Inorg. Chem. 1991, 30, 2540–2547

up relative to d_{yz} and d_{xz}, become degenerate and are equally occupied in the intermediate-temperature regime. On further thermal excitation, where the splitting between the lowest occupied manifold and the unoccupied $d_{x^2-y^2}$ level becomes comparable to kT, the $S = 2$ state becomes the lowest energy configuration for the metal center. If this model is valid, it implies that the change in the electron density at the iron atom in going from a d_{yz}^2, d_{xz}^2, d_{xy}^2 configuration is a d_{yz}^2, d_{xz}^2, d_{xy}, d_z configuration is sufficiently small that neither the infrared (i.e., the frequency of the CN stretching mode) nor the ^{57}Fe Mossbauer hyperfine parameters differ sufficiently for the two states to be resolvable by these spectroscopic techniques. Because of the apparent degeneracy between these two states ($S = 0$ and $S = 1$) and the large magnetic field dependence of μ_{eff}, it is suggested that, at $T < 300$ K, the ground state is a spin-mixed state that has a varying contribution from the LS and IS states as a function of temperature and magnetic field. In the high-temperature regime, promotion of an electron from the d_{xz}, d_{yz} level to the unoccupied $d_{x^2-y^2}$ level is reflected in a major shift of the IR-active CN stretching mode of the pseudohalide ligand, permitting spectroscopic distinction between the LS/IS states, on the one hand, and the HS state, on the other. Clearly, additional experimental data (e.g., a temperature-dependent spin resonance study in an appropriate diluent matrix,[16] magnetic circular dichroism, corresponding crystallographic data, etc.) will be required to test further the proposed interpretation of the presently available characterizations.

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(16) Exploratory experiments with neat solid samples were unsuccessful due to the short spin–lattice relaxation times under these conditions. An appropriate spin-inert solvent has not yet been found for such experiments. We are indebted to Prof. H. J. Schugar for fruitful discussion of these problems.

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Homo- and Heteropolychalcogenide Anions Ch^{2-}, HCh^-, Ch_2^{2-}, Ch_3^{2-}, and Ch_4^{2-} (Ch = Se and/or Te): Solution ^{1}H, ^{77}Se, ^{123}Te, and ^{125}Te NMR Study

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The homo- and heteropolychalcogenide anions, Ch_n^{2-} ($n = 1, 2, 3, 4$; Ch = Se and/or Te) and the hydrochalcogenide anions, HCh^-, have been prepared and characterized in solution by ^{1}H, ^{77}Se, ^{123}Te and ^{125}Te nuclear magnetic resonance spectroscopy. The polychalcogenide anions were prepared in ethylenediamine and/or liquid ammonia by the reaction of the alkali-metal monochalcogenide with the appropriate chalcogen in the presence or absence of 2,2,2-crypt or by the direct reaction of the alkali metal with the chalcogen in liquid ammonia. With the exception of the pyramidal shaped $TeSe_3^{2-}$ anion, the polychalcogenide anions have open-chain structures. In addition, the more electronegative selenium atoms are found to be in terminal positions in the heteropolychalcogenide anions $Te_nSe_{3-n}^{2-}$ and $Te_mSe_{4-m}^{2-}$ ($n = 1, 2$; $m = 2, 3$), which can be rationalized by using the topological charge stabilization rule. The chemical shifts and unusually large spin–spin coupling constants are reported for the polychalcogenide anions and their trends discussed.

