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Preparation and Multinuclear Magnetic Resonance Study of the Zintl Anions $HgCh_2^{2-}$, $CdCh_2^{2-}$, $SnCh_3^{2-}$, $TlCh_3^{3-}$, $SnCh_4^{4-}$, and $Tl_2Ch_2^{2-}$ (Ch = Se and/or Te). Chemical Shift and Coupling Constant Correlations

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Multinuclear magnetic resonance spectroscopy is ideally suited to the study of the solution chemistry and structures of Zintl anions, as every post-transition-metal element forming a Zintl phase possesses at least one natural-abundance isotope that is NMR active, many of which are spin $^1/_2$ nuclei. In the present work several new series of classical anions have been prepared and characterized by multinuclear magnetic resonance, while in other cases previously unreported examples of other series for which isolated examples were already known have also been characterized. All of the anions have been obtained by extraction of the appropriate ternary or quaternary Zintl phases of the type KM(Te/Se) or NaM(Te/Se), where M = Hg, Cd, Tl, or Sn, with ethylenediamine or liquid ammonia in the presence of 2,2,2-crypt. These studies include (1) the linear $HgCh_2^{2-}$ (Ch = Se and/or Te) and $CdCh_2^{2-}$ anions, (2) the trigonal-planar $TlCh_3^{3-}$ and $SnCh_3^{2-}$ anions, (3) the tetrahedral $SnCh_4^{4-}$ anions, and (4) the cyclic $Tl_2Ch_2^{2-}$ anions, which are presumed to have the same "butterfly"-shaped geometry known for $Tl_2Te_2^{2-}$. All of these anions have been fully characterized in ethylenediamine or liquid-ammonia solutions by $^{203,205}Tl$, ^{199}Hg, ^{125}Te, ^{119}Sn, ^{113}Cd, and ^{77}Se NMR spectroscopy. Relevant chemical shifts are reported and their trends discussed. An abundance of heavy-element spin–spin couplings are also reported, enabling structural comparison to be made within and betweeen series after the nuclear dependence has been removed (to give reduced coupling constants), and allowances have been made for relativistic effects, of major importance in the species studied.

Introduction

Many of the heavy main-group elements form intermetallic phases (Zintl phases) with the alkali metals that give soluble products in liquid NH_3 or ethylenediamine (en). About 50 years ago, Zintl and co-workers[2-4] described electrochemical studies on solutions of such sodium alloys together with the results of exhaustive alloy extractions. The homopolyatomic anions Sn_9^{4-}, Pb_9^{4-}, Bi_7^{3-}, Sb_7^{3-}, and Te_4^{2-} were among the first species to be identified. However, any attempt to isolate these anionic species by evaporation of the solvent resulted in the formation of amorphous products or reversion to a known binary alloy phase(s) in the particular system. The macrobicyclic ligand 2,2,2-crypt[5] has been successfully used to complex the alkali-metal counterion (Na^+ or K^+) in these solutions. This prevents the formation of other more stable intermetallic phases on removal of the solvent and generally increases the solubility of the anion(s) in the above solvents. The 2,2,2-crypt ligand contains a three-dimensional intramolecular cavity lined with six oxygen and two nitrogen binding sites and forms inclusion complexes in which the alkali metal is contained inside the molecular cavity. The use of cryptating agents has led to the stabilization and X-ray crystallographic characterization of a variety of novel homopolyatomic anions of widely varying geometries, i.e. Sn_9^{4-} (C_{4v}),[6] Sn_5^{2-} (D_{3h}) and Pb_5^{2-} (D_{3h}),[7] Ge_9^{2-} (D_{3h}) and Ge_9^{4-} (C_{4v}),[8] Sb_7^{3-} (C_{3v}),[9] and As_{11}^{3-} (D_3).[10]

Mixed-metal anionic systems are also known. Elements like mercury and thallium, with their relatively low number of valence electrons, can be combined with less electropositive, more electron-rich elements to give heteropolyatomic species such as the tricapped trigonal-prismatic $TlSn_8^{3-}$ and the bicapped square-antiprismatic $TlSn_9^{3-}$ clusters,[11] the butterfly-shaped $Tl_2Te_2^{2-}$ anion,[12] and the linear $HgTe_2^{2-}$ anion.[13] Heteropolyatomic anions in which all elements are relatively electron rich have likewise been characterized, including the tetrahedral $Sn_2Bi_2^{2-}$ and $Pb_2Sb_2^{2-}$ species,[14,15] and the $As_2Se_6^{2-}$ anion, which consists of a six-membered ring in a chair conformation with two exocyclic selenium atoms attached to the two opposed arsenic atoms in the ring.[16]

The use of multinuclear magnetic resonance spectroscopy is particularly suited to the study of the solution chemistry and structures of Zintl anions, as every post-transition-metal element forming a Zintl phase possesses at least one natural abundance isotope that is NMR active. A large number of these elements possess naturally occurring isotopes that are spin $^1/_2$ (nonquadrupolar) nuclei and are capable of providing additional valuable structural information based upon their hetero- and homonuclear spin–spin couplings.[17]

Previous studies by Rudolph and co-workers of the $Na_{1\rightarrow 2}Sn$, $NaSn_{2.25}$, NaSnPb, NaGeSn, KGeSn, and $NaSnTl_{1.5}$ alloy extracts in en and liquid NH_3 in the absence of a cryptating agent have led to the characterization of Sn_4^{2-}, Sn_9^{4-}, Pb_9^{4-}, and the mixed-metal anions $Sn_{9-n}Pb_n^{4-}$ (n = 1–8), $Sn_{9-n}Ge_n^{4-}$ (n = 1–8), and $TlSn_8^{5-}$ in solution by ^{119}Sn and ^{207}Pb NMR spectroscopy.[18-20] Interestingly, all of the nine-atom species have been found to be fluxional on the NMR time scale, and this therefore underscores the importance of multinuclear magnetic resonance spectroscopy as a complementary structural tool to X-ray crystallography in the study of these species.

Much of the early work on Zintl anions and work until the present have produced cluster, cage, or ring cluster species. It is only recently that a few examples of heteroatomic classically bonded anions extracted from Zintl alloys have come to light. These include the aforementioned $HgTe_2^{2-}$ anion, while extraction of an NaSnTe alloy in en has led to the formation of $SnTe_4^{4-}$,[20] which recently has been shown to have a tetrahedral structure

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(2) Zintl, E.; Goubeau, J.; Dullenkopf, W. *Z. Phys. Chem. Abt. A*, **1931**, *154*, 1.

(3) Zintl, E.; Harder, A. *Z. Phys. Chem., Abt. A* **1931**, *154*, 47.

(4) Zintl, E.; Dullenkopf, W. *Z. Phys. Chem., Abt. B*, **1932**, *16*, 183.

(5) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49.

(6) Corbett, J. D.; Edwards, P. *J. Am. Chem. Soc.* **1977**, *99*, 3313.

(7) Edwards, P.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 903.

(8) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163.

(9) Adophson, D. G.; Corbett, J. D.; Merryman, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 7234.

(10) Belin, C. H. E. *J. Am. Chem. Soc.* **1980**, *102*, 6036.

(11) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 2808.

(12) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2627.

(13) Burns, R. C.; Corbett, J. D. *Inorg. Chem.* **1981**, *20*, 4433.

(14) Critchlow, S. C.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3286.

(15) Corbett, J. D.; Critchlow, S. C.; Burns, R. C. "Rings, Clusters and Polymers of the Main Group Elements"; Cowley, A. H., Ed.; American Chemical Society: Washington, DC, 1983; ACS Symp. Ser. No. 232, Chapter 6, p 95.

(16) Berlin, C. H. E.; Charbonnel, M. M. *Inorg. Chem.* **1982**, *21*, 2504.

(17) Harris, R. K. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 1, p 1.

(18) Rudolph, R.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4629.

(19) Rudolph, R. W.; Taylor, R. C.; Young, D. C. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; p 997.

(20) Rudolph, R.; Wilson, W. L.; Taylor, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 2480.

0020-1669/85/1324-2615$01.50/0

Table I. NMR Parameters for the $HgCh_2^{2-}$ Anions

	chem shift, δ				coupling const J, Hz	
	^{199}Hg		^{125}Te	^{77}Se	^{199}Hg–^{125}Te	^{199}Hg–^{77}Se
anion	obsd	calcd	obsd	obsd		
$HgTe_2^{2-}$	−2169	−2180	−726.4		6500	
$HgTeSe^{2-}$	−1516	−1494	−889.4	−30.5	6470	2270
$HgSe_2^{2-}$	−796	807		−142.27		2258

in the Zintl phase Na_4SnTe_4.[21]

In the present work, we have sought to investigate and to extend the range of known classically bonded heteropolyatomic anions of the immediate post-transition-metal and main-group elements, using multinuclear magnetic resonance spectroscopy as the primary tool for their identification. The synthetic rationale used here was to stabilize Zintl anions containing the (relatively) valence-electron-poor elements by preparing mixed species having a significant number of very electron-rich atoms, namely selenium and/or tellurium, which are fairly easily reduced and as such can effectively act as pseudohalogens (i.e., Se^- or Te^- are isovalent with a halogen atom), thus allowing the central metal atom to become extensively coordinated.

Results and Discussion

The experimental approach involved the syntheses of ternary or quaternary alloys of the type M–X–Te, M–X–Se, and M–X–Te–Se where M = alklai metal (Na or K) and X = Hg, Cd, Sn, or Tl. The resulting Zintl phases were extracted in a suitably basic solvent, en or liquid NH_3, always in the presence of 2,2,2-crypt, and the resulting solutions investigated by multinuclear magnetic resonance spectroscopy. In all cases residual solid remained after extraction, but these residues were not investigated in view of the lack of data concerning the appropriate ternary or quaternary systems except to note that the majority were, like the initial alloy compositions themselves, hydrolytically unstable.

Identification of the Zintl anions observed in this study was dependent upon correct NMR assignments. The reliability of the assignments was assured by a combination of two or more of the following criteria: (1) distinctive heteronuclear NMR coupling patterns arising from isotopically dilute spin $^1/_2$ nuclides (see Supplementary Material for a table of observed and theoretical satellite intensities); (2) isotopic enrichment in either ^{77}Se or ^{125}Te to give the appropriate spin multiplicities corresponding to the number of ligands; (3) identification and consistent behavior of peaks from the same species in the spectra of two or more nuclei; (4) systematic variation of the relative intensities of species as the ratio of tellurium to selenium was changed; (5) for the tin-containing species, corroboration of the NMR assignments by ^{119}Sn Mössbauer spectroscopy. Mössbauer studies on the anions studied in this work and on related systems have been reported in a previous paper.[22] In addition, the NMR assignments have been found to be consistent with empirical and periodic trends noted throughout the course of this work.

