf{Formation of Sn(IV) Selenide Anions}

As has been summarized in Tables 6.1 and 6.2, a large number of other species was also observed in the solution NMR spectra (Figure 6.4) and often the M$_{2}$Se$_{3}$$^{2-}$ anions (M = Sn, Pb) were found to be only minor species. One of the species which could be identified was the SnSe$_{4}$$^{4-}$ anion, showing that some of the Sn(II) starting material, SnSe, was oxidized. As all the selenides used in the preparations were in the -2 oxidation state, it is possible that a redox disproportionation of the Sn(II) species took place in solution to form Sn(IV) species and tin metal according to
equation (6.4)

\[
2 \text{ Sn(II)} \rightarrow \text{ Sn(IV)} + \text{ Sn}^* 
\] (6.4)

Reduction of the solvent or the complexing ligand also cannot be ruled out. The selenium and tin environments of one of the new species, Q, could be identified from its satellite doublet splitting. Furthermore, from the IS/IC ratios it was evident that the Sn atom was bonded to three equivalent selenium atoms but Se was bonded to only one Sn atom. The $^{119}$Sn chemical shift (-276 ppm) and the $^{1}J$(Se-$^{119}$Sn) coupling constant (1953 Hz) are very similar to those of the trigonal planar SnSe$_3^{2-}$ anion (-264 ppm and 2051 Hz).\textsuperscript{49} This suggests that the new species has trigonal planar SnSe$_3$ units. A similar phenomena has also been observed for some new tin telluride anions as discussed in Section B. Although a large number of other new species were observed in the solution NMR spectra, their low concentrations and lack of spin satellites do not allow any further detailed understanding of their structures.
(B) REACTIONS OF K₂Te WITH SnTe

(i) Solution NMR Studies

As was noted in the Introduction to this Chapter, Sn(II) compounds were oxidized to Sn(IV) telluride anions when allowed to react with polytelluride anions. In order to prepare Sn(II) telluride anions this oxidation could possibly be avoided by reaction of SnTe directly with Te²⁻. As the trigonal bipyramidal Pb₂Te₃²⁻ anion has been shown to exist (Chapter 4), it was of interest to determine if the corresponding Sn(II) telluride anion, Sn₂Te₃²⁻, could be prepared by reaction (6.5)

\[
\text{Te}^{2-} + 2 \text{SnTe} \xrightarrow{\text{2,2,2-crypt}} \text{Sn}_2\text{Te}_3^{2-} \quad (6.5)
\]

Consequently when a K₂Te/2SnTe mixture was allowed to react in en and 2,2,2-crypt later added to the solution, formation of a considerable amount of violet solid occurred. The appearance of violet solid was similar to the 2,2,2-crypt-K⁺ salt of Te₂²⁻ (Chapter 5), indicating that Te₂²⁻ may have been oxidized in solution.

Three new intense peaks were found in both the ¹²⁵Te and ¹¹⁹Sn NMR spectra of the solution, all of which had satellites (Figures 6.6, 6.7 and 6.8). By comparison of the satellite doublet spacing it was evident that one tellurium and one tin environment were spin coupled to one another.
Figure 6.6 $^{125}\text{Te}$ NMR spectrum (78.917 MHz) of the solution resulting from the reaction of $\text{K}_2\text{Te}$ with $2\text{SnTe}$ in en in the presence of 2,2,2-crypt. Peaks labeled $x'$, $y'$ and $z'$ are $^{119}\text{Sn}$ satellites; peaks labeled $x''$, $y''$ and $z''$ are $^{117}\text{Sn}$ satellites.
Figure 6.7 $^{119}\text{Sn}$ NMR spectrum (93.276 MHz) of the solution resulting from the reaction of $\text{K}_2\text{Te}$ with $2\text{SnTe}$ in en in the presence of 2,2,2-crypt. Peaks labeled $x'$, $y'$ and $z'$ are $^{125}\text{Te}$ satellites; peaks labeled $x''$ are $^{123}\text{Te}$ satellites.
Figure 6.8 $^{117}\text{Sn}$ NMR spectrum (89.128 MHz) of species X in en. Peaks labeled $X''$ and $X'''$ are $^{125}\text{Te}$ and $^{123}\text{Te}$ satellites, respectively.
Furthermore, the values for the satellite peak/central peak height ratios, $I_s/I_C$, showed that each tin environment is bonded to three Te atoms and each tellurium environment is bonded to only one tin atom. Consequently, none of the three new tin telluride anions, $X$, $Y$ and $Z$, can be the unknown Sn$_2$Te$_3^{2-}$ anion. Rather, the large values for the spin-spin coupling constants, $^1J(^{125}\text{Te},^{117,119}\text{Sn})$, indicate a Sn(IV) species. In general, no spin coupling constants have been reported for Sn(II)-Te bonded species but one can estimate them to be in the range 800 - 1500 Hz by using relativistically corrected reduced coupling constants $^1k_{\text{RC}}(\text{Se-Sn(II)})$ for the Sn$_2$Se$_3^{2-}$ and Sn(SePh)$_3^{2-}$ anions (see Section D(iii) Chapter 1). The observed coupling constants for the new species are much larger and, in fact, correspond well with the values reported for Sn(IV)-Te bonded species which are in the range 2000 - 5000 Hz.$^{49,156,157}$ Evidently any Sn(II) telluride species which might have formed were unstable and were oxidized to Sn(IV) telluride anions, possibly by redox disproportionation as shown by equation (6.4). Interestingly, the unknown species $X$ and $Z$ were also observed from extracts of the NaSnTe, NaSn$_2$Te$_1.5$ and NaSn$_1.5$Te alloys although the chemical shifts of the species differ by 5 - 11 ppm and the coupling constants by 0 - 40 Hz.$^{53}$ However, in these NaSn$_x$Te$_y$ alloy extracts, the SnTe$_3^{2-}$ and SnTe$_4^{4-}$ anions were also present in relatively high
concentrations as well as a large number of other minor species.

Even though only three major species were observed in the solution from reaction (6.5), in contrast with the large number of species observed in the NaSn$_x$Te$_y$ alloy extracts, it was of interest to prepare a solution in which one of the species X, Y or Z would be the major species present. Therefore, K$_2$Te was allowed to react with SnTe in 1:1 and 1:4 ratios in en and 2,2,2-crypt added to the solutions when all the K$_2$Te had reacted (equation (6.6))

\[
\text{Te}^{2-} + n \text{SnTe} \underset{\text{en}}{\overset{2,2,2\text{-crypt}}{\longrightarrow}} \text{Sn}_k\text{Te}_l^{m-} \quad (6.6)
\]

where \( n = 1 \) or 4. In general, the reactions behaved in a manner similar to reaction (6.5), i.e., an intense orange solution formed which turned yellow-brown with the precipitation of a violet solid upon addition of 2,2,2-crypt to the solution. The solution NMR spectra revealed that the same new species X, Y and Z had formed although in somewhat different relative concentrations and greater amounts of minor species were evident (Table 6.4).

In order to avoid the redox reactions which appear to take place when 2,2,2-crypt is added to the solutions in the presence of the alloy residue, the orange solution resulting from the reaction of K$_2$Te with 2SnTe was decanted off the alloy residue into the NMR tube of the reaction vessel
containing a stoichiometric amount of 2,2,2-crypt. The solution turned from orange to red-orange but did not become brown-yellow in color nor did any violet solid material form as occurred when the alloy residue was present. The presence of species X, Y and Z was evident from the solution $^{125}\text{Te}$ NMR spectrum but now Z had the highest concentration among the three species. Peaks arising from SnTe$_3^{2-}$ and HTe$^-$ were also observed as well as a new, relatively intense peak, at -169 ppm with $^{117,119}\text{Sn}$ satellites (species U). The new tellurium environment was bonded to one Sn atom and the magnitudes of the satellite doublet splittings are very similar to the $^{1J}(^{125}\text{Te}-117,119\text{Sn})$ values of the SnTe$_4^{4-}$ anion (2727 and 2851 Hz for $^{117}\text{Sn}$ and $^{119}\text{Sn}$, respectively).\textsuperscript{49} The NMR data for the solution has been summarized in Table 6.4.

When reaction (6.5) was carried out in liquid ammonia, a similar dark orange solution formed as well as a violet solid when 2,2,2-crypt was added to the reaction mixture. However, the solution $^{125}\text{Te}$ NMR spectrum showed that now only species X and Y had formed. The chemical shifts for X and Y are somewhat different than in en as would be expected for a change in solvent and temperature. Interestingly, there was no evidence for broadening of the sharp peaks, even at temperatures as low as -67°C.
Table 6.4

$^{125}\text{Te}$ and $^{119}\text{Sn}$ NMR parameters and $I_{w}/I_{c}$ Ratios for the
$\text{K}_2\text{Te}/\text{SnTe}/2,2’,2’’$-crypt System in Ethylenediamine Solvent

<table>
<thead>
<tr>
<th>Chemical Shift</th>
<th>Coupling Constants</th>
<th>Satellite</th>
<th>Reaction</th>
<th>Relative Peak Heights (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$ (ppm) $^a$</td>
<td>$^2\text{J}$ (Hz) $^b$</td>
<td>$I_{w}/I_{c}$ (%) $^b$</td>
<td>$\text{K}_2\text{Te}$</td>
<td>$\text{K}_2\text{Te}$</td>
</tr>
<tr>
<td>Species</td>
<td>$^{125}\text{Te}$</td>
<td>$^{119}\text{Sn}$</td>
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<td>3412 $\star$</td>
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<td></td>
<td>4125</td>
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</tr>
<tr>
<td>Y</td>
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<td>4425</td>
</tr>
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<td>Y $^\star$</td>
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<td>3998</td>
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<tr>
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<td>-1036</td>
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<tr>
<td>U</td>
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<td>2867 $\pm$60</td>
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<td>4498</td>
</tr>
<tr>
<td>HTe$^{2-}$</td>
<td>-1079 $\star$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Minor Species

| g | h | i |

---

- a Error limits were ±2 ppm for chemical shifts and ±6 Hz for $^2\text{J}$.
- b Estimated from the peak heights of the satellite and central peaks.
- c Relative concentration estimated from the height of the peaks in the $^{125}\text{Te}$ NMR spectra. Asterisks denote other relatively intense peaks.
- d The solution was decanted of the alloy residue before 2,2,2-crypt added.
- e Spin coupling between $^{125}\text{Te}^\star$ and $^{119}\text{Sn}^\star$.
- f Doublet arising from $^2\text{J}^{(\text{H}^{+},^{125}\text{Te}^\star)} = 140$ Hz.
- g Small peaks also observed at -945, -953, -990 and -1075 ppm in the $^{125}\text{Te}$ NMR spectrum.
- h Small peaks observed at -929, -956 and -1077 ppm in the $^{125}\text{Te}$ NMR spectrum.
- i Minor peak at -234 ppm in the $^{125}\text{Te}$ NMR spectrum.
- j Measured at -87 °C in liquid ammonia for the reaction $\text{K}_2\text{Te} + 2\text{SnTe} +$ crypt. Relative peak heights 75% and 25% for I and Y, respectively.
- k The $^{119}\text{Sn}$ and $^{119}\text{Sn}$ satellites were not resolved.
(ii) Possible Structures for the New Tin Telluride Anions

As can be seen from Table 6.4, the new species X, Y, and Z are always present in the solutions but in somewhat varying concentrations. This suggests the anions are formed by similar mechanisms and/or from the same precursor. Moreover, this relationship among the anions is further supported by the fact that the $^{125}\text{Te}$ and $^{119}\text{Sn}$ chemical shifts for the anions are very similar and roughly additive, suggesting they possess related structures. It was clear from the $I_S/I_C$ ratios for the Te and Sn environments that the three species were based on SnTe$_3$-type units, similar to the trigonal planar structure of SnTe$_3^{2-}$. A further support for this relation of species X, Y and Z to SnTe$_3^{2-}$ is evident from their similar $^{119}\text{Sn}$ chemical shifts and one-bond spin-spin coupling constants, $^{1}J(^{125}\text{Te-117},^{119}\text{Sn})$. It would therefore appear that the anions X, Y and Z have structures composed of trigonal planar SnTe$_3$ units as no other simple structure can presently be assigned to the anions. Interestingly, there is no indication of any satellite doublets other than the one-bond $^{1}J(^{125}\text{Te-117},^{119}\text{Sn})$ coupling, indicating that tin and tellurium environments are entirely "decoupled" from their next nearest neighbors. It is unlikely that additional satellites were too low in intensity to be observed as the $^{123}\text{Te}$ satellites, whose intensities are only 1.34 % of the central peak intensity,
could be easily observed in the $^{117}\text{Sn}$ NMR spectrum of species X (Figure 6.8).