Introduction

Numerous homopolychalcogenide anions of selenium and tellurium have been structurally characterized in the solid state, e.g., Se_2^{2-},[1] Se_3^{2-},[2] Se_4^{2-},[3-5] Se_5^{2-},[5-7] Se_6^{2-},[8,9] Te_2^{2-},[10] Te_3^{2-},[11,12] Te_4^{2-},[13,14] and Te_5^{2-}.[8] Many of the crystalline homopolychalcogenide anion salts were isolated from solutions of main-group or transition-metal chalcogenide anions, suggesting complex equilibria and the existence of mixtures of anions in solution.[5,8,13] Furthermore, our previous solution NMR studies of the mixed Se/Te main-group metal chalcogenide anions suggested that homo- and heteropolychalcogenide anions played an important role in main-group metal chalcogenide anion formation.[15,16] In general, the chemistry of heteropolychalcogenide anions has been less well studied,[17] and only the structures of the K_2TeSe_4,[18] Na_2TeSe_3,[19] and K_2TeSe_3[19] phases have been reported in the literature.

The present paper reports a systematic investigation of the selenium, tellurium, and selenium/tellurium polyanions in ethylenediamine (en) and/or liquid ammonia solvents using multinuclear magnetic resonance spectroscopy. Multi-NMR spectroscopy is particularly well suited for structurally characterizing and studying the chemistry of homo- and heteropolychalcogenide anions of selenium and tellurium in solution as both elements have naturally occurring NMR-active spin-$^1/_2$ isotopes, namely, ^{77}Se (7.58%), ^{125}Te (6.99%), and ^{123}Te (0.89%).[20]

Results and Discussion

Solution NMR Studies of Polychalcogenide Anions, Ch_n^{2-}. Preparation of Ch_n^{2-} Anion Solutions. The general approach to the syntheses of polychalcogenide anions involved the reaction of the potassium monochalcogenide with an appropriate amount of

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Table I. ^{77}Se and ^{125}Te NMR Parameters for the Ch^{2-}, HCh^-, Ch_2^{2-}, Ch_3^{2-}, and Ch_4^{2-} Anions (Ch = Se and/or Te)[a]

	chem shifts,[b] ppm			
anion	$\delta(^{77}Se)$	$\delta(^{125}Te)$	^1J(A–B), Hz	temp, °C
Se^{2-}	−435			24
Te^{2-}		−1430		24
HSe^{-}[c]	−495		24 (^1H–^{77}Se)	24
HTe^{-}[d]		−1095	140 (^1H–^{125}Te)	24
Te_2^{2-}[e]		−1080	3645 ± 20 (^{123}Te–^{125}Te)	−54
Te_2^{2-}[f]		−1074		24
Se_3^{2-}	304 (Se_t) 278 (Se_b)		262 ± 6 ($^{77}Se_t$–$^{77}Se_b$)	24
Te_3^{2-}		−286 (Te_1) −367 (Te_b)	2175 ± 6 ($^{125}Te_t$–$^{125}Te_b$)	50
Te_3^{2-}		−298 (Te_t) −372 (Te_b)		24
$TeSe_2^{2-}$	−92	536	670 ± 6 (^{77}Se–^{125}Te)	53
Te_2Se^{2-}[g]	−134	−266 (Te_t) 106 (Te_b)	621 ± 6 (^{77}Se–$^{125}Te_b$) 2235 ± 20 ($^{125}Te_t$–$^{125}Te_b$)	53
Se_4^{2-}[h]	321 (Se_t) 608 (Se_b)		130 ± 12 ($^{77}Se_t$–$^{77}Se_b$)	−75
Te_4^{2-}[i]		7 ± 4		5
Te_4^{2-}[i]		19 ± 8		24
$TeSe_3^{2-}$	468	1087	214 ± 12 (^{77}Se–^{125}Te)	24
$TeSe_3^{2-}$[j]		1077	189 ± 12 (^{77}Se–^{125}Te)	−78
$Te_2Se_2^{2-}$[k]	−59	656	650 ± 30 (^{77}Se–^{125}Te)	5
$Te_2Se_2^{2-}$	−55	666		24
Te_3Se^{2-}[l,m]	−64	632 ($Te_b'\underline{Te_b}Se_t$) 175 ($Te_b\underline{Te_b'}Te_t$) −180 ($Te_bTe_b'\underline{Te_t}$)	430 ± 30 ($^{77}Se_t$–$^{125}Te_b$)	5