(I) Zintl Anions Extracted from KHgTe, KHgSe, and KHgTe$_{0.5}$Se$_{0.5}$ Alloys. The only member of the $HgCh_2^{2-}$ series known prior to this work was $HgTe_2^{2-}$. This anion has been characterized by a single-crystal X-ray study and shown to possess a linear geometry ($D_{\infty h}$ symmetry).[13]

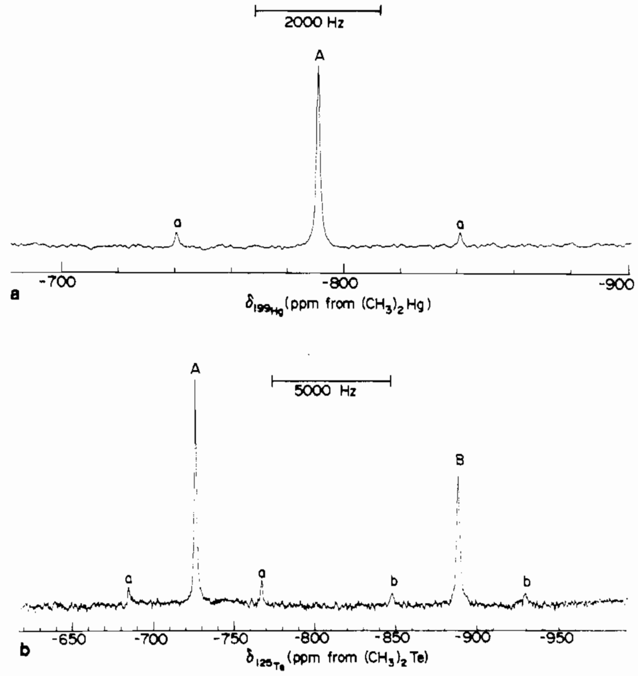

Figure 1. (a) ^{199}Hg NMR spectrum, obtained at 44.80 MHz, for the $HgSe_2^{2-}$ (A) anion. Peaks labeled a denote ^{77}Se satellites. (b) ^{125}Te NMR spectrum of the $HgCh_2^{2-}$ series of anions, obtained at 78.92 MHz: (A) $HgTe_2^{2-}$; (B) $HgTeSe^{2-}$. Peaks labeled a and b denote ^{199}Hg satellites.

Table II. NMR Parameters for the $CdCh_2^{2-}$ Anions

	chem shift, δ		coupling const J, Hz	
anion	^{113}Cd	^{125}Te	^{113}Cd–^{125}Te	^{111}Cd–^{125}Te
$CdTe_2^{2-}$	−487.7 (−500.2)[a]	−1159.0	2148 (2203)	2058
$CdTeSe^{2-}$	−343.3 (−347.8)			
$CdSe_2^{2-}$	−69.0 (−69.1)			

[a] Data recorded for $CdCh_2^{2-}$ in liquid NH_3 is given in parentheses.

Extraction of the alloy KHgTe in en in the presence of 2,2,2-crypt gave a deep yellow solution as previously noted,[13] while extraction of KHgTe$_{0.5}$Se$_{0.5}$ and KHgSe gave progressively paler solutions. The entire series of $HgCh_2^{2-}$ anions was identified and characterized by obtaining the natural-abundance ^{199}Hg (16.84%), ^{125}Te (6.99%), and ^{77}Se (7.58%) NMR spectra of these extracts. The assignments are unambiguous as only one species was observed for each of the ternary alloy systems and all three species were observed in the extract from the quaternary alloy system. Assignments were confirmed, as indicated above, by observation of satellite doublets of appropriate intensity arising from one-bond ^{199}Hg–^{77}Se and ^{199}Hg–^{125}Te couplings in the NMR spectra of each pair of coupled nuclei (Figure 1). The chemical shifts and coupling constants for the series of $HgCh_2^{2-}$ anions are listed in Table I, and it may be noted that the ^{199}Hg chemical shifts are additive in nature. Trends among chemical shifts and coupling constants will be summarized in a later section.

(II) Zintl Anions Extracted from KCdTe, KCdSe, and KCdTe$_{0.5}$Se$_{0.5}$ Alloys. With the preparation and characterization of the $HgCh_2^{2-}$ series of anions, it seemed likely that the analogous, but unknown, cadmium species should exist. Accordingly, the alloys KCdTe, KCdTe$_{0.5}$Se$_{0.5}$, and KCdSe were prepared and extracted as for the corresponding mercury alloys, giving yellow-orange, yellow, and pale yellow solutions, respectively. Examination of these extracts by natural-abundance ^{113}Cd (12.26%), ^{125}Te, and ^{77}Se NMR provided evidence for a new series of $CdCh_2^{2-}$ anions by analogy with the related mercury system on the basis of the same criteria. However, while all chemical shift and coupling constant data were obtained for $CdTe_2^{2-}$, the $CdSe_2^{2-}$ and $CdTeSe^{2-}$ anions were not soluble enough to enable other than ^{113}Cd chemical shift data to be recorded. Similar results were obtained when liquid NH_3 was used as the solvent. All data are listed in Table II, and, interestingly, the ^{113}Cd chemical shifts do not exhibit the highly additive nature exhibited by the ^{199}Hg chemical shifts of the related $HgCh_2^{2-}$ series of anions. As for the $HgCh_2^{2-}$ series of anions, the $CdCh_2^{2-}$ anions are each assumed to have a linear geometry like that of $HgTe_2^{2-}$.[13]

(III) Zintl Anions Extracted from KSnTe$_{2-x}$Se$_x$ (x = 0, $^1/_2$, $^3/_2$, 2) and NaSnTe$_{1-x}$Se$_x$ (x = 0, $^1/_3$, $^2/_3$, 1) Alloys. In view of the fact that Rudolph and co-workers[20] had already observed the ^{119}Sn and ^{125}Te NMR spectra of $SnTe_4^{4-}$ and the crystal structures of Na_4SnTe_4 and $Na_4SnSe_4 \cdot 16H_2O$ have recently been reported,[21,22] two tin-containing ternary alloys were prepared, one tellurium

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[21] Eisenmann, B.; Schäfer, H.; Schrod, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 921.

[22] Krebs, B.; Hinter, H.-U. *Z. Anorg. Allg. Chem.* **1980**, *462*, 143.

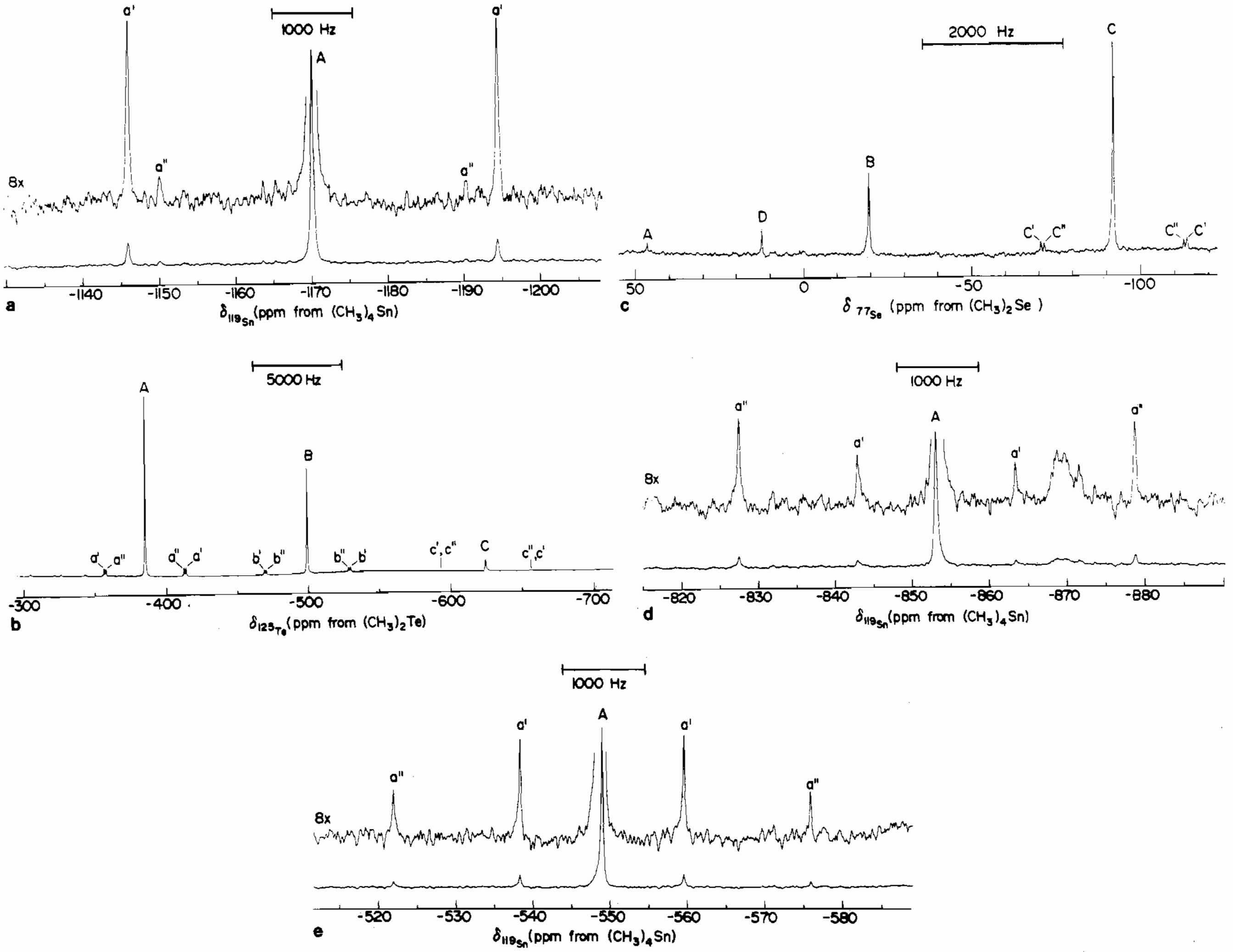


Figure 2. (a) ^{119}Sn NMR spectrum of the $SnTe_3^{2-}$ (A) anion, obtained at 93.27 MHz. Peaks labeled a′ denote ^{125}Te satellites; peaks labeled a″ denote ^{123}Te satellites. (b) ^{125}Te NMR spectrum, obtained at 78.92 MHz, for the $SnCh_3^{2-}$ series of anions. The peak assignments are as follows: (A) $SnTe_3^{2-}$; (B) $SnTe_2Se^{2-}$; (C) $SnTeSe_2^{2-}$. Peaks labeled a′, b′, and c′ denote ^{119}Sn satellites while those labeled a″, b″, and c″ denote ^{117}Sn satellites. (c) ^{77}Se NMR spectrum for the $SnCh_3^{2-}$ series of anions, obtained at 47.70 MHz: (A) $SnTe_2Se^{2-}$; (B) $SnTeSe_2^{2-}$; (C) $SnSe_3^{2-}$; (D) unknown resonance. Peaks labeled c′ and c″ denote ^{119}Sn and ^{117}Sn satellites, respectively; (d) ^{119}Sn NMR spectrum of the $SnTe_2Se^{2-}$ anion, obtained at 93.27 MHz. Peaks labeled a′ denote ^{77}Se satellites; peaks labeled a″ denote ^{125}Te satellites. (e) ^{119}Sn NMR spectrum of the $SnTeSe_2^{2-}$ anion, obtained at 93.27 MHz. Peaks labeled a′ denote ^{77}Se satellites; peaks labeled a″ denote ^{125}Te satellites.