The trigonal planar SnTe$_3$ units within each anion would therefore have to be "spinning" fast on the NMR time scale such that, in effect, they are decoupled from the other nuclei in the anion so that only their average $^{125}\text{Te}$ and $^{119}\text{Sn}$ chemical shifts are observed. A structure for one such possible anion which would be consistent with these findings is based on two linked trigonal planar SnTe$_3$ units of the Sn$_2$Te$_6^{2-}$ anion as depicted in Figure 6.9a along with a possible mechanism for rapid intramolecular exchange of the SnTe$_3$ unit. Structures of other anions with more than two SnTe$_3$ units linked together either in a linear or a branched chain are possible, but the SnTe$_3$ units would have to be exchanging fast on the NMR time scale into different positions in the chains. The SnTe$_3$ units can also be linked by other atoms such as in the Te(SnTe$_3$)$_2^{2-}$ anion (Figure 6.9b) where there is only one bridging tellurium atom per every six in the SnTe$_3$ units. Consequently, the $^{125}\text{Te}$ NMR peak of the bridging Te atom would be small relative to the $^{125}\text{Te}$ resonance of the SnTe$_3$ groups and could, in fact, correspond to one of the minor peaks observed in the $^{125}\text{Te}$ NMR spectra of the en solutions. Interestingly, none of the minor peaks could be observed in liquid ammonia solution, perhaps indicating that perhaps species X is, in fact,
Figure 6.9  The proposed structures of the (a) \( \text{Sn}_2\text{Te}_6^{2-} \) and (b) \( \text{Sn}_2\text{Te}_7^{2-} \) anions (only one valence bond structure shown). Also indicated is a possible mechanism for intramolecular "spinning" of the trigonal planar \( \text{SnTe}_3 \) moieties.
\( \text{Sn}_2\text{Te}_6^{2-} \). Furthermore, as the \( \text{Sn}_2\text{Te}_6^{2-} \) anion has the simplest structure of the ones considered above it is expected to be in highest concentration in these solutions as was indeed observed for species \( X \). It is then likely that species \( Y \) and \( Z \) have the longer \( \text{SnTe}_3 \)-chain or \( \text{SnTe}_3 \)-bridged structures.

Only intramolecular exchange averaging of the \( \text{SnTe}_3 \) units has been considered for the structures above. It is unlikely that \( \text{SnTe}_3 \) units would exchange by intermolecular mechanisms as such a mechanism would lead to chemical shift averaging of all the species and only single Sn and Te environments would be observed for each solution, contrary to what is observed.

The identification of tin telluride anions containing only triply coordinated Sn(IV) species in solution is not unusual. The monomer \( \text{SnTe}_3^{2-} \) had been previously shown to exist in solution\(^{49} \) even though only the dimer, \( \text{Sn}_2\text{Te}_6^{2-} \), was found in the solid state.\(^{52} \) Furthermore, from Na/Sn/Te alloy extraction in en in the presence of 2,2,2-crypt, Devereux\(^{53} \) found that the \( \text{SnTe}_3^{2-} \) and \( \text{SnTe}_4^{4-} \) anions coexisted in solution and did not form the expected \( \text{Sn}_2\text{Te}_7^{6-} \left( \text{Te}_3\text{SnTeSnTe}_3^{3-} \right) \) anion. It is to be expected, however, that the new species \( X, Y \) and \( Z \) could dimerize or even polymerize in the solid state. This could be the cause for the, so far, unsuccessful attempts to obtain crystals of the
new anions. In fact, when the en solvent is evaporated off the solutions they become very viscous. Over a period of months a crystalline-appearing material formed which failed to produce an X-ray diffraction pattern. Further attempts to isolate crystals from the more volatile ammonia solvent also gave amorphous material.

(C) REACTIONS OF THE K₂Te/SnTe AND K₂Se/SnTe SYSTEMS

(i) \( \text{K}_2\text{Ch} + 2\text{SnCh}', \text{Ch(Ch')} = \text{Se(Te)/Te(Se)} \)

Although there was no evidence for the formation of the unknown \( \text{Sn}_2\text{Te}_3^{2-} \) anion from the reactions of \( \text{K}_2\text{Te} \) with SnTe, the successful preparation of the \( \text{Sn}_2\text{Se}_3^{2-} \) anion suggested one or both of the mixed Se/Te anions, \( \text{Sn}_2\text{Se}_2\text{Te}^{2-} \) and \( \text{Sn}_2\text{SeTe}_2^{2-} \), could be prepared by a similar route. Consequently, \( \text{K}_2\text{Se} \) (\( \text{K}_2\text{Te} \)) was allowed to react with two equivalents of SnTe (SnSe) in en followed by the addition of stoichiometric amounts of 2,2,2-crypt to the solutions. As was observed for the \( \text{K}_2\text{Te}/\text{SnTe} \) systems, secondary reactions appeared to take place when crypt was added.

Potassium monoselenide, \( \text{K}_2\text{Se} \), was therefore allowed to react with 2SnTe and the solution decanted from the solid residues onto 2,2,2-crypt which was present in the NMR tube. By a similar procedure, \( \text{K}_2\text{Se} \) was allowed to react with a 1:1 mixture of SnSe and SnTe.
The NMR data for the solutions is summarized in Table 6.5. As expected, a large number of new environments was found in the solutions presumably as a result of the formation of mixed Se/Te species. Because of the greater distribution of NMR-active nuclei over a larger number of environments in these solutions, satellites were only observed for a few cases, making detailed assignments difficult. As discussed before, three new tin telluride anions, X, Y and Z, were formed and tentatively assigned in the K₂Te/SnTe system. One would therefore expect that related mixed Se/Te anions should also exist in these solutions. Furthermore, as X, Y and Z appeared to possess trigonal planar SnTe₃ structural units, the magnitudes of changes in the ¹²⁵Te and ¹¹⁹Sn chemical shifts and ¹J(¹²⁵Te-¹¹⁷,¹¹⁹Sn) for their corresponding mixed Se/Te analogues should be similar to those observed for the trigonal planar SnSeₙTe₃₋ₙ²⁻ anions.⁴⁹ Thus, changes of 302 and -120 ppm in the ¹¹⁹Sn and ¹²⁵Te chemical shifts, respectively, for each substitution of Te with Se is expected (see Table 1.3). If these values are used to calculate the ¹¹⁹Sn and ¹²⁵Te chemical shifts of the species resulting from the substitution of one Te with one Se from the corresponding chemical shifts of species X, Y and Z, good agreement is obtained with species labeled X₁, Y₁ and Z₁ in Table 6.2. The corresponding substitution of two Te atoms
with two Se atoms is assigned to the species labeled $X_2$ and $Y_2$ and the tin and tellurium environments are tentatively assigned to these species on this basis. Similarly, an increase of approximately 250 Hz in the value of $^1J(\text{Te}^{119}\text{Sn})$ is expected for the substitution of a single Te atom with a Se atom in anions $X$ and $Y$. Thus, the predicted $^1J(\text{Te}^{119}\text{Sn})$ values of 4555 Hz and 4650 Hz for $X_1$ and $Y_1$, respectively, are in good agreement with measured values of 4500 and 4633 Hz, respectively (Table 6.5).

These findings lend further support to the trigonal planar nature of the SnTe$_3$ units for the species $X$, $Y$ and $Z$ as well as their mixed Se/Te analogues. Based on this assignment for the species $X_n$ ($n = 1-3$ and $X_0 = X$), it is found that their observed $^{119}\text{Sn}$ chemical shifts vary linearly with $n$, the number of selenium atoms,

$$\delta^{119}\text{Sn}(X_n) = 302n + -1217 \text{ ppm} \quad (6.7)$$

as obtained by linear least square analysis (correlation factor; $R = 0.999$). Interestingly, the substitution of all three Te atoms of the SnTe$_3$ unit of $X$ by Se atoms is predicted, on the basis of additivity, to give a species with a $^{119}\text{Sn}$ chemical shift of $-321$ ppm which corresponds well with species $Q$ ($X_3$) observed in the $K_2\text{Se}/\text{SnSe}$ system (Tables 6.1 and 6.2). It should be noted, however, that it is assumed that the $^{119}\text{Sn}$ chemical shift value for each SnCh$_3$
Table 6.5
NMR Parameters and $^{123}$Te/$^{127}$Te Ratios for the
K$_2$Te/2SnCh$_4$/2,2,2-crypt (Ch = Se, Te) in Ethylenediamine Solvent

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical Shifts $\delta$ (ppm)</th>
<th>Relative Peak Heights ($^{123}$Te NMR) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>123$^a$ Te $^{119}$Sn $^{77}$Te</td>
<td>Not Decanted $^{a}$</td>
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<tr>
<td></td>
<td>25nTe</td>
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<td>X</td>
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<td>$Y_2$</td>
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</tr>
<tr>
<td>SnSe$_3^{=2}$</td>
<td>421</td>
<td>253</td>
</tr>
</tbody>
</table>

a Indicates the solution was decanted from the alloy residue before 2,2,2-crypt was added. Asterisk (*) denote weak peaks (< 2%).

b Expected $^{123}$Te and $^{119}$Sn chemical shifts in parentheses as calculated from the chemical shift changes per substitution of Te with Se for the SnCh$_4^{=2}$ anions (see text).

c Satellite splitting of 4498 ± 24 Hz observed which is assigned to $^1 J(^{123}$Te−$^{119}$Sn); measured in a solution resulting from the reaction K$_2$Te + 25nSe (alloy residue present).

d Satellite splittings of 4425 and 4633 Hz (± 24 Hz) were observed for $^1 J(^{123}$Te−$^{127}$Sn) and $^1 J(^{119}$Te−$^{119}$Sn), respectively; measured in a solution resulting from the reaction K$_2$Se + 25nTe (alloy present).

e Spin satellites were also observed at 1837 ± 24 Hz in the $^{119}$Sn NMR spectrum which are assigned to $^1 J(^{127}$Se−$^{119}$Sn). Measured in a solution resulting from the reaction K$_2$Te + 25nSe (alloy residue present).
unit is independent of the number of Se and Te atoms in other SnCh₃ unit(s) in the species.