[a] All the NMR parameters reported for the anions were measured in ethylenediamine in which the potassium cations have been complexed by 2,2,2-crypt unless otherwise indicated. [b] Linear least-squares regression analysis for the $Te_bSe_nTe_{2-n}^{2-}$ series gave $\delta(Te_b) = -360 + 452n$, where the correlation coefficient is $R = 1.000$. [c] Na^+HSe^- dissolved in C_2H_5OH, $\delta(^1H) = -5.4$ ppm. [d] $\delta(^1H) = -12.9$ ppm. [e] Prepared by the reaction 2K + 2Te in liquid ammonia. [f] Prepared by the reaction K_2Te + Te in the absence of 2,2,2-crypt. [g] $^2J(^{77}Se_t$–$^{125}Te_t) = 419 \pm 6$ Hz. [h] Prepared by the reaction Na + 2Se in liquid ammonia. [i] Line widths were usually $\Delta\upsilon_{1/2} = 2000$–$4000$ Hz; see text. [j] Prepared by the reaction K_2Te + 3Se in liquid ammonia. [k] $^2J(^{77}Se_t$–$^{125}Te_b) = 350 \pm 40$ Hz, tentative estimate. [l] The assigned tellurium chemical shift value is for the underlined tellurium environment. [m] Line widths, $\Delta\upsilon_{1/2}$, were 1000 and 200 Hz for Te_t and Te_b, respectively.

chalcogen metal powder in en or liquid ammonia according to eq 1, where Ch = Se/Te. Alternatively, the polychalcogenide anions

$$K_2Ch' + nCh \xrightarrow[\text{en or NH}_3]{} 2K^+ + Ch'Ch_n^{2-} \qquad (1)$$

were prepared by the reaction of the alkali and chalcogen metals in liquid ammonia according to eq 2, where M = Na or K. In

$$2M + nCh \xrightarrow[\text{NH}_3]{} 2M^+ + Ch_n^{2-} \qquad (2)$$

a number of cases, several polychalcogenide anions could be prepared by extracting $KTe_{2.00}$ or $KPb_{0.50}Ch_x$ alloys. The species could often be qualitatively identified by their characteristic colors, i.e., HTe^- (light yellow), Te_2^{2-} (blue), Te_3^{2-} and Te_4^{2-} (deep red), and Se_3^{2-} (green).

The anions in the resulting solutions were identified by direct NMR observation of the spin-$^1/_2$ nuclides ^{77}Se, ^{123}Te, and ^{125}Te at their natural-abundance levels. Comparisons of the magnitudes of satellite doublet spacings observed for each environment were used to establish which environments were spin–spin coupled to one another. Furthermore, the total number of equivalent Se and/or Te atoms bonded to each environment could be deduced from the measured satellite/central peak intensity ratios.

During the course of this work it became clear that peaks in the ^{77}Se and ^{125}Te NMR spectra recorded in en solutions were broadened considerably unless stoichiometric amounts of the complexing ligand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-crypt) were added to the solutions to complex the free alkali-metal cations. Owing to the relatively low solubilities of many polychalcogenide anion salts of the 2,2,2-crypt-K^+ cation, it was necessary to record NMR spectra at elevated temperatures and/or high magnetic field strengths. For some of the anions, the exchange could only be slowed sufficiently in uncomplexed solutions by recording their NMR spectra at low temperatures in liquid ammonia. The results of these solution NMR studies are summarized in Table I.

The preparation of the tri- and tetraheterochalcogenide anions often resulted in mixtures of species. Variation of the relative stoichiometries of Se and Te used in each preparation resulted in relative peak intensity changes that further aided in the assignment of the environments to their respective anions. The assignment of the NMR spectra of the anions as well as discussions of their structures and stabilities are given in detail in the following sections.