rich, the other selenium rich, with the view in mind to observe the $SnSe_{4-n}Te_n^{4-}$ (n = 0–4) series of anions. An alloy of composition $KSnTe_{0.5}Se_{1.5}$ yielded a deep amber solution when extracted with en in the presence of 2,2,2-crypt, while an alloy of composition $KSnTe_{1.5}Se_{0.5}$ produced a reddish-orange solution similar to that of Sn_9^{4-} under the same conditions. These solutions were investigated by ^{119}Sn (8.58% natural abundance), ^{125}Te, and ^{77}Se NMR spectroscopy. A series containing five tetrahedral $SnCh_4^{4-}$ anions was expected. Evidence for only four species in solution was, however, obtained. Efforts to find low concentrations of the Sn_9^{4-}, $SnTe_4^{4-}$, and (see below) $SnSe_4^{4-}$ anions in the ^{119}Sn NMR spectra of these solutions provided no evidence for their presence. Rather, the signals have been assigned to a new series of classical, triply coordinated anions, viz. $SnTe_3^{2-}$, $SnTe_2Se^{2-}$, $SnTeSe_2^{2-}$, and $SnSe_3^{2-}$. The assigned formal charge of 2− for these anions has been deduced from ^{119}Sn Mössbauer spectroscopy on the basis of oxidation state considerations and is discussed in a subsequent section. Members of this series therefore possess 24 valence electrons and thus are isovalent with the CO_3^{2-} anion. Not unexpectedly, extraction of the ternary alloys $KSnTe_2$ and $KSnSe_2$ under the same conditions gave the pure $SnTe_3^{2-}$ and $SnSe_3^{2-}$ anions, respectively. Again, no evidence could be found for the presence of the $SnTe_4^{4-}$ or $SnSe_4^{4-}$ anions in these alloy extracts.

$SnCh_3^{2-}$ (Ch = Te and/or Se). The assignments of the $SnCh_3^{2-}$ species were accomplished by obtaining the ^{119}Sn, ^{125}Te, and ^{77}Se spectra of each new $SnCh_3^{2-}$ anion (Figure 2). In every case, natural-abundance satellite doublets were observed as a result of directly bonded spin–spin coupling between the spin $^1/_2$ nuclei, i.e. ^{119}Sn–^{125}Te, ^{117}Sn–^{125}Te, ^{119}Sn–^{77}Se, and ^{117}Sn–^{77}Se (natural abundance of ^{117}Sn, 7.61%). The observations of natural-abundance satellite spectra enabled unambiguous assignments to be made on the basis of the following considerations: (i) $^{117,119}Sn$–^{125}Te couplings are always larger in a homologous series than $^{117,119}Sn$–^{77}Se couplings by virtue of the larger magnetogyric ratio of ^{125}Te relative to ^{77}Se;[17] (ii) the spin–spin couplings could be observed in the spectra of each pair of spin-coupled nuclei; (iii) relative satellite intensities in the ^{119}Sn spectra confirmed the assignments of (a) $SnTe_2Se^{2-}$ and $SnTeSe_2^{2-}$, as the ^{125}Te satellites in $SnTe_2Se^{2-}$ should be approximately twice the intensity of the more closely spaced ^{77}Se satellites while the opposite intensity distribution is expected for $SnTeSe_2^{2-}$ (Figure 2d,e), and (b) every member of the series by comparison of the integrated intensities of each satellite doublet with those calculated from the percent natural abundances of the ligand atoms.

The relevant chemical shifts, coupling constants, and assignments for the $SnCh_3^{2-}$ series of anions are given in Table III. All of the ^{119}Sn, ^{125}Te, and ^{77}Se NMR assignments are supported by good agreement of the observed chemical shifts with those calculated from a least-squares linear regression analysis of the data, which is discussed in a later section. From Table III it is also apparent that not only are the chemical shifts additive in nature

Table III. NMR Parameters for the $SnCh_3^{2-}$ Anions

	chem shift, δ						coupling const *J*, Hz			
	^{119}Sn		^{125}Te		^{77}Se					
anion	obsd	calcd	obsd	calcd	obsd	calcd	$^{119}Sn-^{125}Te$	$^{117}Sn-^{125}Te$	$^{119}Sn-^{77}Se$	$^{117}Sn-^{77}Se$
$SnTe_3^{2-}$ [a]	−1170.1	−1162.4	−385.2	−383.3			4535	4335		
$SnTe_2Se^{2-}$	−853.1	−860.2	−499.5	−503.2	46.67	47.75	4792	4577	1916	
$SnTeSe_2^{2-}$ [b]	−548.7	−558.0	−625.0	−623.1	−19.52	−21.67	5035	4816	1996	1923
$SnSe_3^{2-}$	−264.3	−255.8			−92.16	−91.09			2051	1959

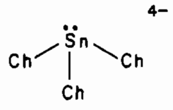
[a] $J_{^{119}Sn-^{123}Te}$ = 3776 Hz. [b] $J_{^{125}Te-^{77}Se}$ = 79.4 Hz.

Table IV. NMR Parameters for the $SnCh_4^{4-}$ Anions

	chem shift, δ						coupling const *J*, Hz			
	^{119}Sn		^{125}Te		^{77}Se					
anion	obsd	calcd	obsd	calcd	obsd	calcd	$^{119}Sn-^{125}Te$	$^{117}Sn-^{125}Te$	$^{119}Sn-^{77}Se$	$^{117}Sn-^{77}Se$
$SnTe_4^{4-}$	−1823.6	−1812.7	−203.3	−199.3			2851	2727		
$SnTe_3Se^{4-}$	−1472.3	−1475.3	−293.4	−298.3	99.6	101.3	3119	2981	1264	
$SnTe_2Se_2^{4-}$	−1124.8	−1137.8	−395.1	−397.3	49.4	47.3	3340	3192	1341	1282
$SnTeSe_3^{4-}$	−791.9	−800.4	−499.4	−496.3	−5.8	−6.7	3571	3418	1402	1342
$SnSe_4^{4-}$	−476.6	−463.0			−61.9	−60.6			1463	1398

but the spin–spin coupling constants are also directly additive. Trends concerning the chemical shifts and coupling constants are discussed in a subsequent section.

Mössbauer Studies. From the relevant NMR satellite intensities and the number of species present, it has already been demonstrated that the central tin atom is triply coordinated in solutions extracted from the $KSnTe_2$, $KSnSe_2$, and $KSnTe_{2-x}Se_x$ (x = 0, $^1/_2$, $^3/_2$, 2) alloys. There are, however, two possible triply coordinated structures that are consistent with these findings. The first is a trigonal-pyramidal structure (I) with a lone pair on tin



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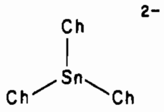

II

so that tin possesses a formal oxidation state of +2, i.e. $SnCh_3^{4-}$, while the second is a trigonal-planar structure (II) where tin has a formal oxidation state of +4, i.e. $SnCh_3^{2-}$. As Sn(II) and Sn(IV) compounds normally give characteristic and well-defined ^{119}Sn Mössbauer isomer shifts,[23] samples of $SnTe_3^{n-}$ and $SnSe_3^{n-}$ as well as the mixed anions were prepared in order to resolve the above ambiguity and to allow assignment of the actual charge on these anions.

The Mössbauer parameters of the various species studied in this work are discussed in detail elsewhere.[24] Importantly, it should be noted here that all isomer shift values for the above samples (ca. 1.6–1.8 mm s^{-1}) were characteristic of tin in the +4 oxidation state whereas Sn(II) resonances are found above that of α-Sn, 2.02 mm s^{-1}.[25]

$SnCh_4^{4-}$ (Ch = Se and/or Te). The two tetrahedral species, $SnTe_4^{4-}$ and $SnSe_4^{4-}$, were prepared by extracting the alloys NaSnTe and NaSnSe with en in the presence of 2,2,2-crypt, while solutions containing the mixed species were obtained by extraction of the quaternary alloys, $NaSnTe_{0.67}Se_{0.33}$ and $NaSnTe_{0.33}Se_{0.67}$, under the same conditions. The chemical shifts and coupling constants for all species are summarized in Table IV and confirm that neither $SnTe_4^{4-}$ nor $SnSe_4^{4-}$ was present in the original K–Sn–Te–Se studies, which led to the formation of the trigonal-planar species. The ^{119}Sn chemical shift and $^{119}Sn-^{125}Te$ coupling constant of $SnTe_4^{4-}$ agree with those previously reported by Rudolph and co-workers,[20] but the ^{125}Te chemical shift quoted by them (−604.4 ppm) differs by almost 400 ppm from our value of −212.4 ppm. After the acquisition parameters were rechecked, one can only conclude that there is a referencing problem associated with the literature result and that the value for the ^{125}Te chemical shift reported in the present work is in fact the correct value. Like the trigonal-planar series of anions, $SnCh_3^{2-}$, the chemical shifts of the tetrahedral $SnCh_4^{4-}$ anions can be fitted by using a least-squares linear regression analysis, and it is also evident from Table IV that the chemical shifts are additive in nature as well as the spin–spin coupling constants. Again, trends among these parameters are dealt with in a later section.

At least two additional species were observed in the ^{125}Te spectrum of the extract of NaSnTe (−436 ppm, −619 ppm), but they have not been thoroughly investigated as of yet. Although no positive assignments can be made at this time, possible candidates include species like $Sn_2Te_7^{6-}$ and $Sn_2Te_6^{4-}$, analogous to the known $M_2Ch_7^{6-}$ and $M_2Ch_6^{4-}$ anions, where M = Ge or Sn and Ch = S or Se.[26]

At this point it is instructive to speculate on the differences observed on extraction of the alloys NaSnCh and $KSnCh_2$ (Ch = chalcogen), which gave the $SnCh_4^{4-}$ and $SnCh_3^{2-}$ species, respectively. In the former, Sn is nominally Sn(I), i.e. $Na^+Sn^+(Ch^{2-})$, while in the latter it is nominally Sn(III), i.e. $K^+Sn^{3+}(Ch^{2-})_2$. Disproportionation of the Sn(I) or Sn(III) in each case can be represented by

$$4Sn^+ \rightarrow Sn^{4+} + 3Sn$$

$$4Sn^{3+} \rightarrow 3Sn^{4+} + Sn$$

This leads to ratios of Ch^{2-}/Sn^{4+} of 4 and 2.67 (~3), in agreement with the products obtained and with the observation that there was *no* evidence for $SnCh_3^{2-}$ species in the extraction of the NaSnCh alloys or $SnCh_4^{4-}$ species on extraction of the $KSnCh_2$ alloys.