No conclusive evidence was found for the formation of the Sn₂Se₂Te²⁻ or Sn₂SeTe₂²⁻ anions in these solutions. In preparations where crypt was added to the solutions in the absence of alloy residues, peaks were found with ¹¹⁹Sn chemical shifts ranging from 250 to 500 ppm and which are in the range expected for Sn(II) species. The formation of mixed Se/Te Sn(II) bonded species is possible although they cannot be characterized further owing to their low intensities in the NMR spectra and consequent inability to observe the satellites that should be associated with these environments. For further characterization of these species by multi-NMR, one could prepare the ¹¹⁹Sn enriched anions from ¹¹⁹Sn enriched SnCh alloy. The consequent increase in the concentrations of ¹¹⁹Sn⁷⁷Se and ¹¹⁹Sn¹²⁵Te isotopomers in solution should allow further characterization of these species based on ¹¹⁹Sn-⁷⁷Se and ¹¹⁹Sn-¹²⁵Te spin-spin couplings and satellite intensities not previously observed in these dilute solutions.
CHAPTER 7
PREPARATION AND SOLUTION NMR STUDY OF SOME
POLYATOMIC THALLIUM-TIN AND THALLIUM-LEAD CLUSTERS

INTRODUCTION

When the alloy, KSnTl, was extracted in ethylenediamine solvent in the presence of 2,2,2-crypt, crystals of
(2,2,2-crypt-K+)3(TlSn93-TlSn83-)4·en formed as the solvent was slowly evaporated from the dark red-brown solution.32
From the subsequent structural characterization of the TlSn83- and TlSn93- anions (Figure 1.2) by X-ray
crystallography, Corbett and Burns32 suggested that the 50:50 composition of the mixture of these anions probably
represented the most insoluble composition. This indicated that other thallium-tin polyatomic anions may be present in
these solutions. Rudolph, Taylor and Wilson39 identified the TlSn85- by 119Sn NMR in ethylenediamine solution. The
charge of the anion was determined by elemental analysis. Interestingly, this anion resulted from the extraction of
the NaSnTl1.5 alloy. The structure proposed for the TlSn85-anion is based on a monocapped square antiprism, similar to
the structure of Sn94- (Figure 1.2), with the Tl atom in the equatorial site (coordination number = 5). This structural
assignment was later supported by Lohr\textsuperscript{158} from relativistically extended Hückel calculations. A solution multi-NMR study of the polyatomic anions $\text{Sn}_9^{-r}\text{Ge}_r^4^-$ ($r = 0 - 8$), $\text{Sn}_9^{-k}\text{Pb}_k^4^-$ ($k = 0 - 9$), $\text{TlPb}_m\text{Sn}_8^{-m}\text{Sn}_m^5^-$ ($m = 0 - 4$), $\text{SbSn}_8^3^-$ and $\text{Sn}_4^2^-$ showed that all the anions were fluxional on the NMR time scale.\textsuperscript{39,41} Although this indicated, with the exception of $\text{Sn}_4^2^-$, that polyatomic Zintl anions were in general fluxional, it should be noted that the structures of these anions are based on the monocapped square antiprism. The nido nine-atom polyhedron can convert to a tricapped trigonal prism with only a minimal change in energy and has been proposed as the mechanism for fluxionality in these anions (also see Section C(i), Chapter 1).\textsuperscript{28} Theoretical calculations also indicate a low-energy pathway for the fluxional behavior of the $\text{Sn}_4^2^-$ anion.\textsuperscript{42} However, it cannot be assumed that all polyhedral polyatomic anion structures have low-energy pathways for interconversion open to them as fluxionality has only been observed for related nido nine-atom polyhedra.

Other polyhedral structures, such as the closo-$\text{TlSn}_8^3^-$ and closo-$\text{TlSn}_9^3^-$ polyhedra, may be nonfluxional on the NMR time scale at room temperature or at lower temperatures. It would therefore be of considerable interest to study these types of clusters by variable temperature NMR spectroscopy in order to observe the dynamics of atom
scrambling directly. Furthermore, as was discussed in Chapter 1, it was evident that alloy extraction in the presence of crypt not only allowed the isolation of stable salts of Zintl anions, but also minimized ion pairing. This latter effect appears to have a significant effect on the stability of many polyatomic anions.65

In light of these facts the present study was undertaken in order to prepare and characterize tin-thallium and tin-lead polyatomic anions in solution and to study them by variable temperature multi-NMR spectroscopy.

RESULTS AND DISCUSSION

(A) EXTRATION OF KSn0.9T10.9 ALLOY IN ETHYLENEDIAMINE

A red-brown solution resulting from the extraction of the KSn0.9T10.9 alloy in en gave an intense doublet at -1136 ppm in the solution 119Sn NMR spectrum. The doublet is assigned to the fluxional T1Sn3 Sn5- anion by comparison with the previously reported NMR parameters.41 Apart from a small peak at -1208 ppm arising from Sn94-, no other peaks could be observed in the spectrum (Table 7.1).

A fresh sample of the KSn0.9T10.9 alloy was again extracted in en, but this time the solution was decanted onto 2,2,2-crypt. No evidence was observed for alloy formation after allowing the solution to stand for several hours, but when the solution was decanted back onto the powdered alloy
residue, small lumps of alloy formed upon standing overnight. Three very broad peaks (Δν1/2 ≈ 900 - 1300 Hz) were observed at -939, -1015 and -1048 ppm in the 119Sn NMR spectrum of the isolated dark yellow-brown solution (Table 7.1). The observation of broad peaks suggested that, unlike Sn₉⁴⁻ and TlSn₉⁵⁻, the tin environments were not exchanging fast on the NMR time scale and therefore indicate the presence of nonfluxional homo- or heteropolyatomic tin cluster(s) in solution. However, as these peaks did not become significantly sharper at lower temperatures (4 °C), their precise nature could not be determined.

A sharp peak (-1316 ppm) and a relatively broad doublet (-1310 ppm) were also observed in the 119Sn NMR spectrum (Table 7.1). A variable temperature 119Sn NMR study of the solution (Figure 7.1) showed that the doublet and the sharp singlet belonged to two different species as the singlet remained sharp whereas the doublet became broader (sharper) at higher (lower) temperatures. A pair of satellites associated with the sharp singlet is assigned to 117Sn-119Sn spin-spin coupling. There can be no Tl atom in this species, since only a singlet was observed, indicating that this Sn environment arises from a homonuclear polyatomic tin cluster, Sn₉⁻, not previously observed in solution. The satellite peak/central peak height ratio, Iₕ/Iₖ, of 14 ±2 % corresponds to a fluxional five atom tin cluster, Sn₅⁻. 
<table>
<thead>
<tr>
<th>Species</th>
<th>117Sn</th>
<th>119Sn</th>
<th>205Tl</th>
<th>119Sn - 205Tl</th>
<th>117Sn - 119Sn</th>
<th>Temp. (°C)</th>
</tr>
</thead>
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<tr>
<td>TlSn2-</td>
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<td>843</td>
<td>647</td>
<td>461</td>
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<td></td>
</tr>
<tr>
<td>Sn2-</td>
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<td></td>
<td></td>
<td>262</td>
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<td></td>
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<tr>
<td>Sn2+</td>
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<td></td>
<td></td>
<td></td>
<td>1935</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>(1250)</td>
<td></td>
<td></td>
<td></td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

a Linewidth (Hz) at half height given in parenthesis.

b Peaks arising from unknown species are labeled with capital letters: a given species may give rise to more than one environment.

c Observed in a solution resulting from extraction of alloy in the absence of crypt.

d Observed in a solution resulting from extraction of alloy in the presence of crypt.

e For assignment see text.

f An unresolved 117/119Sn satellite splitting of 790 ± 60 Hz was also observed.
Figure 7.1 $^{119}$Sn NMR spectra (93.276 MHz) at (a) 54°C, (b) 24°C and (c) 4°C of the solution resulting from the extraction of KSn$_{0.9}$Tl$_{0.9}$ alloy in en solvent in the presence of 2,2,2-crypt. Peaks labeled a' are $^{117}$Sn satellites.
This cluster size would be consistent with the trigonal bipyramidal structure of Sn₅²⁻ (Figure 1.2) reported by Corbett and Edwards. The value of $J(^{117}\text{Sn}^{119}\text{Sn})$ for this species (1940 Hz) is of similar magnitude to those reported for Sn₄²⁻ (1224 Hz) and Sn₂Bi₂²⁻ (1606 Hz) and much larger than the corresponding average values observed for larger fluxional clusters such as Sn⁹⁴⁻ (260 - 290 Hz) and TlSn₈⁵⁻ (410 - 460 Hz). This is to be expected for a small fluxional structure such as Sn₅²⁻. However, extended-Hückel calculations on different geometries of Sn₅²⁻ indicate no viable low-energy pathway for internuclear rearrangement of the trigonal bipyramidal Sn₅²⁻ anion. Furthermore, the chemical shift is far from the expected value of -836 ppm estimated from the average charge on the tin atoms for Sn₅²⁻ by Rudolph and co-workers. Another alternative would be the square pyramidal structure (C₄ᵥ) expected for nido-Sn₅⁴⁻ (Structure I).
The charge per Sn atom is large for such a species and one would, consequently, anticipate the anion to be susceptible to decomposition in solution.

Two thallium environments were observed in the solution $^{205}$Tl NMR spectrum, a relatively broad "triplet" at 3201 ppm and a sharp singlet at 2953 ppm (Table 7.1). No satellites associated with the sharp peak could be observed owing to the relatively low signal to noise ratio for this peak. The relative heights of the outer lines of the "triplet" were found to be 49 ± 4 % of the central line, corresponding to six equivalent tin atoms (50% as given by eq. (3.14) with $p_\beta = p_{119} + p_{117} = 0.0856 + 0.0756 = 0.1614$ and $p_\gamma = 1 - 0.1614 = 0.8386$ when the $^{117}$Sn and $^{119}$Sn satellites are not resolved). The satellite spacing of 790 ± 60 Hz, however, is not in good agreement with the doublet splitting (867 Hz) observed in the $^{119}$Sn NMR spectrum, so one cannot unambiguously assign these multiplets to the same species. In fact, the doublet in the $^{119}$Sn NMR spectrum could simply arise from two different tin environments which are undergoing fast exchange on the NMR time scale at higher temperatures (Figure 7.1).
(B) 

EXTRACTION OF K/Sn/Tl ALLOYS IN LIQUID AMMONIA

(i) 

The KSn$_{0.9}$Tl$_{0.9}$ Alloy

The $^{119}$Sn NMR study of the ethylenediamine solution discussed in Section A indicated the presence of nonfluxional homo- and heteropolyatomic tin clusters. In particular, the large linewidths observed for some of the peaks suggested these tin clusters were undergoing intermediate exchange on the NMR time scale. In order to be able to slow down this exchange at lower temperatures another solvent had to be used as ethylenediamine freezes at 4 °C. Consequently, the KSn$_{0.9}$Tl$_{0.9}$ alloy was extracted in liquid ammonia in the presence of 2,2,2-crypt and the final dark brown solution concentrated and isolated.

The solution $^{119}$Sn NMR spectrum showed an entirely different mixture of species than in ethylenediamine solution (Table 7.2). The effect of solvent on the formation of different clusters has also been reported by Lohr et al.$^{41}$ It is difficult to determine what causes this difference to arise for the two solvent systems, but the nature of the solution-alloy interface could also have a significant effect on the stability of the intermediates necessary for the formation of the final polyatomic cluster in solution. Haushalter et al.$^{44,160}$ have previously reported that complex processes take place at solution-solid interfaces when metals are treated with ethylenediamine solutions containing Sn$_9^{4-}$.
Table 7.2

$^{117}$Sn, $^{119}$Sn and $^{205}$T1 NMR Parameters for Solutions Resulting from Extraction of KSnO, gTlO, g Alloy in Liquid Ammonia in the Presence of 2,2,2-crypt

<table>
<thead>
<tr>
<th>Species</th>
<th>$^{117}$Sn</th>
<th>$^{119}$Sn</th>
<th>$^{205}$Tl</th>
<th>$^{117}$Sn - $^{205}$Tl</th>
<th>$^{119}$Sn - $^{205}$Tl</th>
<th>$^{117}$Sn - $^{119}$Sn</th>
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<td>5542 ± 30</td>
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<td>-1624</td>
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<td></td>
<td>5298 ± 30</td>
<td>1630 ± 30</td>
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<td>-1625</td>
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<td>5548 ± 30</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-13</td>
</tr>
</tbody>
</table>

a Linewidth (Hz) at half height in parenthesis.

b For assignment see text.

c Weak satellites (peaks c''' and c' in Figure 7.3) are approximately 1/3 the height of the main satellite peaks, c' and c''.
and Pb\textsuperscript{4−} anions. It is unlikely that the difference in composition is caused by different extraction temperatures as the solution was allowed to warm to 0 °C as soon as ammonia solvent had been vacuum distilled onto the alloy/crypt mixture.