Monochalcogenide Anions, Ch^{2-}, and Hydrochalcogenide Anions, HCh^-. Strong singlets, assigned to the solvated Ch^{2-} anions, were observed in the ^{77}Se and ^{125}Te solution NMR spectra when the K_2Ch (Ch = Se or Te) phases were treated with 2 equiv of 2,2,2-crypt in en. In addition, a weak doublet was observed at −1430 ppm in the ^{125}Te NMR spectrum of the K_2Te solution. The doublet was also observed in the solution extracts of $LiPbTe_{0.67}Se_{0.33}$ + 12-crown-4 in en, but in much higher concentrations. From proton-decoupling experiments and the measured ^{125}Te satellite/central peak ratios (4%) in the ^{1}H NMR spectrum ($\delta(^1H)$, −12.9 ppm), the doublet in the ^{125}Te spectrum has been assigned to the HTe^- anion. The source of the proton in HTe^- is unclear, but the simplest explanation would be an acid–base reaction between Te^{2-} and the solvent and/or deprotonation of the complexing ligands. Haushalter et al.[21] have recently isolated the PPh_4^+ salt of the HTe^- anion and solved its crystal structure.

The ^{1}H and ^{77}Se NMR spectra of the HSe^- anion were also obtained by dissolving NaHSe in anhydrous C_2H_5OH. The expected doublet for HSe^- in the ^{77}Se spectrum occurred at −495 ppm ($\delta(^1H)$, −5.4 ppm); however, only a singlet was observed in en solutions of NaHSe, indicating that HSe^- is partially or completely deprotonated in the more basic en solvent. The relative ^{1}H chemical shifts of HSe^- and HTe^- are consistent with the

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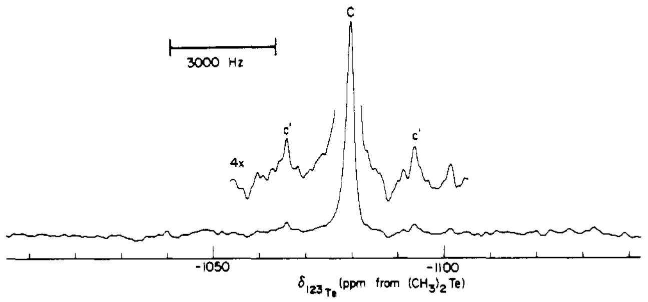
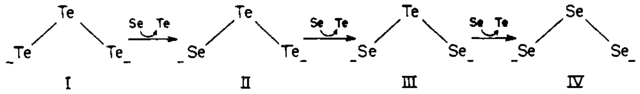


Figure 1. ^{123}Te NMR spectrum (130.89 MHz) of 2K$^+$ + Te$_2^{2-}$ in liquid ammonia at −54 °C. Peak C is due to Te$_2^{2-}$. Peaks c′ arise from $^1J(^{123}Te_t-^{125}Te_t)$ coupling.

Scheme I



anticipated greater hydrido character of hydrogen bonded to the more electropositive tellurium atom.

The Se^{2-} anion is expected to have the most shielded ^{77}Se chemical shift because the paramagnetic shielding term, σ^p, in Ramsey's shielding expression[25] (eq 3) is absent for a spherically

$$\sigma = \sigma^d + \sigma^p \tag{3}$$

symmetric environment. It is of interest that the chemical shift of the Se^{2-} anion is very solvent dependent[22] and is far from being the most shielded selenium environment observed thus far, cf. Se(SiH$_3$)$_2$, −666 ppm,[23] and Li$^+$(SeSiH$_3$)$^-$, −736 ppm.[24] Undoubtedly, the spherical symmetry of Se^{2-} is distorted in solution, giving rise to paramagnetic shielding. A similar solvent dependence of the chemical shift is expected for the Te^{2-} ion if it can be stabilized in a suitable solvent.