(IV) Zintl Anions Extracted from KTlTe, KTlSe, and $KTlTe_{0.5}Se_{0.5}$ Alloys. The only simple heteroatomic ring derived from a Zintl alloy is $Tl_2Te_2^{2-}$, the structure of which has been previously determined by X-ray crystallography.[12] In the hope of producing the mixed Tl_2TeSe^{2-} and $Tl_2Se_2^{2-}$ anions, alloys of composition $KTlTe_{0.5}Se_{0.5}$ and KTlSe were prepared in addition to KTlTe, from which $Tl_2Te_2^{2-}$ has been obtained. In each case, deep reddish-brown solutions resulted upon extraction with en in the presence of 2,2,2-crypt and were investigated by natural-abundance ^{203}Tl (29.50%) and ^{205}Tl (70.50%), ^{125}Te, and ^{77}Se NMR spectroscopy. As anticipated, evidence was obtained for the new anionic species, $Tl_2Se_2^{2-}$ and Tl_2TeSe^{2-}. However, it was immediately evident from the ^{205}Tl and ^{203}Tl spectra that there were more species present than expected for the simple, mixed series $Tl_2Ch_2^{2-}$ (Ch = Te and/or Se). In order to obtain structural information based upon $^{203,205}Tl-^{125}Te$ and $^{203,205}Tl-^{77}Se$ spin multiplicities, two quaternary alloy samples, one containing enriched tellurium (77.3% ^{125}Te)

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(23) Greenwood, N. N.; Gibb, T. C. "Mössbauer Spectroscopy"; Chapman and Hall Ltd.: London, 1971; p 371.

(24) Birchall, T.; Burns, R. C.; Devereux, L. A.; Schrobilgen, G. J. *Inorg. Chem.* **1985**, *24*, 890.

(25) Stevens, J. G. *Hyperfine Interact.* **1983**, *13*, 221.

(26) Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 113.

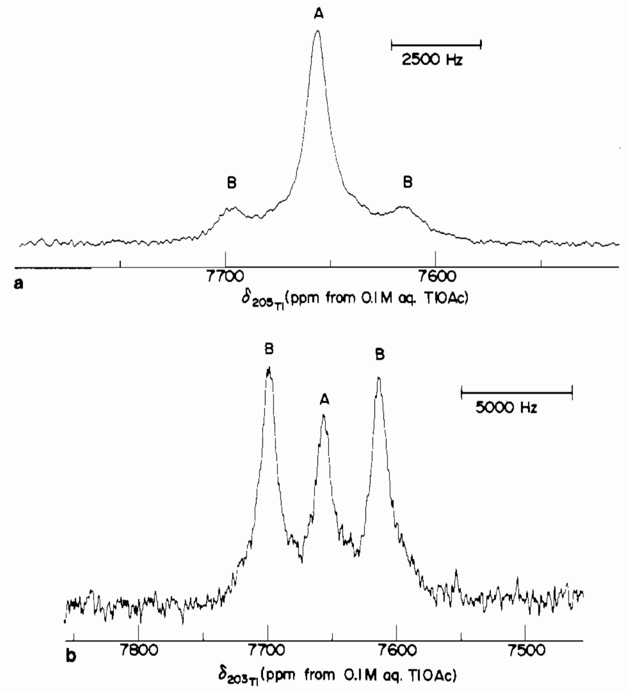

Figure 3. (a) ^{205}Tl and (b) ^{203}Tl NMR spectra of the $Tl_2Se_2^{2-}$ anion, obtained at 57.76 and 57.20 MHz, respectively. The spacing between lines B represents the ^{203}Tl–^{205}Tl spin–spin coupling.

and the other containing enriched selenium (94.4% ^{77}Se) were prepared, extracted, and investigated to accurately determine the nature of the species present in the above solutions. This led to the identification of the $TlCh_3^{3-}$ series of anions, analogous to the $SnCh_3^{2-}$ series of anions discussed above.

$Tl_2Ch_2^{2-}$ (Ch = Te and/or Se). A single resonance at 7656 ppm from 0.1 M thallous acetate was observed in the ^{203}Tl and ^{205}Tl spectra from the resultant en extract of the ternary KTlSe alloy. Evidence for a *two-bond* ^{203}Tl–^{205}Tl coupling was observed in the ^{205}Tl spectrum (Figure 3a), and the corresponding ^{203}Tl spectrum (Figure 3b) confirmed this ^{203}Tl–^{205}Tl coupling, with a magnitude of 5000 Hz. The ^{77}Se spectrum showed a triplet at 405.3 ppm from $(CH_3)_2Se$ with a ^{205}Tl–^{77}Se spin–spin coupling of 2260 Hz (^{203}Tl–^{77}Se coupling could not be resolved owing to a combination of three factors: broad natural line widths, lower natural abundance of ^{203}Tl, and the very similar magnetogyric ratios of ^{203}Tl and ^{205}Tl[17]). The multiplicity pattern and the relative intensities of the peaks led to the assignment of this species as $Tl_2Se_2^{2-}$, which is presumed to possess the same solid-state butterfly geometry as reported for the $Tl_2Te_2^{2-}$ anion.[12]

^{205}Tl and ^{203}Tl NMR studies of the solution extracted from the nonenriched quaternary alloy $KTlTe_{0.5}Se_{0.5}$ indicated the presence of only *two* species in the high-frequency region of the spectra (7654 ppm and 7877 ppm from 0.1 M thallous acetate) which were assigned to the $Tl_2Se_2^{2-}$ and Tl_2TeSe^{2-} anions, respectively. No evidence was obtained for the presence of $Tl_2Te_2^{2-}$, and this is discussed in greater detail below. The above signals occurred at essentially the same chemical shifts (<±1 ppm) for the extracts obtained from the ^{125}Te- and ^{77}Se-enriched alloys. As noted above, the solution extract from KTlSe gave a resonance at 7656 ppm in both the ^{205}Tl and ^{203}Tl NMR spectra for $Tl_2Se_2^{2-}$, which is in good agreement with the former value. Again, ^{203}Tl–^{205}Tl couplings appear as satellite doublets in both the ^{203}Tl and ^{205}Tl NMR spectra, the relative intensities of which are in accord with our assignment of this signal as $Tl_2Se_2^{2-}$. This assignment was also confirmed by the observation of the ^{77}Se spectrum, which exhibited the expected 1:2:1 triplet due to $^{203,205}Tl$–^{77}Se coupling; again the individual ^{203}Tl–^{77}Se and ^{205}Tl–^{77}Se couplings could not be resolved for the reasons given above. For the ^{77}Se-enriched sample, the coupling patterns for the ^{205}Tl and ^{203}Tl resonances of $Tl_2Se_2^{2-}$ were more complicated as a result of the increased ^{77}Se abundance. If the contribution involving spinless selenium (5.6%) is neglected, then each signal would consist of a doublet of triplets ($^{205}Tl^{203}Tl^{77}Se_2^{2-}$) overlapping with a triplet ($^{205}Tl_2{}^{77}Se_2^{2-}$). However, because of the broad natural line width and the two-bond ^{205}Tl–^{203}Tl coupling (5000 Hz) being about twice that of the ^{205}Tl–^{77}Se coupling (2260 Hz)—$^1J_{^{203}Tl-^{77}Se}$ is similar, as noted above—no individual couplings were observed and a "pseudoquintet" occurred for both ^{205}Tl and ^{203}Tl signals, the respective intensity patterns resulting from the different percentage abundances of the two thallium isotopes.

The ^{205}Tl and ^{203}Tl resonances of the Tl_2TeSe^{2-} anion obtained from the extract of the nonenriched quaternary alloy both consisted of broad ($\Delta\nu_{1/2} \sim 3000$ Hz) singlets. This suggests that the two-bond ^{205}Tl–^{203}Tl coupling for this anion is less than about 1000 Hz as *no* evidence of a coupling could be observed. Indeed, it could even be absent. The ^{205}Tl and ^{203}Tl spectra obtained from the ^{77}Se-enriched alloy extract both appear as doublets with a $^{203,205}Tl$–^{77}Se coupling of 2100 Hz. It is apparent, particularly from the ^{203}Tl spectrum (the less abundant thallium isotope) that the ^{205}Tl–^{203}Tl coupling must be considerably less than 1000 Hz, with a maximum value of about 300 Hz on the basis of a crude line-shape analysis of the ^{205}Tl and ^{203}Tl signals for Tl_2TeSe^{2-} and $Tl_2Se_2^{2-}$, those of the latter providing a measure of the natural line width. The ^{205}Tl and ^{203}Tl NMR spectra from the extract of the ^{125}Te-enriched alloy appear as broad, three-line signals. The outer lines arise from a $^{203,205}Tl$–^{125}Te coupling of 3620 Hz while the central line arises as a result of the contribution from an isotopic isomer containing spinless tellurium (and selenium). Although a small central peak would also have been expected in the enriched selenium case, the lower spinless abundance (5.6% vs. 22.7%), smaller coupling constant for selenium to thallium than for tellurium, and broad line width apparently combine to mask its presence. The appearance of the above spectra of Tl_2TeSe^{2-} containing enriched ^{125}Te or ^{77}Se are consistent with a two-bond ^{205}Tl–^{203}Tl coupling constant of between 300 and 0 Hz. The ^{77}Se NMR spectrum of the extract of the ^{77}Se-enriched alloy showed a broad 1:2:1 triplet (along with signals from the $TlCh_3^{3-}$ species, see below) at about 414 ppm, with an apparent coupling of about 2150 Hz. Both the chemical shift and coupling constant are similar to those for $Tl_2Se_2^{2-}$ (which is present in the sample), but no other signal appears that could be attributed to Tl_2TeSe^{2-}. We therefore conclude that the ^{77}Se resonances of $Tl_2Se_2^{2-}$ and Tl_2TeSe^{2-} are almost identical ($\delta_{^{77}Se}$ for $Tl_2Se_2^{2-}$ is 405 ppm, as noted above), and this is supported by the observation that the apparent $^{203,205}Tl$–^{77}Se coupling constant of the triplet, 2150 Hz, is about midway in value between those of $Tl_2Se_2^{2-}$ (2260 Hz) and Tl_2TeSe^{2-} (2100 Hz); note also that the ^{205}Tl and ^{203}Tl NMR spectra show that there are about *equal* concentrations of these anions present in the sample. The ^{125}Te NMR spectrum of the extract of the ^{125}Te-enriched alloy also exhibited a broad 1:2:1 triplet at −114.9 ppm with a $^{203,205}Tl$–^{125}Te coupling constant of 3610 Hz, in addition to signals from the $TlCh_3^{3-}$ species, which are discussed below. This coupling constant is in good agreement with that (3620 Hz) obtained from the ^{205}Tl and ^{203}Tl NMR spectra of the same extract, given above. We thus assign this triplet to the Tl_2TeSe^{2-} anion. Like $Tl_2Se_2^{2-}$, it is proposed that the Tl_2TeSe^{2-} anion has the same butterfly-type geometry established for $Tl_2Te_2^{2-}$ in the solid state.[12]

It is particularly interesting to note that no evidence was found for the existence of the $Tl_2Te_2^{2-}$ anion at room temperature in any of the solutions extracted from the enriched or natural-abundance quaternary $KTlTe_{0.5}Se_{0.5}$ alloys or in those resulting from the extraction of KTlTe by en or liquid NH_3 in the presence of 2,2,2-crypt, although it is from solutions of the latter type that the $Tl_2Te_2^{2-}$ anion was originally obtained as the solid compound $(2,2,2\text{-crypt-}K^+)_2Tl_2Te_2^{2-}\cdot en$. However, when a saturated liquid NH_3 solution obtained by extraction of KTlTe in the presence of 2,2,2-crypt is cooled to −40 °C, a ^{205}Tl resonance was observed at 8128 ppm with accompanying satellites ($J_{^{205}Tl-^{125}Te}$ = 8006 Hz), which we attribute to the $Tl_2Te_2^{2-}$ anion. The chemical shift is comparable to those of $Tl_2Se_2^{2-}$ and Tl_2TeSe^{2-} and is consistent with the formation of $Tl_2Te_2^{2-}$. Based on the line width, the two-bond ^{205}Tl–^{203}Tl coupling constant may be estimated to be