The most interesting feature of the solution \textsuperscript{119}Sn NMR spectrum in liquid ammonia is an intense doublet (5548 Hz) centered at \(-1625\) ppm (Figure 7.2b). The same doublet was also observed at \(-1624\) ppm in the solution \textsuperscript{117}Sn NMR spectrum, but with a splitting of \(5298\) Hz (Figure 7.2a). The doublets are attributed to spin-spin coupling of tin to the spin-\(\frac{1}{2}\) thallium isotopes \textsuperscript{203}Tl and \textsuperscript{205}Tl (not resolved), and their assignments are further confirmed by the agreement of \(J(\textsuperscript{117}Sn-\textsuperscript{203}/\textsuperscript{205}Tl)/J(\textsuperscript{119}Sn-\textsuperscript{203}/\textsuperscript{205}Tl) = 0.955\) with the ratio of the \textsuperscript{117}Sn and \textsuperscript{119}Sn gyromagnetic ratios (Table 1.2), \(\gamma_{117}/\gamma_{119} = 0.956\). The \textsuperscript{119}Sn doublet in Figure 7.2b has two sets of satellite peaks in a 1:1 ratio associated with it which result from two different \textsuperscript{117}Sn-\textsuperscript{119}Sn spin-spin couplings. The \textsuperscript{119}Sn-\textsuperscript{117}Sn couplings are also observed in the \textsuperscript{117}Sn NMR spectrum (Figure 7.2a).

In the previously observed homo- and heteroatomic tin clusters, only one type of tin-tin coupling was observed owing to the fast intramolecular scrambling of the Sn atoms in the clusters.\textsuperscript{41} The observation of two different \textsuperscript{117}Sn-\textsuperscript{119}Sn spin-spin coupling constants for the present species
Figure 7.2 (a) $^{117}$Sn (89.128 MHz) and (b) $^{119}$Sn (93.276 MHz) NMR spectra (-31°C) of species C formed from the extraction of KSn$_{0.9}$Tl$_{0.9}$ alloy in liquid ammonia in the presence of 2,2,2-crypt. The doublets arise from (a) $J(^{117}\text{Sn}-^{203/205}\text{Tl})$ and (b) $J(^{119}\text{Sn}-^{203/205}\text{Tl})$. Peaks labeled $c_1$ and $c_2$ arise from $J(^{117}\text{Sn}-^{119}\text{Sn})$. 
indicates that the doublet arises from a nonfluxional thallium-tin cluster. The nonfluxional nature of the species is also evident from the relatively large values of $J^{(119\text{Sn}-203/205\text{Tl})}$ (5548 Hz) and $J^{(117\text{Sn}-119\text{Sn})}$ (1717 and 620 Hz) when compared to the corresponding values in the fluxional TlSn$_5^{5-}$ anion, which lie in the ranges; $J^{(119\text{Sn}-203/205\text{Tl})}$ = 646 – 800 Hz and $J^{(117\text{Sn}-119\text{Sn})}$ = 412 – 456 Hz.41

A single tin environment suggests a cluster having a relatively high symmetry. Furthermore, the relatively low values of the satellite peak/doublet peak ratios, $I_{\text{S1}}/I_{\text{C}} = 7.6 \pm 0.5 \%$, for the $^{119}\text{Sn}$ doublet indicate only a small number of neighboring tin atoms as expected for a nonfluxional cluster. In fact, the value of $I_{\text{S1}}/I_{\text{C}}$ corresponds to a value of 8.2 % for two tin atoms in chemically and magnetically equivalent environments (calculated from equation (3.14) where $n = 2$, $P_{\text{117}} = P_{\text{119}} = 0.0761$ and $P_{\gamma} = 0.9239$; the $^{119}\text{Sn}$ isotopes are taken as inactive in chemically equivalent environments when $^{119}\text{Sn}$ is the observed nucleus).

A possible thallium-tin cluster structure having one Tl atom which would be consistent with the observed $^{117}\text{Sn}$ and $^{119}\text{Sn}$ doublets is a planar five-membered ring of tin atoms capped with a Tl atom, i.e., nido-TlSn$_5^{5-}$ (Structure II). The 1:1 intensity ratio of the one-bond and two-bond couplings, $J^{(117\text{Sn}-119\text{Sn})}$, is consistent with the 1:1
intensity ratio of the two different $^{117}\text{Sn}$ satellite peaks in the $^{119}\text{Sn}$ NMR spectrum (or $^{119}\text{Sn}$ satellites in the $^{117}\text{Sn}$ NMR spectrum). A similar structure based on a square planar Sn$_4$ ring capped with a Tl atom can be excluded owing to the 2:1 intensity ratio expected for the one-bond and two-bond $^{117}\text{Sn}-^{119}\text{Sn}$ couplings of the planar Sn$_4$ unit. Another less likely possibility is represented by Structure III and consists of a Tl atom sandwiched between two square planar Sn$_4$ rings (D$_{4d}$). In this isomer of the TlSn$_8^{5-}$ anion, the 1:1 intensity ratio of various $^{117}\text{Sn}-^{119}\text{Sn}$ couplings would correspond to intra- (J) and interplanar (J') couplings assuming the diagonal intra- and interplanar coupling constants are too small to be resolved.
Although all of the tin atoms are chemically equivalent in the two structures, one could use $^{203}/^{205}$Tl NMR spectroscopy to distinguish between them as the Tl atom has five and eight neighboring tin atoms for Structures II and III, respectively. The two structures can be ruled out as it was found from the $^{205}$Tl NMR spectrum (Figure 7.3) that the $I_{S_{1}}/I_{C}$ ratio of $35 \pm 2$ % for the Sn satellite (the $^{117}$Sn and $^{119}$Sn satellites were treated as unresolved) corresponds to only four equivalent neighboring tin atoms (theoretical ratios: 3 Sn, 28 %; 4 Sn, 35 %; 5 Sn, 41 %).

It is possible that chemical equivalence among the tin atoms results from fast chemical exchange involving an intermediate step in a more complex multi-step intramolecular exchange mechanism which, if fast enough on the NMR time scale, would lead to averaging of the tin environments. However, a simple exchange mechanism for a thallium-tin cluster based on commonly observed polyhedral structures\textsuperscript{35} having one Tl atom leads to too many equivalent neighboring tin atoms for the thallium and/or the tin environments. Furthermore, the satellite peaks of the $^{119}$Sn doublet did not broaden significantly relative to the doublet peak at lower temperatures, indicating exchange averaging cannot be caused by a fast exchange step. The $^{119}$Sn and $^{205}$Tl NMR spectra, therefore, must result from a static, but highly symmetrical, polyhedral thallium-tin anion having more
Figure 7.3 $^{205}\text{Tl}$ NMR spectrum (57.708 MHz, -30°C) of the solution resulting from the extraction of KSn$_{0.9}$Tl$_{0.9}$ alloy in liquid ammonia in the presence of 2,2,2-crypt. Peaks labeled c' and c''' are $^{119}\text{Sn}$ satellites and peaks labeled c'' and c'v are $^{117}\text{Sn}$ satellites.
than one Tl atom.

A structure which would account for the NMR findings is based on a square antiprism of tin atoms, Sn₈, with two Tl atoms capping opposite square faces, as expected for the closo-Tl₂Sn₈⁴⁻ anion (Structure IV)

![Diagram of Tl₂Sn₈⁴⁻](image)

The anticipated ¹¹⁹Sn-²⁰³/²⁰⁵Tl coupling constant (¹J) and two different ¹¹⁷Sn-¹¹⁹Sn coupling constants (J and J') are indicated in Structure IV. However, it has been assumed that diagonal ¹¹⁹Sn-¹¹⁷Sn spin-spin couplings that are within or between the square planar Sn₄ rings are too small to be resolved. Moreover, it is assumed that there is no ¹¹⁷,¹¹⁹Sn-²⁰³,²⁰⁵Tl spin-spin coupling between the Tl atom
and the Sn atoms in the square planar ring when they are not nearest neighbors to the Tl atom. Consequently, each Tl atom "sees" only four Sn atoms.

Although the Sn atoms are all chemically equivalent in Structure IV, each type of isotopomer, even those having the same isotopic composition, will give rise to different NMR subspectra. Consequently, the above calculated values for the satellite peak/doublet peak intensity ratios for the $^{117}$Sn (8.2 %) and $^{119}$Sn satellites (9.3 %) in their respective $^{119}$Sn and $^{117}$Sn NMR doublet spectra are inaccurate. In order to obtain accurate values for the $I_{Sl}/I_{C}$ ratios, the calculated intensities of one of the $^{119}$Sn doublet peaks and its associated $^{117}$Sn satellite peaks are given in Table 7.3 for the most important isotopomers, namely, $^{119}$Sn$_k^{na}$Sn$_{8-k}$ (k = 1 - 8), $^{119}$Sn$^{117}$Sn$^{na}$Sn$_6$, $^{119}$Sn$_2^{117}$Sn$^{na}$Sn$_5$, $^{119}$Sn$^{117}$Sn$_2^{na}$Sn$_5$, $^{119}$Sn$_3^{117}$Sn$^{na}$Sn$_4$, $^{119}$Sn$_2^{117}$Sn$_2^{na}$Sn$_4$ and $^{119}$Sn$^{117}$Sn$_3^{na}$Sn$_4$. The calculated $I_{Sl}/I_{C}$ ratios for the satellites were 8.0 % for a Sn$_8$ square antiprism, in good agreement with the observed ratio of 7.6 ± 0.5 %.

It was clear from the $^{205}$Tl NMR spectrum of the species that there was no evidence for $^{203}$Tl-$^{205}$Tl spin-spin coupling. The absence of spin-spin coupling between the two thallium atoms is not unexpected for Structure IV as the two atoms are relatively far apart. However, it is somewhat
<table>
<thead>
<tr>
<th>Isotopomer(s) $^a$</th>
<th>Total Number of Equivalent Isotopomers Contributing to Satellite and Central peaks</th>
<th>Intensities (%) $^b$</th>
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</thead>
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<tr>
<td>$^{119}\text{Sn}<em>{1}^{117}\text{Sn}</em>{5}^{n} \text{Sn}_{6-r-s}$ ($\times 10^{-4}$)</td>
<td>$^N$ $J$ $J'$ $C$</td>
<td>$^m \times N \times P_A \times 100$</td>
</tr>
<tr>
<td>$\sum_{k=1}^{8} C_k \ n(P_{119})<em>k(P</em>{219})_{8-k}$</td>
<td>- - -</td>
<td>- - 39.441</td>
</tr>
<tr>
<td>$^{119}\text{Sn}<em>{1}^{117}\text{Sn}</em>{5}^{n} \text{Sn}_{6}$ (22.628)</td>
<td>16 16 24</td>
<td>1.810 1.810 5.431</td>
</tr>
<tr>
<td>$^{119}\text{Sn}<em>{2}^{117}\text{Sn}</em>{6}^{n} \text{Sn}_{5}$ (2.317)</td>
<td>96 96 144</td>
<td>1.112 1.112 3.336</td>
</tr>
<tr>
<td>$^{119}\text{Sn}<em>{2}^{117}\text{Sn}</em>{6}^{n} \text{Sn}_{5}$ (2.055)</td>
<td>48 48 40 $^c$</td>
<td>0.493 0.493 0.658</td>
</tr>
<tr>
<td>$^{119}\text{Sn}<em>{3}^{117}\text{Sn}</em>{6}^{n} \text{Sn}_{4}$ (0.481)</td>
<td>320 320 360 $^c$</td>
<td>0.285 0.285 0.854</td>
</tr>
<tr>
<td>$^{119}\text{Sn}<em>{3}^{117}\text{Sn}</em>{6}^{n} \text{Sn}_{4}$ (0.2103)</td>
<td>240 240 160 $^c$</td>
<td>0.252 0.252 0.337</td>
</tr>
<tr>
<td>$^{119}\text{Sn}<em>{4}^{117}\text{Sn}</em>{6}^{n} \text{Sn}_{4}$ (0.187)</td>
<td>56 56 32 $^c$</td>
<td>0.052 0.052 0.060</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>4.004</strong></td>
<td><strong>50.117</strong></td>
</tr>
</tbody>
</table>

$a$ The probability of isotopomer occurrence, $P_A = (P_{117})^{r}(P_{119})^s(P_{219})^{8-r-s}$, is given in parentheses; where $P_{117} = 0.0761$, $P_{119} = 0.0858$ and $P_{219} = 0.8381$.