Dichalcogenide Anions, Ch$_2^{2-}$. A single, sharp line was observed in the ^{123}Te and ^{125}Te NMR spectra of the K/Te liquid ammonia solution as expected for the Te$_2^{2-}$ anion (eq 2). In addition, the Te$_2^{2-}$ one-bond coupling constant $^1J(^{123}Te-^{125}Te)$ could be determined from the natural-abundance ^{123}Te and ^{125}Te satellites (Figure 1) and was found to be 3645 Hz, representing the largest indirect spin–spin coupling constant presently known for bonded tellurium nuclei.

The NMR spectra of the TeSe^{2-} and Se$_2^{2-}$ anions could not be measured owing to their low solubilities and/or instabilities of their 2,2,2-crypt-K$^+$ salts. Sharp and Koehler[26] have previously reported that the Se$_2^{2-}$ anion only exists in low concentrations and in equilibrium with Na$_2$Se and Se$_3^{2-}$ in liquid ammonia.

Trichalcogenide Anions, Ch$_3^{2-}$. Only a single, broad peak was observed in the ^{125}Te NMR spectrum of K$_2$Te/2Te in en (Figure 2a). However, the expected two peaks, in a 2:1 ratio (Te$_t$:Te$_b$), were observed when 2,2,2-crypt was added to the solution (Figure 2b); and are consistent with the V-shaped Te$_3^{2-}$ anion (structure I in Scheme I). 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 exchanged-averaged ^{125}Te environments in the noncryptated 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. These results are not unexpected as it has been found that the size of the countercation affects the geometry of the Te$_3^{2-}$ anion.[12]

The green triselenide anion (structure IV) was prepared and characterized by a method analogous to that used for the tritelluride anion (Figure 3c). The Se$_3^{2-}$ anion was also synthesized by allowing the KPb$_{0.50}$Se$_{2.00}$ alloy to react with 2,2,2-crypt in en with subsequent formation of a gray-black insoluble residue, presumed to be PbSe.