Table V. NMR Parameters for the $Tl_2Ch_2^{2-}$ Anions

anion	chem shift, δ			coupling const *J*, Hz		
	^{205}Tl	^{125}Te	^{77}Se	$^{205}Tl-^{203}Tl$	$^{205}Tl-^{125}Te$	$^{205}Tl-^{77}Se$
$Tl_2Te_2^{2-}$ [a]	8128			<200	8006	
Tl_2TeSe^{2-}	7877	−114.9	~414	<300	3615	2100
$Tl_2Se_2^{2-}$	7655		405.3	5000		2260

[a] Data on $Tl_2Te_2^{2-}$ were recorded at −40 °C in liquid NH_3. All other data were recorded in ethylenediamine at room temperature.

no greater than 200 Hz and, like the Tl_2TeSe^{2-} anion, could even be absent. A summary of all chemical shift and coupling constant data for $Tl_2Se_2^{2-}$, Tl_2TeSe^{2-}, and $Tl_2Te_2^{2-}$ is given in Table V. In passing, we note that there is a considerable decrease in the (two-bond) $^{205}Tl-^{203}Tl$ coupling constant on going from $Tl_2Se_2^{2-}$ to both Tl_2TeSe^{2-} and $Tl_2Te_2^{2-}$. This is presumably related to progressively weaker bonding in the series arising on replacement of selenium by tellurium. This results from the reduced involvement of the 5s orbitals (on Te) compared to the 4s orbitals (on Se) in the bonding, and the less efficient overlap of tellurium relative to selenium.[12,27]

The presence of signals from $Tl_2Te_2^{2-}$ at −40 °C but not at room temperature in liquid NH_3 (or en) suggests that this anion is involved in equilibrium 1. It should be admitted that no evidence

$$2TlCh_3^{3-} \rightleftarrows Tl_2Ch_2^{2-} + 2Ch_2^{2-} \qquad (1)$$

was found for the existence of Te_2^{2-} in the low-temperature study in liquid NH_3 and may be due to reduced solubility at these temperatures and the low natural abundance of ^{125}Te. However, in the case of selenium the equilibrium has shifted to the right at room temperature (only $Tl_2Se_2^{2-}$ was observed on extraction of KTlSe, as noted above), and in the ^{77}Se spectrum of the extract of $KTlTe_{0.5}Se_{0.5}$ (^{77}Se enriched), which contains both trigonal-planar and butterfly-type species, an intense signal occurred at about −436 ppm, which can be attributed to the Se^{2-} anion. The chemical shift of this anion is known to occur at −437 ppm, as observed for a solution obtained by extraction of K_2Se with en in the presence of 2,2,2-crypt.[28]

Now in liquid NH_3, equilibrium 2 below is known to exist with the value of K' ($=K_{eq}/K_{sp}$) equal to about 5 × 10⁶ M^{-3}.[29] A

$$2Na_2Se_2 \rightleftarrows Na_2Se + Na_2Se_3 \qquad (2)$$

similar equilibrium appears to exist in en,[28] so that the presence of Se^{2-} can be accounted for. However, Se_3^{2-} would also be expected to appear, but its presence was not detected. While Se^{2-} has been observed, the equilibria in this *quaternary* system are probably complicated by the likely presence of species such as $TeSe^{2-}$, Te_2Se^{2-}, and $TeSe_2^{2-}$, all presently unknown, which may account for the lack of Se_3^{2-}. We are currently working on these systems and shall report data on these and related homoatomic species in the near future.

$TlCh_3^{3-}$ (Ch = Te and/or Se). The ^{205}Tl and ^{203}Tl NMR spectra of the solutions obtained from the extraction of the ^{125}Te and ^{77}Se *enriched* quaternary alloys produced, in addition to the previously discussed $Tl_2Ch_2^{2-}$ anions, evidence for a group of four other signals, some with complex multiplicity patterns (Figure 4a). In fact, a new series of classical anions was observed, which, from the number of signals present and the relative intensities of the multiplet peaks in the ^{205}Tl NMR spectra, conclusively established a $TlCh_3^{n-}$ stoichiometry. We propose that this series of anions is isovalent with the $SnCh_3^{2-}$ series, and hence with CO_3^{2-}, making the anionic charge 3− with thallium having a formal +3 oxidation state. The multiplicity patterns observed in the ^{205}Tl NMR spectra for $TlTe_3^{3-}$, $TlTe_2Se^{3-}$, and $TlTeSe_2^{3-}$ (77.3% ^{125}Te enriched) and $TlSe_3^{3-}$, $TlTeSe_2^{3-}$, and $TlTe_2Se^{3-}$ (94.4% ^{77}Se enriched) were virtually identical with those calculated on the basis of ^{125}Te and ^{77}Se abundances and the statistical distributions of the selenium and tellurium ligand atoms for the assumed trigonal-planar structures. An example of the origin of such patterns is given diagramatically in Table VI for the most complex case, $TlTe_3^{3-}$, along with a listing of the relative intensities for the other isotopically enriched species. For $TlTe_3^{2-}$, important isotopic isomers are listed in Table VI, and a series of subspectra arising for each possible combination of spin-active and spinless contributions of ^{125}Te to the coupling with the central thallium atom is also given. It should be noted that natural-abundance ^{77}Se and/or ^{125}Te (as appropriate) satellite couplings were also observed in the ^{205}Tl NMR spectra of both the nonenriched and enriched ^{125}Te or ^{77}Se series of $TlCh_3^{3-}$ anions.

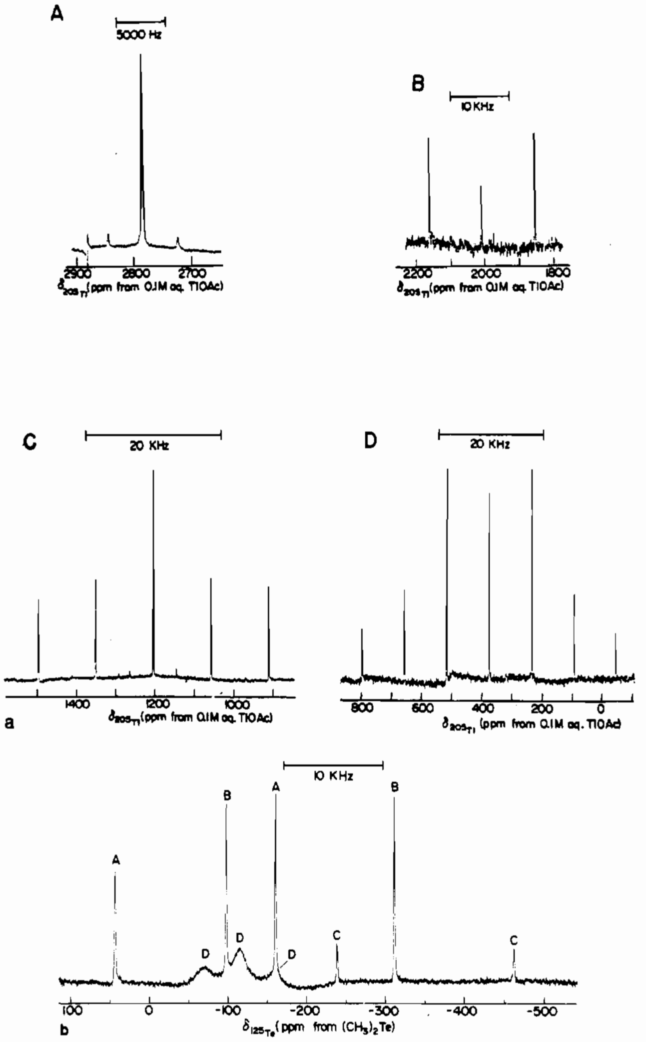

Figure 4. (a) ^{205}Tl NMR spectra, obtained at 57.76 MHz, for the $TlCh_3^{3-}$ series of anions containing ^{125}Te enriched to 77.3%. The multiplet patterns are assigned as follows: (A) $TlSe_3^{3-}$; (B) $TlSe_2Te^{3-}$; (C) $TlSeTe_2^{3-}$; (D) $TlTe_3^{3-}$. (b) ^{125}Te NMR spectrum for the $TlCh_3^{3-}$ series of anions, obtained at 78.97 MHz, containing ^{125}Te enriched to 77.3%. The doublet resonances are as follows: (A) $TlTe_3^{3-}$; (B) $TlTe_2Se^{3-}$; (C) $TlTeSe_2^{3-}$. The triplet resonance, D, is assigned to Tl_2TeSe^{2-}.

Tellurium-125 NMR spectroscopy confirmed the presence of the three tellurium-containing $TlCh_3^{3-}$ anions that gave rise to a series of doublets in the ^{125}Te spectra of the extracts of the quaternary alloys (Figure 4b). The doublet multiplicities arise from $^{203,205}Tl-^{125}Te$ spin–spin coupling. Again, the individual ^{203}Tl and ^{205}Tl components of the couplings could not be completely

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(27) Burns, R. C.; Gillespie, R. J.; Barnes, J. A.; McGlinchey, M. J. *Inorg. Chem.* **1982**, *21*, 799.

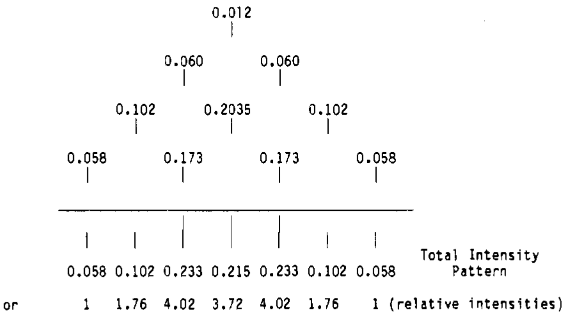
(28) Bjӧrgvinsson, M.; Schrobilgen, G. J., manuscript in preparation.

(29) Sharp, K. W.; Koehler, W. H. *Inorg. Chem.* **1977**, *16*, 2258.