$b$ The factor, $m$, is $\frac{1}{2}$ for the satellite peaks, $J$ and $J'$, and 1 for the central line, $C$.

$c$ The central line, $C$, of an isotopomer triplet is counted as $\frac{1}{2}$ for $C$; contributions from a doublet of doublets is not counted.
surprising that the "two-bond" $^{203,205}Tl-117,119Sn$ spin-spin coupling is too small to be observed for Structure IV. It is conceivable that the high p character of the skeletal bonding orbitals results in very small values for spin-spin coupling constants, particularly when the atoms are not directly bonded to each other.

In general, the two $^{117}Sn-^{119}Sn$ spin-spin coupling constants cannot be unambiguously assigned to either J or J'. However, in the structures of $Sn_9^{4-}$, $^{28}TlSn_9^{3-}$, $^{32}Sn_9Cr(CO)_3^{4-}$, $^{37}$ the intraplanar Sn-Sn distances of the square planar $Sn_4$ units are longer than those of the interplanar $Sn_4$ units. If one assumes the spin-spin couplings are large for shorter Sn-Sn distances, the larger coupling can be assigned to J'. Interestingly, yet another set of $^{117}Sn$ and $^{119}Sn$ satellites, c''' and c''', were observed as shoulders on peaks c' and c'' in the $^{205}Tl$ NMR spectrum (Figure 7.3). The peaks c'''' and c''' are approximately 1/3 the height of peaks c' and c'', indicating that perhaps one of the Sn atoms in each square planar $Sn_4$ unit is shifted slightly towards the Tl atom.

Although the species giving rise to the $^{119}Sn$ doublet has a high solution concentration, an intense peak arising from $Sn_9^{4-}$ was observed in the $^{119}Sn$ NMR spectrum. Furthermore, a relatively intense, broad triplet at -992 ppm attributed to a new tin species was also observed. Other
smaller peaks of unknown tin species were also observed in the solution $^{119}$Sn NMR spectrum, but owing to their low intensities they were not studied further. In addition to the peak at 9707 ppm in the $^{205}$Tl NMR spectrum, a new, relatively intense peak was observed at 10,439 ppm. Clearly, there are other thallium species present in the solution, but owing to the large chemical shift ranges of the $^{203}$Tl and $^{205}$Tl nuclei in these solutions, they were not studied further. The NMR data for all the species observed in solutions resulting from extraction of KSn$_{0.9}$Tl$_{0.9}$ alloy in liquid ammonia in the presence of 2,2,2-crypt are summarized in Table 7.2.

(ii) **The High Temperature KSnTl Alloy**

The high temperature alloy, KSnTl, was prepared in a molybdenum tube and extracted in a manner similar to that used for the KSn$_{0.9}$Tl$_{0.9}$ alloy. However, it was immediately evident from the solution $^{205}$Tl NMR spectrum that the peak at 10,456 ppm was now much more intense than the peak at 9707 ppm. This large difference in the composition is attributed to different conditions used in the two alloy preparations. The KSn$_{0.9}$Tl$_{0.9}$ alloy was prepared in a glass ampule where the alloy was kept in a molten state for only a few minutes whereas the KSnTl alloy was maintained at ca. 950 °C overnight. Consequently, the KSn$_{0.9}$Tl$_{0.9}$ alloy is expected
to be richer in the kinetically more stable phases while the KSnTl alloy would be expected to be richer in the thermodynamically more stable phases, and could lead to different compositions for the solution extracts.

The solution $^{203}$Tl and $^{205}$Tl NMR spectra of the species at 10,463 ppm are depicted in Figure 7.4. In the $^{203}$Tl spectrum, peaks $d_1$ and $d_2$ are higher in intensity relative to peak D than in the $^{205}$Tl spectrum (Figure 7.4b). This indicates that lines $d_1$ and $d_2$ may be associated with a splitting pattern arising from $^{203}$Tl-$^{205}$Tl spin-spin coupling. As the natural abundance of $^{205}$Tl (70.5 %) is higher than that of $^{203}$Tl (29.5 %), peaks $d_1$ and $d_2$ are expected to be more intense relative to peak D in the $^{203}$Tl NMR spectrum. Moreover, it follows that peaks $d_1$, $d_2$ and D arise from a species having two chemically equivalent Tl atoms where the central line D is assigned to the isotopomers $^{205}$Tl$_2$ and $^{203}$Tl$_2$ in their respective $^{205}$Tl and $^{203}$Tl NMR spectra. Peaks $d_1$ and $d_2$ are assigned to doublets resulting from $^{203}$Tl-$^{205}$Tl spin-spin coupling (21,679 Hz) attributed to the $^{203}$Tl$^{205}$Tl isotopomer (Table 7.4).

Interestingly, peaks $d_1$ and $d_2$ are not symmetrically disposed around the central line, D, in either the $^{203}$Tl spectrum or the $^{205}$Tl spectrum. The D-$d_1$ peak separation is 11,041 Hz while the D-$d_2$ separation is 10,638 Hz, yielding an asymmetry of 403 Hz. This asymmetry arises from the large
Figure 7.4  (a) $^{203}\text{Tl}$ (57.08 MHz) and (b) $^{205}\text{Tl}$ (57.708 MHz) NMR spectra (24°C) of the solution resulting from the extraction of the high-temperature KSnTl alloy in liquid ammonia in the presence of 2,2,2-crypt. Peaks labeled $d_1$ and $d_2$ arise from $J(203\text{Tl} - 205\text{Tl})$ and peaks labeled $d'$, $d''$, $d'_1$, $d'_1'$, $d'_2'$ and $d'_2''$ are unresolved $^{117/119}\text{Sn}$ satellites (see Table 7.5). The asterisk (*) denotes a fold-in from the resonance at 9662 ppm.
Figure 7.5 Expansion of the $^{205}$Tl multiplet in Figure 7.4b showing satellites associated with (a) the central line D and (b) peak $d_1$. Peaks labeled $d''$ arise from spin systems $AA'N_2$, $AA'NX$ and $AA'X_2$ and peaks labeled $d'$ arise from spin systems $AA'X$, $AA'N$, $XAA'X$, $XAA'N$ and $NAA'N$ (see Table 7.5). Peaks labeled $d_1'$, $d_1''$ and $d_1'''$ are unresolved $^{117/119}$Sn satellites.
Table 7.4
Peak Separations of the $^{203\text{Tl}}, \, 205\text{Tl}, \, 117\text{Sn} \, \text{and} \, 119\text{Sn} \, \text{Multiplets}$

<table>
<thead>
<tr>
<th>$J(A-B)$ $^b$ (Hz)</th>
<th>$^{203\text{Tl}}$</th>
<th>$^{205\text{Tl}}$</th>
<th>$117\text{Sn}$</th>
<th>$119\text{Sn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$21.679 , (^{203\text{Tl}-205\text{Tl}})$</td>
<td>$d_1 - d_2$</td>
<td>$11.041$</td>
<td>$11.041$</td>
<td>$2404 - 2470$</td>
</tr>
<tr>
<td></td>
<td>$d_3 - d_3$</td>
<td>$10.638$</td>
<td>$10.638$</td>
<td>$714$</td>
</tr>
<tr>
<td></td>
<td>$d_4 - d_4$</td>
<td>$555$</td>
<td>$555$</td>
<td>$269$</td>
</tr>
<tr>
<td>$2780 \pm 50 , (^{117/119\text{Sn}-203/205\text{Tl}})$</td>
<td>$d_1' - d_1'$</td>
<td>$2780$</td>
<td>$2795$</td>
<td>$269$</td>
</tr>
<tr>
<td></td>
<td>$d_2' - d_2'$</td>
<td>$2780$</td>
<td>$2825$</td>
<td>$116$</td>
</tr>
<tr>
<td></td>
<td>$d_3' - d_3'$</td>
<td>$49$</td>
<td>$49$</td>
<td>$116$</td>
</tr>
<tr>
<td></td>
<td>$d_4' - d_4'$</td>
<td>$2155$</td>
<td>$2166$</td>
<td>$2155$</td>
</tr>
<tr>
<td></td>
<td>$d_5' - d_5'$</td>
<td>$598$</td>
<td>$592$</td>
<td>$598$</td>
</tr>
<tr>
<td></td>
<td>$d_6' - d_6'$</td>
<td>$280$</td>
<td>$226$</td>
<td>$280$</td>
</tr>
</tbody>
</table>

---

a The peak labeling schemes are given in Figures 7.4, 7.5 and 7.6.

For assignments of the peaks see Table 7.5.

b The chemical shifts, measured at 24 °C, were 10,463 ppm for $\delta(^{203\text{Tl}})$ and $\delta(^{205\text{Tl}})$ and -981 ppm for $\delta(^{117\text{Sn}})$ and $\delta(^{119\text{Sn}})$. 
value of $J^{(203\text{TL}-205\text{TL})}$, which is no longer insignificant when compared to the resonance frequency difference of 579,510 Hz for the $^{203}\text{TL}$ and $^{205}\text{TL}$ environments. The NMR spectra of the $^{203}\text{TL}^{205}\text{TL}$ isotopomers are therefore not first order AX spectra but second order AB spectra.\textsuperscript{161} The asymmetry, $b$, in each pair of transitions of the AB spin system about its chemical shift is given by equation (7.1)

$$b = \sqrt{(J(A-B))^2 + \Delta \nu_{AB}^2 - 2\Delta \nu_{AB} \cos \theta}$$

(7.1)

where $J(A-B)$ is the spin-spin coupling constant between nuclei A and B and $\Delta \nu_{AB}$ is the difference in their chemical shifts given in Hz. Using equation (7.1), the asymmetry is calculated to be 405 Hz and is in excellent agreement with the measured value of 403 Hz (Table 7.5).