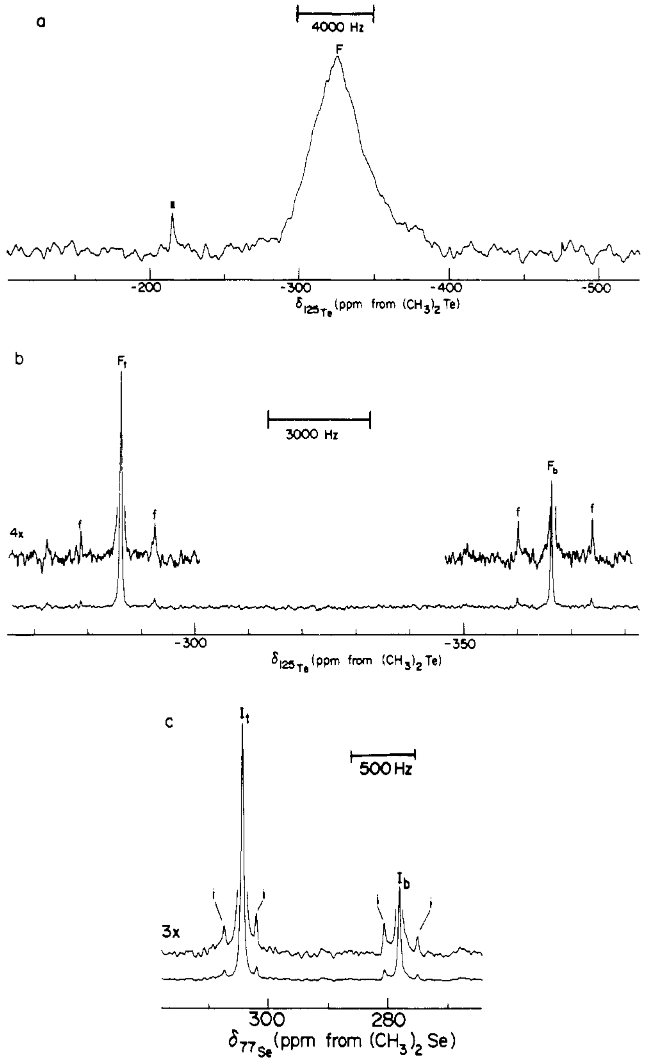


Figure 2. ^{125}Te NMR spectra of (a) 2K$^+$ + Te$_3^{2-}$ (78.917 MHz) and (b) (2,2,2-crypt-K$^+$)$_2$Te$_3^{2-}$ (157.792 MHz) and the ^{77}Se NMR spectrum (47.704 MHz) of (c) (2,2,2-crypt-K$^+$)$_2$Se$_3^{2-}$ in en solvent: Peak F is due to Te$_3^{2-}$ (exchange averaged); peaks F$_t$ and F$_b$ are due to Te$_t$ and Te$_b$ of Te$_3^{2-}$ and peaks I$_t$ and I$_b$ to Se$_t$ and Se$_b$ of Se$_3^{2-}$. Satellite peaks f and i arise from $^1J(^{125}Te_t-^{125}Te_b)$ and $^1J(^{77}Se_t-^{77}Se_b)$ couplings, respectively. The peak denoted with an asterisk is a spurious spike.

Single resonances having the same satellite spacings were observed in both the ^{77}Se and the ^{125}Te NMR spectra of the green cryptated en solution of K$_2$Te/Se (1:2) and are assigned to the TeSe$_2^{2-}$ anion (structure III). The TeSe$_2^{2-}$ anion has been further characterized by a single-crystal X-ray structure determination of the en-solvated 2,2,2-crypt-K$^+$ salt and reported in a forthcoming paper.[27] A considerable amount of the pyramidal TeSe$_3^{2-}$ anion was also observed in the NMR spectra of these solutions (see below).

The NMR spectra of cryptated K$_2$Se/Te (1:2) en solutions gave ^{77}Se and ^{125}Te resonances arising from the TeSe$_3^{2-}$, TeSe$_2^{2-}$, and Te$_3^{2-}$ anions. In addition, two new tellurium environments and one new selenium environment, all spin coupled to one another, were observed (Figure 3). These resonances are assigned to the novel V-shaped Te$_2$Se^{2-} anion having a terminal selenium atom (structure V). The assignments of the terminal selenium (Se$_t$) and tellurium (Te$_t$) resonances are based on the observation that their chemical shifts and one-bond coupling constants are very similar to those of the corresponding environments in the TeSe$_2^{2-}$ and Te$_3^{2-}$ anions. Moreover, the chemical shifts of the bridging tellurium atoms (Te$_b$) in the trichalcogenide anions Te$_b$Ch$_2^{2-}$ were

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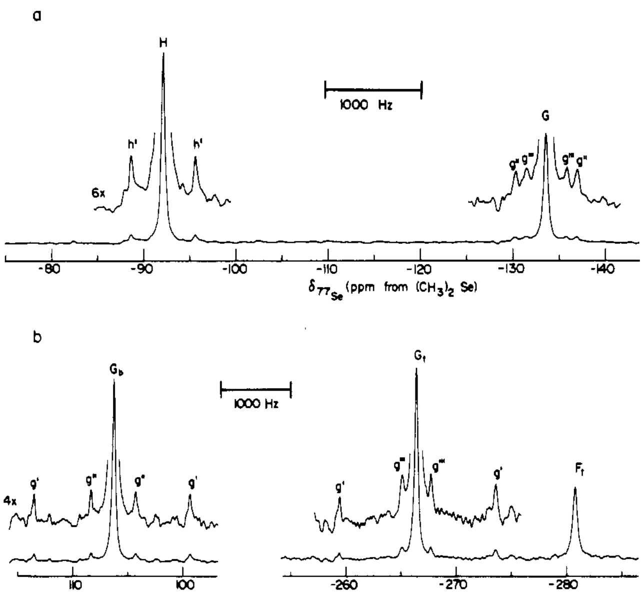
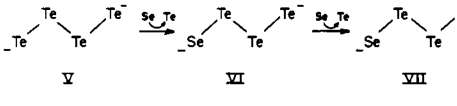