Table VI. ^{205}Tl NMR Spectral of the $TlCh_3^{3-}$ Anions (Example: $TlTe_3^{3-}$ (77.3% ^{125}Te))

isotopic isomer[a]	multiplicity and binominal intens	statistical factor (s)	probability % (p)	abundance (sp)
TeTeTe	1	1	$(0.227)^3$	0.012
*TeTeTe	1:1	3	$(0.773)(0.227)^2$	0.119
*Te*TeTe	1:2:1	3	$(0.773)^2(0.227)$	0.407
*Te*Te*Te	1:3:3:1	1	$(0.773)^3$	0.462

Multiplicity Pattern for $TlTe_3^{3-}$



species		relative line intens: 77.3% ^{125}Te/94.4% ^{77}Se
$TlTe_3^{3-}$	calcd	1:1.76:4.02:3.72:4.02:1.76:1/1
	obsd	1:1.82:4.15:3.76:4.11:1.77:0.96/1
$TlTe_2Se^{3-}$	calcd	1:1.17:2.34:1.17:1/1:0.12:1
	obsd	1:1.19:2.49:1.23:1.12/1:0.15:0.97
$TlTeSe_2^{3-}$	calcd	1:0.59:1/1:0.24:2.01:0.24:1
	obsd	1:0.60:1.06/1:0.27:2.16:0.25:0.96
$TlSe_3^{3-}$	calcd	1/1:0.36:3.04:0.71:3.04:0.36:1
	obsd	1/1:0.35:3.11:0.78:3.18:0.38:0.99

[a] *Te denotes a spin-active tellurium atom (^{125}Te).

resolved for the reasons stated previously. Assignments were made by comparison with the ^{205}Tl–^{125}Te couplings observed in the ^{205}Tl NMR spectra of the ^{125}Te-enriched series. Likewise, a series of doublets was observed in the ^{77}Se NMR spectra of the extract of the ^{77}Se-enriched quaternary alloy, corresponding to ^{203,205}Tl–^{77}Se spin–spin coupling in the $TlCh_3^{3-}$ species (note that $TlSe_3^{3-}$ was not observed because of its low concentration as a result of the equilibrium discussed above in this particular extraction). Again, assignments were made by comparison with the ^{205}Tl–^{77}Se couplings observed in the corresponding ^{205}Tl NMR spectrum.

Relevant chemical shifts and coupling constants for this trigonal-planar series of anions are given in Table VII. The assignments of the $TlCh_3^{3-}$ anions are unambiguous on the basis of spin–spin coupling multiplicities, intensities, and coupling constant congruencies among the ^{205}Tl, ^{125}Te, and ^{77}Se NMR spectra. As for the other series of anions, the observed chemical shift data are subjected to a least-squares linear-regression analysis, which is discussed in the following section. The additive nature of the chemical shifts and coupling constants, as observed for the isovalent $SnCh_3^{2-}$ series of anions, is again apparent.

Comparison of NMR Parameters for the $HgCh_2^{2-}$, $CdCh_2^{2-}$, $SnCh_3^{2-}$, $TlCh_3^{3-}$, and $SnCh_4^{4-}$ Series of Anions. (I) Chemical Shift (δ). Nuclear shielding (screening) is usually discussed according to the terminology originated by Ramsey.[30] Thus one can define both a diamagnetic (σ^d) and a paramagnetic (σ^p) component of the shielding constant (σ) such that

$$\sigma = \sigma^d + \sigma^p$$

where σ^d involves free rotation of electrons about the nucleus while σ^p describes the restriction to this rotation caused by other electrons and other nuclei in the molecule.

The general trend found in this work with respect to the central nucleus, Hg, Cd, Tl, and Sn, is that an increase in the electron-withdrawing ability of the ligand atoms attached to the central metal leads to a decrease in the shielding of that nucleus. In principle this may be correlated with a change in the electron density on the central nucleus, thus giving a diamagnetic contribution to shielding. However, the observed changes, although showing the expected trend, are too large to be attributed to this inductive effect so that the paramagnetic term in Ramsey's shielding expression must be primarily responsible for the observed shifts of the central nuclides. The ^{125}Te and ^{77}Se (ligand) chemical shift trends for every series of anions indicate a progressive increase in shielding on replacing tellurium by selenium, which appears contrary to that expected on the basis of simple inductive effects caused by a varying number of tellurium or selenium atoms in a particular geometry. As σ^d and σ^p are generally of opposite sign,[31] this again reflects the dominance of the paramagnetic term in the chemical shift trends of these elements.

For all series of anions each component element was subjected to a linear least-squares regression analysis of the chemical shift data as a function of n, the number of tellurium substituent atoms, when $n \leq 3$. The equations governing the chemical shifts of those nuclei observed for each series of anions are given below:

$$HgSe_{2-n}Te_n^{2-}\text{:}\quad \delta_{^{199}Hg} = -685.5n - 807.2 \tag{3}$$

$$CdSe_{2-n}Te_n^{2-}\text{:}\quad \delta_{^{113}Cd} = -209.4n - 90.7 \tag{4}$$

$$\begin{aligned} SnSe_{3-n}Te_n^{2-}\text{:}\quad \delta_{^{119}Sn} &= -302.2n - 255.8 \\ \delta_{^{125}Te} &= 119.9n - 743.0 \\ \delta_{^{77}Se} &= 69.42n - 91.09 \end{aligned} \tag{5}$$

$$\begin{aligned} TlSe_{3-n}Te_n^{3-}\text{:}\quad \delta_{^{205}Tl} &= -802.8n + 2797.2 \\ \delta_{^{125}Te} &= 146.1n - 496.7 \\ \delta_{^{77}Se} &= 95.2n + 138.1^{32} \end{aligned} \tag{6}$$

$$\begin{aligned} SnSe_{4-n}Te_n^{4-}\text{:}\quad \delta_{^{119}Sn} &= -337.4n - 463.0 \\ \delta_{^{125}Te} &= 99.0n - 595.3 \\ \delta_{^{77}Se} &= 54.0n - 60.6 \end{aligned} \tag{7}$$

It was found that the calculated values for the chemical shifts were generally in excellent agreement with the observed shifts, and they support the assignments of all of these species on the basis of the criteria originally used for their identification. Linear behavior between the chemical shift and the number of tellurium atoms present in a species is illustrated by correlation factors, R,[33] of greater than 0.9994 for all of the above equations except for $CdCh_2^{2-}$, for which R is 0.9843. This agreement is certainly helped by the fact that most chemical shift values (and this also applies to coupling constants) were obtained from single solutions containing a majority of the range of species, which minimized the effects of temperature, viscosity, and ion-pair formation. Furthermore, little or no concentration dependence of chemical shift for any of these species was noted. While the first of the agreement factors given above is impressive, closer examination of the differences between observed and calculated chemical shifts show that, in each case, the chemical shift trend could be fitted better by a higher order equation, as is usually the case for "additivity" relationships. This is not evident in the case of the $CdCh_2^{2-}$ series of anions.

(II) Coupling Constants (*J* and *K*). As indicated previously, the spin–spin coupling constants for each of the trigonal-planar $SnCh_3^{2-}$ and $TlCh_3^{3-}$ and tetrahedral $SnCh_4^{4-}$ systems are directly additive and also have the same trends on interchanging ligand atoms, that is, an increase in coupling constant on substituting selenium for tellurium. In the case of $SnCh_3^{2-}$ and $TlCh_3^{3-}$, this suggests a similarity in bonding between these isostructural, isovalent series of anions. In the case of $HgCh_2^{2-}$ we note, however, the opposite trend to that described above. Unfortunately, the lack of data available for $CdCh_2^{2-}$ precludes a comparison for this isovalent system.

The interaction of nuclear spins with the surrounding electrons gives rise to spin–spin coupling. In high-resolution NMR spec-

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(30) Ramsey, N. F. *Phys. Rev.* **1953**, *91*, 303.

(31) Reference 17, Chapter 3, p 53.

(32) Equation based on two points only (i.e. $n = 2$).

(33) The correlation coefficient is defined as $R = (n\sum xy - \sum x\sum y)/[(n\sum x^2 - (\sum x)^2)(n\sum y^2 - (\sum y)^2)]^{1/2}$, where all symbols have their usual meanings.

Table VII. NMR Parameters for the $TlCh_3^{3-}$ Anions

	chem shift, δ						coupling const *J*, Hz	
	^{205}Tl		^{125}Te		^{77}Se			
anion	obsd	calcd	obsd	calcd	obsd	calcd	^{205}Tl–^{125}Te	^{205}Tl–^{77}Se
$TlTe_3^{3-}$	376	389	−58.45	−58.44			16214	
$TlTe_2Se^{3-}$	1204	1192	−204.50	−204.53	373.5	373.5	16986	6834
$TlTeSe_2^{3-}$	2008	1994	−350.64	−350.63	278.3	278.3	17746	7040
$TlSe_3^{3-}$	2784	2797			*a*	183.1[b]		7250

[a] Not observed; see text. [b] Calculated from eq 5.

troscopy spin–spin coupling is usually dominated by the Fermi contact mechanism. If this is true, one-bond coupling constants can be discussed on the basis of the formalism developed by Pople and Santry,[34] and given by eq 8 and 9, where all symbols have

$$^{1}J_{AB} = \frac{16\pi^2}{9h}\left(\frac{g\beta h}{2\pi}\right)^2 \gamma_A\gamma_B|\psi_{ns,A}(0)|^2|\psi_{ns,B}(0)|^2\pi_{AB} \tag{8}$$

$$\pi_{AB} = 4\sum_{i}^{\text{occ}}\sum_{j}^{\text{unocc}}\frac{C_{is,A}C_{is,B}C_{js,A}C_{js,B}}{E_j - E_i} \tag{9}$$

their usual meanings and/or values, $|\psi_{ns,A}(0)|^2$ and $|\psi_{ns,B}(0)|^2$ are the s-electron densities for the *ns* valence orbitals at the nuclei of atoms A and B, π_{AB} is the mutual polarizability of the *ns* orbitals on A and B, $C_{n,A}$ and $C_{n,B}$ are the LCAO coefficients of the s-type atomic orbitals centered on A and B, and E_i and E_j are the energies of the occupied and unoccupied molecular orbitals, respectively.

From eq 8 one can see that the observed (one-bond) coupling constant, $^1J_{AB}$, is dependent upon the nuclear properties of the coupled nuclei, specifically the magnetogyric ratios, as well as on electronic terms (i.e. s-electron density and π_{AB}). It is necessary to remove this nuclear dependence in order to look at structurally related effects on the spin–spin coupling. If it is assumed that the Fermi contact mechanism is dominant, then the reduced coupling constant, $^1K_{AB}$, as defined in the generalized equation (10), gives a better representation of the electronic environments

$$^{n}K_{AB} = \frac{4\pi^2}{h\gamma_A\gamma_B}{}^{n}J_{AB} \tag{10}$$

in molecules. The reduced coupling constants for the $HgCh_2^{2-}$, $CdTe_2^{2-}$, $SnCh_3^{2-}$, $TlCh_3^{3-}$, and $SnCh_4^{4-}$ anions are presented in Table VIII.

An empirical relationship between the square root of the reduced coupling constant, $^1K_{AB}$, and the atomic number, Z_A, of the changing nucleus in a series of isovalent and isostructural molecules involving no lone pairs on the central atom has been developed by Reeves:[35–38]

$$(^{1}K_{AB})^{1/2} = CZ_A + D \tag{11}$$

Thus, good correlations have been observed for a variety of non-metal methyl or hydride species, such as those of group 14.[48] Unfortunately, in our studies, we have data for a comparison of the two series of trigonal-planar anions only and for $CdTe_2^{2-}$ and $HgTe_2^{2-}$. Ideally, data on the lighter congeneric analogues would be welcome, but many of these involve quadrupolar nuclei in environments of less than cubic symmetry and, as such, are unlikely to be forthcoming in the near future. The tetrahedral series of anions would appear to be more encouraging, and we are currently working on the germanium and lead systems. Nevertheless, we do note that for the two series of trigonal-planar anions and for $CdTe_2^{2-}$ and $HgTe_2^{2-}$ the heavier congeneric analogues have considerably higher ^1K values, as expected for neutral or charged species that *do not* have lone pairs of electrons.[39] The fact that the heavier congeners have ^1K values so much larger than those of the lighter species is partially attributable to relativistic effects, which are dealt with in the following section. For the pair of trigonal-planar anions $SnTe_2Se^{2-}$–$TlTe_2Se^{3-}$ we note that $^1K_{Sn-Te}/^1K_{Sn-Se}$ and $^1K_{Tl-Te}/^1K_{Tl-Se}$ are almost equivalent (1.509 vs. 1.500), while for the pair $SnTeSe_2^{2-}$–$TlTeSe_2^{3-}$ the same ratios are again very close (1.523 vs. 1.521). This suggests that the bonding for each anion in a pair is very similar. Unfortunately, data for $CdTeSe^{2-}$ are not available for comparison with data from $HgTeSe^{2-}$.