There are two pairs of satellite peaks associated with peaks $d_1$ and $d_2$ in Figure 7.4 (also see Table 7.4), i.e., $d_1'$, $d_1''$ and $d_2'$, $d_2''$. The two satellite doublets (2155 Hz and 2780 Hz) are assigned to spin coupling to $^{117/119}\text{Sn}$. The ratio of the two satellite splittings is 0.775 and because this ratio is much smaller than the value of 0.956 expected for the ratio of the $^{117}\text{Sn}$ and $^{119}\text{Sn}$ gyromagnetic ratios, the two satellite doublets must arise from two different kinds of $^{203,205}\text{TL}_{117/119}\text{Sn}$ spin-spin coupling. Unfortunately, the $^{117}\text{Sn}$ and $^{119}\text{Sn}$ satellite
Table 7.5
Contribution of Different Spin Systems to the $^{203}\text{Tl}$, $^{205}\text{Tl}$ and $^{119}\text{Sn}$

Multiplets of the Proposed $\text{Tl}_2\text{Sn}_2^k$-Cluster Anion (Species D)\(^a\)

<table>
<thead>
<tr>
<th>Spin System</th>
<th>203\text{Tl} (B)</th>
<th>205\text{Tl} (A)</th>
<th>119\text{Sn} (N)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td></td>
<td></td>
<td>D</td>
<td>Asymmetry, $b = 205$ Hz see eq. (7.1)</td>
</tr>
<tr>
<td>BB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>$d_1, d_2$</td>
<td>$d_1, d_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AAN</td>
<td></td>
<td></td>
<td>$d'$</td>
<td>$4d, D$</td>
</tr>
<tr>
<td>AAX</td>
<td></td>
<td></td>
<td>$d'$</td>
<td>$4d, D$</td>
</tr>
<tr>
<td>BBN</td>
<td>$d'$</td>
<td>$d'$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBX</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BAN</td>
<td>$d_1''', d_2'''$</td>
<td>$d_1', d_2'$</td>
<td>$1d, 4d$</td>
<td></td>
</tr>
<tr>
<td>ABN</td>
<td>$d_1''', d_2''$</td>
<td>$d_1''', d_2'''$</td>
<td>$1d, 4d$</td>
<td>$J_1(\text{Tl-Sn}) &gt; J_2(\text{Tl-Sn})$</td>
</tr>
<tr>
<td>BAX</td>
<td>$d_1''', d_2'''$</td>
<td>$d_1', d_2'$</td>
<td>$1d, 4d$</td>
<td>$J_1(\text{Tl-Sn})$ and $J_2(\text{Tl-Sn})$ are of opposite sign</td>
</tr>
<tr>
<td>ABX</td>
<td>$d_1', d_2$</td>
<td>$d_1'', d_2''$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\{\)

| NAAN        | $d'$            |                 | $4d$            |         |
| NBN         |                 |                 | $4d$            |         |
| XAN         |                 |                 | $3d, 6d$        | $J(X-N) = J'$ f |
| XBN         | $d'$            |                 | $1d, 6d$        |         |
| NAEN, NBAN  | $d$             |                 | $1d, 4d$        |         |
| XAEN, XBAN  | $d$             |                 | $1d, 3d, 6d$    | $J(X-N) = J'$ f |

\(\})

| AAN$_2$     | $d'''$, D       |                 | $4d$            |         |
| BEN$_2$     |                 |                 | $4d$            |         |
| AANX        | $d'''$, D       | $d''$, C        | $2d, 5d$        | $J(X-N) = J$ f |
| BENX        |                 |                 | $2d, 5d$        |         |
| AEEN$_2$, BEAN$_2$ | $d_1, d_2$ | $d_1, d_2$ | $1d, 4d$ | $J(X-N) = J$ f |
| AEENX, BEANX| $d_1', d_2'$   | $d_1', d_2'$    | $1d, 2d, 5d$    |         |

\(\)

\(a\) For labeling of peaks see Figures 7.4, 7.5, and 7.6 and Table 7.4.  
\(b\) $A = ^{205}\text{Tl}$, $B = ^{203}\text{Tl}$, $N = ^{119}\text{Sn}$ and $X = ^{117}\text{Sn}$.  
\(c\) Not all the peaks were observed or resolved in the four-spin systems.  
\(d\) Only the $d'''$ peaks were observed in the $^{203}\text{Tl}$ and $^{205}\text{Tl}$ spectra of these spin systems. 
\(f\) Tentative assignment (see text).
peaks are not resolved, resulting in relatively large linewidths for the satellite peaks (Figure 7.5a).

The observation of two different $J^{(203,205\text{Ti}-117/119\text{Sn})}$ values shows that the Ti atoms have two different groups of neighboring Sn atoms. The $d_1'/d_1$ and $d_1''/d_1$ ($d_2'/d_2$ and $d_2''/d_2$) intensity ratios were measured to be 29 ± 3% and correspond to three equivalent Sn atoms (28% calculated from eq. (3.14) where $n = 3$, $p_\beta = 0.1619$ and $p_\gamma = 0.8381$; $^{117}\text{Sn}$ and $^{119}\text{Sn}$ satellites not resolved). From this it may be concluded that each of the two different neighboring groups of Sn atoms consists of three Sn atoms.

In general, a doublet of doublets is expected in the A-part of an AB'N spin system. The two-spin systems AB'N and BA'N have different values for $J(A-N)$ (Structure V and VI, respectively) and will therefore give rise to two different sets of doublets of doublets.

![Diagram of structures V and VI](image)

Consequently, the two different sets of doublets of doublets in the $^{205}\text{Ti}$ (or $^{203}\text{Ti}$) NMR spectrum, i.e., doublets $d_1'$, $d_2'$ and doublets and $d_1''$, $d_2''$, are assigned to the spin systems ABN, ABX and BAN, BAX, respectively, where $A = ^{205}\text{Ti}$, $B = ^{203}\text{Ti}$.
$^{203}\text{Tl}$, $N = ^{119}\text{Sn}$ and $X = ^{117}\text{Sn}$ (Table 7.5). The two unique coupling constants are hereafter denoted $J_1(\text{Tl-Sn})$ and $J_2(\text{Tl-Sn})$. Owing to the large value of the $\text{Tl-Tl}$ spin coupling, the thallium NMR spectra of isotopomers which give rise to $\text{AA'}N$, $\text{AA'}X$, $\text{BB'}N$ and $\text{BB'}X$ spin systems, are strongly dependent on the relative signs of $J_1(\text{Tl-Sn})$ and $J_2(\text{Tl-Sn})$.\textsuperscript{161} The central line, D, of the $^{205}\text{Tl}$ NMR spectrum and its associated satellites are shown in Figure 7.5b. From Figure 7.5b it is clear that the satellite peaks $d'$ are separated by ca. 300 Hz from peak D (Table 7.4). Such small values for the satellite separations are only possible if $J_1(\text{Tl-Sn})$ and $J_2(\text{Tl-Sn})$ are of opposite sign. Thus, the line separations are approximately equal to their average value, i.e., $\frac{1}{2}| J_1(\text{Tl-Sn}) + J_2(\text{Tl-Sn}) | = 310$ Hz.\textsuperscript{161} The assignments of the peaks $d_1'$, $d_1''$, $d_2'$ and $d_2''$ arising from different spin systems are given in Table 7.5.

The $^{119}\text{Sn}$ NMR spectrum of the solution showed the expected multiplet for $\text{Sn}_9^{4-}$ at $-1280$ ppm, the previously observed doublet at $-1639$ ppm (Section B(i)) and a multiplet at $-981$ ppm. The latter environment was much more intense than when observed in the $\text{KSn}_{0.9}\text{Tl}_{0.9}$ alloy extract, indicating this tin environment arose from the same species that gave rise to the $^{203}\text{Tl}$ and $^{205}\text{Tl}$ multiplets. The $^{117}\text{Sn}$ and $^{119}\text{Sn}$ NMR spectra of the tin environment at $-981$ ppm are shown in Figure 7.6 and the separations of peaks $1d$, $2d$, $3d$, $4d$.
Figure 7.6  (a) $^{117}$Sn (89.128 MHz) and (b) $^{119}$Sn (93.276 MHz) NMR spectra (24°C) of the solution resulting from the extraction of the high-temperature KSnIII alloy in liquid ammonia in the presence of 2,2,2-crypt. For assignments of peaks 1d, 2d, 3d, 4d, 5d and 6d see text and for their separations from the central peak D, see Table 7.4. Assignments are given in Table 7.5.
$4d$, $5d$ and $6d$ from the central line, D, are listed in Table 7.4.

The separation of the intense peaks $4d$ from D is 296 Hz in the $^{119}\text{Sn}$ NMR spectrum and corresponds to the average value of $J_1(\text{Ti-Sn})$ and $J_2(\text{Ti-Sn})$ given above, as expected for virtual coupling of strongly coupled systems such as $\text{AA}'\text{N}$, $\text{BB}'\text{N}$, $\text{ABN}$ and $\text{BAN}$ (Tables 7.4 and 7.5). However, peaks $1d$ in the $^{119}\text{Sn}$ multiplet ($^{117}\text{Sn}$ multiplet) are separated from the central line, D, by approximately the numerical average of the coupling constants, $\frac{1}{2}(|J_1(\text{Ti-Sn})| + |J_2(\text{Ti-Sn})|) = 2470$ Hz, which arise from the $\text{ABN}$ and $\text{BAN}$ ($\text{ABX}$ and $\text{BAX}$) spin systems (Tables 7.4 and 7.5).

The $2d$, $3d$, $5d$ and $6d$ peaks therefore arise from the NMR spectra of isotopomers having $^{117}\text{Sn}-^{119}\text{Sn}$ spin-spin coupling. It was evident from the $^{203}\text{Ti}$ and $^{205}\text{Ti}$ spectra that the Ti atoms have two different neighboring Sn atoms. Consequently, two unique $^{117}\text{Sn}-^{119}\text{Sn}$ spin-spin coupling constants are expected as a result of coupling within ($J$) and between ($J'$) the two groups of tin atoms. This will result in isotopomers giving rise to spin systems $\text{XAA}'\text{N}$ (VII) and $\text{AA}'\text{NX}$ (VIII).

![Diagram VII](VII)

![Diagram VIII](VIII)
Consequently, the spin systems XAA'N and AA'XN, as well as XABN and ABXN, will have different $^{119}\text{Sn}$ (or $^{117}\text{Sn}$) NMR spectra (Table 7.5).

In order to determine values for the two expected unique $^{117}\text{Sn}$-$^{119}\text{Sn}$ couplings, a series of $^{119}\text{Sn}$ NMR spectra (note $^{119}\text{Sn} = N$) corresponding to the spin systems XAA'N, XABN, XBAN, AA'XN, ABXN and BAXN (Table 7.5) were calculated$^{162}$ using the observed $J_1(\text{Tl-Sn})$ and $J_2(\text{Tl-Sn})$ values and by varying the $J(\text{$^{117}\text{Sn}$-$^{119}\text{Sn}$})$ values. The peaks in the calculated $^{119}\text{Sn}$ NMR spectrum vary somewhat between each spin system, but for $J(\text{$^{117}\text{Sn}$-$^{119}\text{Sn}$}) = 800 \text{ Hz}$, peaks at 710 and 125 Hz with respect to the central line, D, were common for these spin systems, and correspond reasonably well to peaks 2d and 5d, respectively. A similar calculation with $J(\text{$^{117}\text{Sn}$-$^{119}\text{Sn}$}) = 400 \text{ Hz}$ gives peaks at 560 and 60 Hz corresponding to peaks 3d and 6d. However, it should be noted that the positions of the calculated peaks are not only dependent upon the values of $J(\text{$^{117}\text{Sn}$-$^{119}\text{Sn}$})$, but are also dependent upon $J_1(\text{Tl-Sn})$ and $J_2(\text{Tl-Sn})$. As the latter values could not be determined more accurately, one can only tentatively assign the values of 800 and 400 Hz to $J(\text{$^{117}\text{Sn}$-$^{119}\text{Sn}$})$. The major peaks calculated for these spin systems are listed in Table 7.5.

A number of additional peaks, attributed to subspectra of other isotopomers, are also present in the
\(^{119}\text{Sn}\) multiplets (Figure 7.6), many of which are only partially resolved. In addition to the \(^{4d}\) peaks, other transitions arise from the spin systems NAA'N, NABN, NBAN, AA'N\(_2\), ABN\(_2\) and BAN\(_2\), and are positioned 10 - 60 Hz around the \(^{4d}\) peaks. These transitions presumably cause broadening of the \(^{4d}\) peaks. Furthermore, the contributions of spin systems arising from isotopomers containing three spin-\(\frac{1}{2}\) nuclei of Sn, i.e., N\(_3\), N\(_2\)X and NX\(_2\), will also be significant in the \(^{119}\text{Sn}\) NMR spectrum. It is impossible to analyze the \(^{119}\text{Sn}\) and \(^{117}\text{Sn}\) multiplets in order determine the values of \(J(\text{Sn}^{117}\text{Sn}^{119}\text{Sn})\) with certainty owing to extensive overlap of peaks from different spin systems.

In addition to \(^{119}\text{Sn}\) peaks arising from Sn\(_9^{4-}\) and Tl\(_2\)Sn\(_8^{4-}\) and small peaks at -1786 and -1810 ppm, it appears that the only \(^{119}\text{Sn}\) multiplet present is that of the new thallium-tin cluster. It is, however, conceivable that the tin environment is bonded to another tin atom which would give rise to satellites whose intensities are too low to be observed.

(iii) A Proposed Structure for the Tl\(_2\)Sn\(_m^{k-}\) Cluster

The \(^{203}\text{Tl}\) and \(^{205}\text{Tl}\) NMR spectra of the solution extract of KSnTl in liquid ammonia show unambiguously for the first time the presence of a thallium-tin polyatomic anion having more than one Tl atom. Furthermore, it was evident
from the relative intensities that each Tl atom "sees" two different groups of Sn atoms, each group containing three Sn atoms. As it appears that all the tin atoms in the cluster were chemically equivalent on the NMR time scale, one can propose a structure based on two TlSn₃ tetrahedra that are bonded through the corners by two Tl atoms (Structure IX). A possible anion having these features (on the NMR time scale) would be \((\text{Sn}_3\text{TlTlSn}_3)^{4-}\). The anion is related to the \(\text{Sn}_4^{2-}\) anion in that Sn has been replaced by Tl⁻ and two such TlSn₃³⁻ tetrahedra are coupled through the Tl atoms. Like the \(\text{Sn}_4^{2-}\) anion, the \(-\text{TlSn}_3^{2-}\) tetrahedron of \((\text{Sn}_3\text{TlTlSn}_3)^{4-}\) utilizes ten electrons for skeletal bonding. Owing to the degeneracy of the half-filled e orbital of an 10-electron TlSn₃ tetrahedron, each tetrahedron is expected to undergo a Jahn-Teller distortion, possibly to a compressed tetrahedron as indicated by theoretical calculations on \(\text{Sn}_4^{2-}\).⁴² The thallium and tin environments would, however,
be equivalent on the NMR time scale as presumably a similar low-energy pathway of interchange consisting of motion through three compressed and three elongated tetrahedra, proposed for the Sn₄²⁻ anion, are also possible for the Tl₃Sn₃ tetrahedra. Furthermore, the proposed structure and mechanism are also consistent with the NMR findings in that there should be no exchange of Sn atoms between tetrahedra nor would the Tl-Tl bond be broken in this exchange mechanism.

It might at first seem odd that a thallium-tin cluster could exist in which thallium is formally in the +3 oxidation state. However, recently the structures of several thallium-iron carbonyl cluster anions, namely, [Tl₂Fe₄(CO)₁₆]²⁻, [Tl₄Fe₈(CO)₃₀]⁴⁻ and [Tl₆Fe₁₀(CO)₃₆]⁶⁻, have been reported which are Tl(III) species. Interestingly, it was reported that when the thallium-iron carbonyl clusters were prepared from Tl(I) salts, metallic thallium precipitated from the reaction. Lumps of alloys also formed when the KSnTl alloy was extracted in liquid ammonia in the presence of 2,2,2-crypt although they were not studied further. The large coupling constant, J(²⁰³Tl-²⁰⁵Tl), observed for the thallium-tin cluster would also be consistent with two Tl(III)-Tl(III) bonded species owing to the high s character resulting from the formally sp³ hybridized Tl atoms. A smaller coupling constant would be
expected between two Tl(I) atoms in a p-bonded cluster.

It is of interest to note that the values for the $^{203,205}_{Tl}^{117,119}_{Sn}$ spin-spin coupling constants of the proposed $(Sn_3TlTlSn_3)^{4-}$ anion are roughly half the values found for the $Tl_2Sn_8^{4-}$ anion. This difference may be attributable to the presence of a lone pair on Tl in $Tl_2Sn_8^{4-}$ such that the "one-bond" Tl-Sn coupling constant increases by roughly 2500 Hz. If a similar increase is also assumed per addition of a lone pair on Tl, the corresponding negative "two-bond" Tl-Sn coupling constant would be very small, and could account for failure to observe this coupling in the proposed $Tl_2Sn_8^{4-}$ anion.

Although the structure proposed for the $(Sn_3TlTlSn_3)^{4-}$ anion is consistent with the NMR data, other clusters cannot be ruled out. No static structure of commonly observed polyhedra was apparent which was consistent with the NMR data. However, a polyhedron having two Tl atoms along one edge of a "semi-fluxional" polyhedron such that each Tl atom sees two chemically equivalent Sn groups on the NMR time scale would also be consistent with the NMR data. One possible way to distinguish between the two types of polyhedra, a coupling of small polyhedra or a single large "semi-fluxional" polyhedron, would be from the relative values of the two $117Sn-119Sn$ coupling constants. The difference would be expected to be large for small
coupled polyhedra whereas they would be comparable for the single and larger polyhedron. However, as was discussed above, the value for \( J(117\text{Sn}-119\text{Sn}) \) could not be reliably determined from this study.

(C) **ATTEMPTS TO PREPARE TlSn\(_9\)\(^{3-}\) AND TlPb\(_9\)\(^{3-}\) AND EVIDENCE FOR A NEW THALLIUM-LEAD CLUSTER**

Thallium and tin solution NMR studies of alloy extractions (Sections A and B) failed to produce direct evidence for the TlSn\(_9\)\(^{3-}\) and TlSn\(_9\)\(^{3-}\) anions in these solutions. Interestingly, the closo-TlSn\(_9\)\(^{3-}\) cluster is related to the nido-Sn\(_9\)\(^{4-}\) cluster by the addition of Tl\(^{+}\) cation to the latter anion. The syntheses of the TlSn\(_9\)\(^{3-}\) and TlPb\(_9\)\(^{3-}\) anions were attempted by allowing Tl\(^{+}\) cation to react with Sn\(_9\)\(^{4-}\) and Pb\(_9\)\(^{4-}\) anions in ethylenediamine according to equations (7.2) and (7.3)

\[
\begin{align*}
\text{Tl}^+ + \text{Sn}_9^{4-} & \xrightarrow{\text{en}} \text{TlSn}_9^{3-} \quad (7.2) \\
\text{Tl}^+ + \text{Pb}_9^{4-} & \xrightarrow{\text{en}} \text{TlPb}_9^{3-} \quad (7.3)
\end{align*}
\]

A previous NMR study had shown that extraction of K/Sn and K/Pb alloys in en gave the Sn\(_9\)\(^{4-}\) and Pb\(_9\)\(^{4-}\) anions as the dominant species in solution.\(^{41}\) However, when the solutions resulting from the extraction of the KSn\(_{2.25}\) and KPb\(_{2.25}\) alloys were mixed with ethylenediamine solutions of TlNO\(_3\) or
TlI in the absence of crypt, lumps of grey spongy alloys formed and the solution decolorized. Evidently, the TlSn₉³⁻ anion and the unknown TlPb₉³⁻ anion cannot be prepared by this synthetic route.

The ²⁰⁷Pb NMR spectrum of the solution resulting from the extraction of the Kpb₀.₉Tl₀.₉ alloy in en gave a single peak at -4110 ppm assigned to the Pb₉⁴⁻ anion,¹¹ and a doublet at -4008 ppm. The doublet is assigned to a new T₁₉Pb₉ᵏ⁻ anion with a coupling constant, 2⁰³/2⁰⁵T₁-2⁰⁷Pb, of 4608 Hz. Unfortunately, the ²⁰⁵T₁ NMR spectrum of the new species could not be located owing to the low concentration of the species and large dynamic chemical shift range of the ²⁰⁵T₁ nuclei. Consequently, the number of Pb atoms in the T₁₉Pb₉ᵏ⁻ anion could not be determined. It is unlikely, however, that the new thallium-lead cluster is the lead analog of the TlSn₈⁵⁻ anion, i.e., T₁Pb₈⁵⁻, owing to the large coupling constant, J(²⁰³/²⁰⁵T₁-²⁰⁷Pb) = 4608 Hz. In fact, the large value of the coupling constant suggests the new species is related to the proposed T₂Sn₈⁴⁻ anion, i.e., T₂Pb₈⁴⁻.

The extraction of the Kpb₀.₉Tl₀.₉ in ethylenediamine in the presence of 2,2,2-crypt gave a dark green solution. However, no peaks could be observed in the ²⁰⁷Pb NMR spectrum.
CHAPTER 8
CONCLUSIONS AND DIRECTIONS FOR FUTURE RESEARCH

(A) INTRODUCTION

The introduction of the alkali metal cation complexing agent 2,2,2-crypt by Corbett et al.\textsuperscript{65} allowed the isolation of a large number of stable crystalline salts of Zintl anions which were subsequently characterized by X-ray crystallography. However, Rudolph and co-workers\textsuperscript{38} showed that many Zintl anions not previously isolated in the solid state could be structurally characterized directly in solution by multi-NMR. This development was of great importance as often times the isolated crypt salts did not represent the true nature of these complex solutions. The power of multi-NMR for the characterization of mixtures of polyanions in solution was further illustrated by Schrobilgen et al.\textsuperscript{49} in their study of a large number of novel classical metal chalcogenide anions. In a continuing study of polyanions in basic media, the majority of this Thesis has described the preparation and structural characterization of classically as well as nonclassically bonded main-group polyanions in solution by multi-NMR and, when suitable single crystals were attainable, in the solid state by X-ray
crystallography.

(B) **METHOD FOR CALCULATIONS OF SATELLITE AND CENTRAL PEAK INTENSITIES IN NMR SPECTRA**

In order to be able to conveniently determine the number of atoms bonded to an element from the measured satellite and central NMR peak intensities of the element's NMR-active nucleus, relatively simple expressions for the satellite peak/central peak intensity ratio, $I_s/I_c$, were derived for commonly encountered systems. Specifically, the probability of different possible isotopomers and their consequent NMR spectra where derived algebraically. The final expression for $I_s/I_c$ was then arrived at by superimposing the different subspectra for each isotopomer algebraically. The most commonly observed systems, $AX_n$ and $A_k$ (two spin-$\frac{1}{2}$ isotopes for element A) were considered and also the more complex systems $AX_nY_m$ and $A_kX_n$.

Even though only first order spectra of spin-$\frac{1}{2}$ nuclei were considered, the generality of the derivation greatly simplifies the analysis of more complex systems such as those giving rise to second order spectra.
DILEAD(II) CHALCOGENIDE ANIONS, Pb₂Ch₃²⁻ (Ch= Se, Te)

A novel series of dilead chalcogenide anions, Pb₂SeₙTe₃₋ₙ²⁻ (n = 0 - 3) was prepared in ethylenediamine and subsequently structurally characterized by ⁷⁷Se, ¹²⁵Te and ²⁰⁷Pb NMR spectroscopy. The NMR data was consistent with trigonal bipyramidal structures where the Pb atoms occupied the axial sites and the chalcogen atoms were in the equatorial positions. The comparison of the NMR parameters of the Pb₂SeₙTe₃₋ₙ²⁻ anions with the metal chalcogenide anions studied previously⁴⁹ indicated a dominant use of p orbitals of both Pb and Ch in the Pb-Ch bonds.