Table VIII. Reduced Coupling Constants, ^1K, and Relativistically Corrected Reduced Coupling Constants, $^1K_{RC}$, for the Anions $SnCh_4^{4-}$, $SnCh_3^{2-}$, $TlCh_3^{3-}$, $CdTe_2^{2-}$, and $HgCh_2^{2-}$

	^1K[a]		$^1K_{RC}$[a]	
anion	M–Te	M–Se	M–Te	M–Se
$SnTe_4^{4-}$	2.016		0.982	
$SnTe_3Se^{4-}$	2.205	1.481	1.075	0.899
$SnTe_2Se_2^{4-}$	2.361	1.571	1.151	0.954
$SnTeSe_3^{4-}$	2.525	1.642	1.230	0.997
$SnSe_4^{4-}$		1.714		1.041
$SnTe_3^{2-}$	3.206		1.562	
$SnTe_2Se^{2-}$	3.388	2.245	1.651	1.363
$SnTeSe_2^{2-}$	3.560	2.338	1.735	1.420
$SnSe_3^{2-}$		2.403		1.459
$TlTe_3^{3-}$	7.403		1.682	
$TlTe_2Se^{3-}$	7.756	5.171	1.762	1.464
$TlTeSe_2^{3-}$	8.103	5.327	1.841	1.508
$TlSe_3^{3-}$		5.486		1.553
$CdTe_2^{2-}$	2.552		1.215	
$HgSe_2^{2-}$		5.531		1.525
$HgSeTe^{2-}$	9.563	5.560	2.116	1.533
$HgTe_2^{2-}$	9.608		2.126	

[a] *K* and K_{RC} are in SI units of N A^{-2} m^{-3} when *J* is measured in Hz. All *K* and K_{RC} values are to be multiplied by a factor of 10^{22}. M = Sn, Tl, Cd, or Hg.

Relativistic Corrections for Heavy Metals. Although factoring out the product of the magnetogyric ratios $\gamma_A\gamma_B$ of the directly bonded coupled nuclei in eq 8 does give comparable reduced coupling constants, $^1K_{AB}$, within series of anions possessing the same central atom, there is a considerable difference in ^1K values for homologous series possessing different central atoms, e.g. Sn and Tl in the MCh_3^{n-} anions (Table VIII). Such differences would be expected to be dominated by the s-electron density terms in the Fermi contact expression (eq 8). This has already been intimated in the previous section where it was noted that there was a dependence of $(^1K)^{1/2}$ values on *Z* and hence on s-electron density. However, this crude approach does not take into account relativistic effects, which are extremely important in spin–spin coupling of heavy-metal elements, i.e. particularly Hg and Tl in this case. These nuclei, with $Z = 80$ and 81, respectively, are very near the gold maximum for relativistic effects at $Z = 79$.[40,41]

It is possible to factor out relativistic effects by using multiplicative correction factors, such as those calculated by comparison of hyperfine radial integrals obtained from relativistic and nonrelativistic hydrogenic wave functions, as listed in the literature.[42]

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(34) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1.
(35) Reeves, L. W.; Wells, E. J. *Can. J. Chem.* **1963**, *41*, 2698.
(36) Reeves, L. W. *J. Chem. Phys.* **1964**, *40*, 2128, 2132, 2423.
(37) Inglefield, P. T.; Reeves, L. W. *J. Chem. Phys.* **1964**, *40*, 2424, 2425.
(38) Feeney, J.; Haque, R.; Reeves, L. W.; Yue, C. P. *Can. J. Chem.* **1968**, *46*, 1389.
(39) Pyykkö, P.; Wiesenfeld, L. *Mol. Phys.* **1981**, *43*, 557.
(40) Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276.
(41) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271.
(42) Pyykkö, P.; Pajanne, E.; Inokuti, M. *Int. J. Quantum Chem.* **1973**, *7*, 785.

More recently, Pyykkö and Wiesenfeld[39] have tabulated values of the relativistic (and nonrelativistic) $ns_{1/2}$ (hyperfine) integral v_{-1} (among others) for the main-group elements calculated by using a sum-over-states, relativistically parameterized, extended-Hückel method with all parameters coming from relativistic or nonrelativistic Hartree–Fock calculations, together with Pyykkö's relativistic theory of spin–spin coupling.[43] A comparison of the anticipated relativistic effect for a particular element may be made by considering the ratio $(|\psi_{ns}(0)|^2)_{rel}/(|\psi_{ns}(0)|^2)_{nonrel}$, where

$$|\psi_{ns}(0)|^2 = -(c/2\pi)v_{-1} \qquad (12)$$

in the nonrelativistic limit.[39,43] The ratios are Se = 1.155, Cd $\simeq$ 1.45, Sn = 1.426, Te = 1.439, Hg $\simeq$ 3.13, and Tl = 3.059 (data for Cd and Hg are from ref 44 and 45). Thus, for the anions studied in this work, in the most extreme case of $^1K_{Hg-Te}$, a factor of 4.50 for a relativistic correction would apply while in the least extreme case of $^1K_{Sn-Se}$ coupling only a factor of 1.65 would result. This illustrates the care needed in comparing coupling constants involving heavy elements with those involving lighter elements.

A list of "relativistically corrected" reduced coupling constants, $^1K_{RC}$, is given in Table VIII. We now note that for the trigonal-planar $SnCh_3^{2-}$ and $TlCh_3^{2-}$ series of anions and for $CdTe_2^{2-}$ and $HgTe_2^{2-}$ the $^1K_{RC}$ values are much closer although the heavier congeners are, in each case, still greater as would be expected because there still exists a dependence on s-electron density.

As noted earlier, in cases where orbital and dipolar contributions to the spin–spin coupling are deemed unimportant, the spin–spin coupling is dominated by the Fermi contact term and depends upon the amount of s-character in the bond joining the nuclei (eq 8). Empirical relationships between the coupling constants ^1J and percentage s-character of the atomic orbitals forming the σ bond between the coupled nuclei have been formulated for constant pairs of nuclei in different bonding situations, as given in eq 13, where

$$C|^1J(Y,Z)| = \%s_Y \ \%s_Z \qquad (13)$$

C is an experimentally determined proportionality constant.[46] Thus, for $SnCh_4^{4-}$ and $SnCh_3^{2-}$, where the %s character in the (ligand) selenium or tellurium bonding orbitals is essentially constant, there is an increase in ^1J on moving from $SnCh_4^{4-}$ to $SnCh_3^{2-}$, corresponding to an increase in %s character in the bonding contribution of the central metal (i.e. $sp^3 \rightarrow sp^2$ hybridization). More generally, we can write the equation

$$C'|^1K(M,Ch)| = \%s_M \ \%s_{Ch} \qquad (14)$$

However, comparisons between species with different central elements are clouded by the dependence of ^1K (and $^1K_{RC}$) on $|\psi_{ns}(0)|^2$, even assuming differences in π_{AB} are not overriding. Comparisons are therefore best made for elements where Z values are close. For $HgCh_2^{2-}$ and $TlCh_3^{3-}$, where $|\psi_{ns}(0)|^2$ differs by about 8% (10% using nonrelativistic values), we note that the ^1K values for $HgCh_2^{2-}$ are greater than those of $TlCh_3^{3-}$, reflecting the greater %s bonding character of mercury (sp) than thallium (sp^2). For $CdTe_2^{2-}$, $SnTe_3^{2-}$, and $SnTe_4^{4-}$, the $|\psi_{ns}(0)|^2$ values increase by a factor of two (relativistic or nonrelativistic values) from cadmium to tin ($Z = 48 \rightarrow 50$) so that comparisons are no longer valid. Indeed, ^1K for $CdTe_2^{2-}$ (sp), while still greater than ^1K for $SnTe_4^{4-}$ (sp^3), is actually less than ^1K for $SnTe_3^{2-}$ (sp^2), reflecting the dominance of the $|\psi_{ns}(0)|^2$ term.

Conclusions

The extraction of Zintl phases in the present study has led to the realization that "classically bonded" Zintl anions are more prevalent than hitherto realized. Evidence for at least 16 new anions was found during this work, whereas only $SnTe_4^{4-}$, $SnSe_4^{4-}$, $Tl_2Te_2^{2-}$, and $HgTe_2^{2-}$ were previously known. The $Tl_2Te_2^{2-}$ anion, as well as the two new butterfly-shaped species, Tl_2TeSe^{2-} and $Tl_2Se_2^{2-}$, may be regarded as being classically bonded or, alternatively, as being derivable from a trigonal bipyramid by the loss of one (equatorial) vertex, giving a nido-type cluster in each case ($2n + 4$ skeletal electrons).

It is interesting to note that while all of the anions studied in this work have been prepared in nonaqueous solution, many are known to be stable in aqueous solution in the absence of atmospheric oxygen, e.g. $SnTe_4^{4-}$ and $SnSe_4^{4-}$. Indeed, many were first prepared under such conditions.[26] Also, many other species, such as the bridged species $Sn_2Ch_6^{4-}$ (the dimer of $SnCh_3^{2-}$) and $Sn_2Ch_7^{6-}$ (Ch = S, Se, or Te) were not formed under the conditions used in our studies. Currently, we are investigating the formation of these species, as well as germanium and lead analogues, and hope to report data on them in the near future.

The unambiguous characterization of complex mixtures of the anions studied in this work in ethylenediamine or liquid NH_3 solution was achieved by using a fully multinuclear approach to NMR spectroscopy and serves to illustrate the merits of such an approach. A wealth of novel NMR data, i.e., spin–spin couplings and chemical shifts, has been obtained.

The simplicity of these anions makes them ideally suited to theoretical and semiempirical considerations. Thus, it has been demonstrated that, within each of the series of anions $HgCh_2^{2-}$, $SnCh_3^{2-}$, $TlCh_3^{3-}$, and $SnCh_4^{4-}$, the chemical shifts of the individual nuclides are rigorously additive. Consideration of the coupling constant, $^1J_{AB}$, in each case has been made and the dependence on the magnetogyric ratios of the directly bonded coupled nuclei removed to give $^1K_{AB}$, the reduced coupling constant. This reduced coupling constant has been further factored to remove relativistic effects, giving $(^1K_{AB})_{RC}$, a "relativistically corrected" reduced coupling constant. Comparison of $^1K_{AB}$ and $(^1K_{AB})_{RC}$ values has further emphasized the importance of considering relativistic effects in any discussion of spin–spin couplings involving heavy nuclides and hence the care required in their interpretation and comparison.