The detailed geometries of the Pb₂Se₃²⁻ and Pb₂Te₃²⁻ anions were obtained from the crystal structures of the compounds (2,2,2-crypt-K⁺)₂Pb₂Se₃²⁻ and (2,2,2-crypt-K⁺)₂Pb₂Te₃²⁻. These anions were found to have compressed trigonal bipyramidal structures as was evident from the small bond angles Ch-Pb-Ch = 90 and 92° and Pb-Ch-Pb = 71 and 67° for Ch = Se and Te, respectively. The compressed geometry of the anions gave rise to an unusually short Pb-Pb distance. However, the short Pb-Pb distance is not believed to signify a bonding interaction.

The characterization of the Pb₂Ch₃²⁻ anions illustrated their apparently close relationship to the butterfly shaped Tl₂Ch₂²⁻ ³³ and Sb₂Se₄²⁻ ¹⁰³ anions by the removal and addition of Ch²⁻. The presence of Se²⁻ in the
solutions in which the Pb$_2$Ch$_3$$^{2-}$ and Tl$_2$Ch$_2$$^{2-}$ anions were prepared as well as the apparent exchange broadening of Tl$_2$Ch$_2$$^{2-}$ anions$^{49}$ lend further credence to this relationship.

(D) **THE POLYCHALCOGENIDE ANIONS CH$_n$$^{2-}$ (n = 1 - 4) AND TeS$_m$Se$_{3-n}$$^{2-}$ (m = 0 - 3)**

From previous studies of metal chalcogenide anions$^{49}$ it was postulated that the simple polychalcogenide anions played a significant role in the chemistry of these systems. A much better understanding of the solution chemistry and NMR spectroscopy of polychalcogenide anions of selenium and tellurium was therefore needed. In order to gain a better insight into their chemistry and their role in classical metal chalcogenide anion chemistry, solution multi-NMR studies of polychalcogenide anions were undertaken.

The homopolychalcogenide anions, Se$_n$$^{2-}$ and Te$_n$$^{2-}$ (n = 1 - 4) as well as the HSe$^{-}$ and HTe$^{-}$ anions, were prepared and characterized in solution by $^1$H, $^{77}$Se, $^{123}$Te and $^{125}$Te NMR spectroscopy. In addition, the new series of chain-like heteropolychalcogenide anions of selenium and tellurium, Te$_3$-$k$Se$_k$$^{2-}$ and Te$_4$-$r$Se$_r$$^{2-}$ (k = 1, 2 and r = 1, 2), and the pyramidal TeSe$_3$$^{2-}$ anion were prepared and structurally characterized in solution by $^{77}$Se and $^{125}$Te NMR spectroscopy. The structures of the trichalcogenide and tetrachalcogenide anions of selenium and tellurium could be rationalized by use
of the principle\textsuperscript{127} that substitution of Te by Se resulted in a structure in which the Se atom occupied the position having the highest electron charge density.

The complex solution chemistry of the polychalcogenide anions was evident from NMR studies. In particular, this was evident from intermolecular chemical exchange which resulted in broadening of NMR peaks. The NMR study showed that exchange could be slowed sufficiently by eliminating or weakening ionic pairing by complexation of the alkali metal cations with 2,2,2-crypt. This was particularly evident in the case of the trichalcogenide anions. Furthermore, it was evident from NMR studies that ionic pairing has a significant effect on the stabilities and equilibria of the longer chain polyselenide anions Se\textsubscript{3}\textsuperscript{2\text{--}}, Se\textsubscript{4}\textsuperscript{2\text{--}} and Se\textsubscript{6}\textsuperscript{2\text{--}}.

The large values of the spin-spin coupling constants for the Ch\textsubscript{T}–Ch\textsubscript{B} bonds of chain anions indicated the nature of these bonds was different from that of the Ch\textsubscript{B}–Ch\textsubscript{B} bonds. Consequently, a simple model was proposed in which the Ch\textsubscript{T}–Ch\textsubscript{B} bond is polarized towards Ch\textsubscript{B} owing to the high s character and consequent higher electronegativity of the atomic hybrid orbital used in bonding.

The detailed geometries of the V-shaped TeSe\textsubscript{2}\textsuperscript{2\text{--}} anion and the pyramidal TeSe\textsubscript{3}\textsuperscript{2\text{--}} anions were obtained from the crystal structure of (2,2,2-crypt-K\textsuperscript{+})\textsubscript{2}TeSe\textsubscript{2}\textsuperscript{2\text{--}}•en and (2,2,2-
crypt-\(\text{K}^+\)\(\text{TeSe}_3^{2-}\)-en. The large bond angle (111°) observed for the \(\text{TeSe}_2^{2-}\) anion was, like the NMR data, consistent with a bonding model in which there is a high s character in the atomic hybrid of the \(\text{Ch}_B\) atom. Furthermore, the bond lengths of \(\text{TeSe}_3^{2-}\) indicated a bond order of 1 1/3 for the Te-Se bond, as expected from the dominant resonance structures.

The series of anions, \(\text{TeS}_m\text{Se}_{3-m}^{2-}\), were prepared in ethylenediamine solution and subsequently structurally characterized by \(^{77}\text{Se}\) and \(^{125}\text{Te}\) NMR spectroscopy. Interestingly, the trends in the NMR parameters \(\delta(^{77}\text{Se})\), \(\delta(^{125}\text{Te})\) and \(^{1}J(^{77}\text{Se}-{^{125}}\text{Te})\) indicated that S was more electronegative than Se in this system.

(E) **TIN CHALCOGENIDE ANIONS**

The novel Sn(II) species, \(\text{Sn}_2\text{Se}_3^{2-}\) and \(\text{SnPbSe}_3^{2-}\) were formed and subsequently characterized by \(^{77}\text{Se}, 117\text{Sn}, 119\text{Sn}\) and \(^{207}\text{Pb}\) NMR spectroscopy when \(\text{K}_2\text{Se}\) was allowed to react directly with \(\text{SnSe}\) and \(\text{PbSe}\). The anions were found to be isostructural with the \(\text{Pb}_2\text{Ch}_3^{2-}\) anions in which the Sn and Pb atoms were in axial positions and the Se atoms in the equatorial positions. However, the NMR parameters of the \(\text{Sn}_2\text{Se}_3^{2-}\) and \(\text{SnPbSe}_3^{2-}\) anions indicated that the anions were distorted from their "ideal" bipyramidal geometries.

No Sn(II) tellurium anions could be prepared by this route. Rather, these anions appeared to be unstable and lead
to the formation of new tin(IV) telluride anions. The structures of these anions could not be determined unambiguously by NMR owing to fast exchange. However, the NMR parameters indicated that these anions consisted of trigonal planar SnTe₃ units linked together. Furthermore, the SnTe₃ units were undergoing fast intramolecular "spinning" on the NMR time scale such that they were in effect "decoupled" from the remaining environments in the anions.

(F) THALLIUM-TIN AND THALLIUM-LEAD CLUSTERS

This study illustrated the remarkable dependency of the stability and formation of thallium-tin clusters resulting from alloy extraction upon (1) the presence of the alkali metal complexing agent 2,2,2-crypt during alloy extraction, (2) the solvent used for extraction and (3) the method used for the preparation K/Sn/Tl alloys. Thus, a completely different kind of species formed when one or more of these parameters were altered.

The presence of two novel thallium-tin cluster anions in liquid ammonia having two Tl atoms was evident from the ¹¹⁷Sn, ¹¹⁹Sn, ²⁰³Tl and ²⁰⁵Tl NMR studies. For one of the anions, two Tl atoms in the cluster could be unambiguously determined. Although these anions could not be characterized in detail from this study, the structure of the anions was
shown by multi-NMR to be consistent with square antiprism of Sn₈ capped with two Tl atoms, Sn₈Tl₂⁴⁻, and a structure consisting of coupled TlSn₃ tetrahedra, i.e., (Sn₃TlTlSn₃)⁴⁻.

A different attempt to synthesize the TlSn₉³⁻ anion and the hitherto unknown TlPb₉³⁻ anion by direct reaction of the Tl⁺ cation with Sn₉⁴⁻ and Pb₉⁴⁻ anions in ethylenediamine proved unsuccessful. However, a new TlₙPbₘ⁻ anion in en could be identified in the ⁴⁻ Pb NMR spectrum in the extract of the KPb₀.₉Tl₀.₉ alloy.

(G) FUTURE DIRECTIONS FOR RESEARCH

The successful preparation and characterization of the TeSₘSe₃₋ₘ²⁻ series of anions and the recent characterization of the Pb₂SₘCh₃₋ₘ²⁻ anions (Ch = Se and/or Te)¹⁶⁴ suggest the series of anions TlSₘCh₃₋ₘ³⁻, Tl₂SₘCh₂₋ₘ²⁻, SnSₘCh₃₋ₘ³⁻, SnSₘCh₄₋ₘ³⁻, SₘCh₃₋ₘ²⁻ and SₘCh₄₋ₘ²⁻, where Ch = Se and/or Te, could be prepared and characterized in solution in a similar manner. This would also be of considerable interest as it would allow one to compare the effects of S and Se upon trends in NMR parameters and to determine the relative electronegativities of S and Se in these anions. This would especially become important for the SₘSe₃₋ₘ²⁻ and SₘSe₄₋ₘ²⁻ anion series owing to the different isomers possible having S or Se in the terminal positions and their rationalization using the
Topological Charge Stabilization Rule.\textsuperscript{127}

Although new Sn(IV) tellurium anions could be prepared in ethylenediamine or liquid ammonia, attempts to isolate crystals of their 2,2,2-crypt-K\textsuperscript{+} salts proved unsuccessful. In order to obtain crystalline compounds containing these anions, a different complexing ligand such as 18-Crown-6 could be used. Furthermore, salts of other large nonpolarizing cations such as t-butylammonium or tetraphenylphosphonium halides (Cl\textsuperscript{-} or Br\textsuperscript{-}) could also be added to solutions containing these anions. Using this approach, Haushalter \textit{et al.}\textsuperscript{52} have isolated a number of crystalline salts of the Zintl anions.

It was evident from the 119Sn NMR spectra of the proposed (Sn\textsubscript{3}Tl\textsubscript{2}Sn\textsubscript{3})\textsuperscript{4\textsuperscript{-}} anion that the subspectra of a four and higher spin system consisting of isotopomers containing 117Sn and 119Sn were needed in order to determine the J(117Sn-119Sn) spin-spin coupling constant. Consequently, 117,119Sn enriched samples would be required for this purpose. Note both isotopes, 117Sn and 119Sn, are needed in the sample in order to observe Sn-Sn spin coupling between two chemically equivalent Sn environments. Undoubtedly, there will be extensive overlap of the lines from the higher spin systems in the 119Sn NMR spectrum. Their analysis should be simplified, however, as the lines from the 119Sn subspectra could be measured allowing the determination of
the coupling constants by interactive spectral fitting procedures.

The study of the thallium-tin cluster anions strongly suggests that other species could be prepared. Thus, the extraction of the high-temperature KSnTl alloy in ethylenediamine will presumably lead to formation of new thallium-tin clusters. Furthermore, the high-temperature KPbTl alloy could be prepared and extracted in ethylenediamine and/or liquid ammonia in the presence of 2,2,2-crypt and the resulting thallium-lead cluster anions characterized by $^{203}$Tl, $^{205}$Tl and $^{207}$Pb NMR spectroscopy.
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