Experimental Section

Apparatus and Materials. The majority of compounds used and prepared during this work were air and moisture sensitive. Consequently, all manipulations were carried out under anhydrous conditions on glass vacuum lines or in a nitrogen-atmosphere drybox (Vacuum Atmospheres Model DLX). Drybox moisture and oxygen levels were routinely less than 0.01 ppm.

Potassium (MCB) and sodium (BDH, 99.8%) were used as received, and freshly cut samples were handled only in the drybox. Thallium (BDH, 99.999%), tin (Baker Analyzed, 99.9%), cadmium (Spex Industries Inc., 99.9999%), mercury (Johnson Matthey, triply distilled), tellurium (Alfa Inorganics, 99.5%), and selenium (Alfa Inorganics, 99.9%) were used directly as obtained. Enriched ^{125}Te metal (77.3%) was obtained from TeO_2 (Techsnabexport, Moscow) by dissolution in concentrated HNO_3 followed by reduction of the resulting aqueous solution of Te(VI) according to the method outlined by Vogel.[47] Enriched ^{77}Se metal (94.4%) was obtained from Union Carbide, Oak Ridge, TN and used directly as received. The 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was obtained from Merck and also used as received. Ethylenediamine (Fisher Scientific Co.) was dried over CaH_2 (MCB) for several weeks and then vacuum distilled onto and stored over fresh CaH_2 for at least 1 week prior to use. Liquid NH_3 (Canadian Liquid Air) was dried with sodium at −33 °C and stored over sodium at −78 °C for at least 1 week before use.

Preparation of Alloys. All alloys were prepared by fusion of the appropriate components in the required mole ratios in either Pyrex or quartz vessels. This was generally accomplished in two stages. First, the alkali metal and Hg, Cd, Sn, or Tl were first fused to give the respective binary alloy. The required amounts of tellurium and/or selenium were then premixed and added to the binary alloy in the drybox, and the

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[43] Pyykkö, P. *Chem. Phys.* **1977**, *22*, 289.

[44] Jokissaari, P.; Räisänen, K.; Lajunen, L.; Passoja, A.; Pyykkö, P. *J. Magn. Reson.* **1978**, *31*, 121.

[45] Jokissaari, P.; Räisänen, K.; Kuonanoja, J.; Pyykkö, P.; Lajunen, L. *Mol. Phys.* **1980**, *39*, 715.

[46] Reference 17, Chapter 3, p 73.

[47] Vogel, A. I. "Quantitative Inorganic Analysis", 3rd ed.; Longmans: London, 1961; p 508.

[48] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

mixture was fused once more. After complete reaction, the ternary/quaternary alloy was allowed to cool, transferred to the drybox, powdered, and stored in a glass vial until required. In every case a homogeneous alloy was obtained accept for the Na–Sn–Te–Se alloys, which invariably produced a plug of tin metal (even though the binary alkali-metal–tin alloy had been previously formed), which amounted to between 20 and 30% of the initial mass of tin added. This plug was removed, so that it should be appreciated that the alloys NaSnTe, NaSnSe, $NaSnTe_{0.33}Se_{0.67}$; and $NaSnTe_{0.67}Se_{0.33}$ have somewhat less than the indicated amount of tin.

Extraction of Alloy Phases. Typically, a stoichiometric amount of 2,2,2-crypt corresponding to the alkali metal was added and thoroughly mixed with 150–200 mg of powdered alloy in a glass ampule. After evacuation, approximately 10 cm^3 of en or liquid NH_3 was vacuum distilled onto the mixture and the tube and contents were allowed to warm to room temperature. Complete extraction of the alloys generally took place within 3–7 days. Samples were periodically agitated during the extraction period.

Preparation of NMR Samples. Following extraction of the alloy phases, the undissolved materials were allowed to settle before the clear solutions were decanted into precision 10-mm (o.d.) (thick-walled tubes for liquid NH_3) NMR tubes attached to the reaction vessels. The solutions were concentrated for NMR analysis through evaporation by cooling the portion of the reaction vessel containing the residual alloy in an ice–water bath. Slow static distillation of en or liquid NH_3 from the NMR tube back onto the alloy was allowed to continue until a solvent column height suitable for NMR analysis was obtained or until a saturated solution had formed. After being cooled to 0 °C in the case of en or −78 °C for liquid NH_3, the NMR tube and contents were isolated by flame sealing.

In general, concentrations of the anions ranged from about 0.25 *m* down to 0.05 *m* for extractions of the ternary alloys. However, in the case of the cadmium species, concentrations are estimated to be only 0.02 *m* or lower. For the extractions from the quaternary alloys the concentrations necessarily vary over a wider range because of the distribution of species depending on the alloy composition, with the concentrations of the principal species in the range 0.20–0.10 *m*. The approximate distributions of the anions extracted from the quaternary alloys were estimated from relative signal intensities and are as follows.

$KHgTe_{0.5}Se_{0.5}$: 48% $HgTe_2^{2-}$, 28% $HgTeSe^{2-}$, 24% $HgSe_2^{2-}$. $KCdTe_{0.5}Se_{0.5}$: 73% $CdTe_2^{2-}$, 22% $CdTeSe^{2-}$, 5% $CdSe_2^{2-}$. $KSnTe_{1.5}Se_{0.5}$: 45% $SnTe_3^{2-}$, 45% $SnTe_2Se^{2-}$, 10% $SnTeSe_2^{2-}$, <1% $SnSe_3^{2-}$. $KSnTe_{0.5}Se_{1.5}$: <1% $SnTe_3^{2-}$, 10% $SnTe_2Se^{2-}$, 35% $SnTeSe_2^{2-}$, 55% $SnSe_3^{2-}$. $NaSnTe_{0.67}Se_{0.33}$: 19% $SnTe_4^{4-}$, 38% $SnTe_3Se^{4-}$, 31% $SnTe_2Se_2^{4-}$, 12% $SnTeSe_3^{4-}$, <1% $SnSe_4^{4-}$. $NaSnTe_{0.33}Se_{0.67}$: <1% $SnTe_4^{4-}$, 3% $SnTe_3Se^{4-}$, 19% $SnTe_2Se_2^{4-}$, 43% $SnTeSe_3^{4-}$, 35% $SnSe_4^{4-}$. $KTlTe_{0.5}Se_{0.5}$ (average): 12% $TlTe_3^{3-}$, 15% $TlTe_2Se^{3-}$, 4% $TlTeSe_2^{3-}$, ≤2% $TlSe_3^{3-}$, <1% $Tl_2Te_2^{2-}$, 32% Tl_2TeSe^{2-}, 35% $Tl_2Se_2^{2-}$.

NMR studies showed that, in addition to signals for the species listed above, a number of other signals were observed in the spectral ranges investigated for the extracts of some ternary and quaternary alloys. These were always of low concentration (< ca. 1% of total) as shown, for example, in Figure 2c,d. Many of these are currently under investigation.

Multinuclear Magnetic Resonance Spectroscopy. All NMR spectra were recorded on pulse spectrometers equipped with cryomagnets and consequently were run unlocked (field drift <0.1 Hz/h) at 24 °C. With the exception of those for ^{203}Tl and ^{205}Tl, NMR spectra were recorded at an external applied field strength of 5.8719 T on a Bruker WM-250 spectrometer using a 10-mm probe that was broad-banded over the frequency range 23–103 MHz. The observing frequencies were ^{77}Se (47.704 MHz), ^{113}Cd (55.457 MHz), ^{119}Sn (93.273 MHz), ^{125}Te (78.917 MHz), and ^{199}Hg (44.800 MHz). Free-induction decays were typically accumulated in a 32K memory. Spectral width settings of 50 or 100 kHz were employed, yielding data point resolutions of 3.0 and 6.1 Hz and acquisition times of 0.328 and 0.164 s, respectively. No relaxation delay was applied. The number of free-induction decays accumulated varied with concentration and sensitivity of the nucleus under consideration, with 4000–300 000 scans being typical for these dilute samples. Pulse widths corresponding to bulk magnetization tip angles, θ, of approximately 90° were 20 (^{77}Se), 15 (^{113}Cd), 10 (^{119}Sn), 20 (^{125}Te), and 25 μs (^{199}Hg) on the WM-250 spectrometer. Line broadening parameters used in exponential multiplication of the free-induction decays were 10–20 Hz.

Because ^{203}Tl and ^{205}Tl resonate outside the dynamic range of the Bruker WM-250 high-range probe (142.87 and 144.27 MHz, respectively, at 5.8719 T), spectra of these nuclei were obtained on a Bruker WP-100 SY/SC (Bruker Canada Applications Laboratory, Milton, Ontario) at an applied field of 2.3488 T. This was achieved by using a 10-mm broad-band probe from a Bruker WM-360, which tuned over the range 16–146 MHz and which physically fit the WP-100 cryomagnet. The WP-100 console was broad banded, so it was possible to obtain spectra of both thallium isotopes (θ = 90° with pulse widths of 10 μs) at 57.199 (^{203}Tl) and 57.760 MHz (^{205}Tl).

The respective nuclei were referenced to neat samples of $(CH_3)_2Hg$, $(CH_3)_2Cd$, $(CH_3)_2Se$, $(CH_3)_2Te$, and $(CH_3)_4Sn$ and to a 0.1 M aqueous TlOAc solution at 24 °C. The chemical shift convention used is that a positive sign signifies a chemical shift to high frequency of the reference compound and vice versa.

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Registry No. $HgTe_2^{2-}$, 79172-65-9; $HgTeSe^{2-}$, 96913-60-9; $HgSe_2^{2-}$, 96913-61-0; $CdTe_2^{2-}$, 96913-62-1; $CdTeSe^{2-}$, 96913-63-2; $CdSe_2^{2-}$, 96913-64-3; $SnTe_3^{2-}$, 94781-10-9; $SnTe_2Se^{2-}$, 94800-03-0; $SnTeSe_2^{2-}$, 94800-05-2; $SnSe_3^{2-}$, 94800-01-8; $SnTe_4^{4-}$, 76858-69-0; $SnTe_3Se^{4-}$, 96913-65-4; $SnTe_2Se_2^{4-}$, 96913-66-5; $SnTeSe_3^{4-}$, 96913-67-6; $SnSe_4^{4-}$, 94781-07-4; $Tl_2Te_2^{2-}$, 77321-80-3; Tl_2TeSe^{2-}, 96913-68-7; $Tl_2Se_2^{2-}$, 96913-69-8; $TlTe_3^{3-}$, 96913-70-1; $TlTe_2Se^{3-}$, 96913-71-2; $TlTeSe_2^{3-}$, 96913-72-3; $TlSe_3^{3-}$, 96913-73-4; ^{203}Tl, 14280-48-9; ^{205}Tl, 14280-49-0; ^{199}Hg, 14191-87-8; ^{125}Te, 14390-73-9; ^{119}Sn, 14314-35-3; ^{113}Cd, 14336-66-4; ^{77}Se, 14681-72-2.

Supplementary Material Available: A table of observed and theoretical satellite intensities (including errors) for natural-abundance heteronuclear coupling patterns (2 pages). Ordering information is given on any current masthead page.