Figure 3. (a) ^{77}Se NMR spectrum (95.383 MHz) and (b) ^{125}Te NMR spectrum (157.792 MHz) of the en solution resulting from the reaction of K_2Se with 2Te in the presence of 2,2,2-crypt. Peak H is due to $TeSe_2^{2-}$, peak G is due to Te_2Se^{2-}, peaks G_b and G_t are due to Te_b and Te_t, respectively, and peak F_t is due to Te_t of Te_3^{2-}. Peaks g′, g″ (and h′), and g‴ arise from $^{125}Te_t$–$^{125}Te_b$, $^{77}Se_t$–$^{125}Te_b$, and $^{77}Se_t$–$^{125}Te_t$ couplings, respectively.

Scheme II



V VI VII

VIII IX

found to vary linearly with the number of selenium atoms bonded to them (Table I), indicating a homologous series of anions.

The coexistence of $TeSe_2^{2-}$, Te_2Se^{2-}, and Te_3^{2-} in the tellurium-rich solution (K_2Se/Te (1:2)) suggests an equilibrium among the species that is consistent with eq 4. The total number of

$$2Te_2Se^{2-} \rightleftharpoons TeSe_2^{2-} + Te_3^{2-} \qquad (4)$$

Te_b–Se_t and Te_b–Te_t bonds does not change in equilibrium (4) so that the energy difference is expected to be small. An analogous equilibrium involving Te_2Se^{2-}, $TeSe_2^{2-}$, and Se_3^{2-} does not occur to an appreciable extent in the selenium-rich solution (K_2Te/Se (1:2)) and may be attributed to the higher stabilities of species having selenium atoms in the terminal positions.

Tetrachalcogenide Anions, Ch_4^{2-}. The single spin-coupled resonances in the ^{77}Se and ^{125}Te NMR spectra of the yellow-orange K_2Te/Se (1:2) en and ammonia solutions are assigned to the trigonal-pyramidal-shaped (C_{3v}) $TeSe_3^{2-}$ anion (structure IX in Scheme II). The $TeSe_3^{2-}$ anion has been further characterized by single-crystal X-ray structure determinations of the en solvated 2,2,2-crypt-K^+ salt, reported in a forthcoming paper,[27] and in the Na_2TeSe_3 and K_2TeSe_3 phases.[19]

In attempts to prepare the remaining mixed Se/Te tetrachalcogenide anions, samples were prepared by allowing the mixtures K_2Se/Se/Te (1:1:2) and K_2Se/Te (1:3) to react in en, followed by complexation of the potassium cations with 2,2,2-crypt. Two new ^{77}Se NMR peaks (Figure 4a) and two new ^{125}Te NMR peaks (Figure 4b) were observed along with intense sharp peaks for $TeSe_3^{2-}$. The new resonances in each spectrum were found to vary in relative intensities with sample composition and are consequently attributed to different species. On the basis of similar chemical shift values for each pair of Se and Te environments and the fact the ^{77}Se chemical shifts are close to those of Se_t in $TeSe_2^{2-}$ and Te_2Se^{2-}, the resonances are assigned to the Te_b–Se_t^- units of the new anions Te_3Se^{2-} and $Te_2Se_2^{2-}$ depicted by structures VI and VII, respectively. The environments at higher frequency are assigned to the $Se_2Te_2^{2-}$ anion as their intensities were found to be greater in the selenium-rich sample. The remaining two Te environments of Te_3Se^{2-} ($^-Te_tTe_bTe_b'Se_t^-$), Te_t and Te_b', were only found as broad, weak peaks at −180 and 175 ppm, respectively, suggesting slow chemical exchange was occurring. The assignment was further supported by the observation that the chemical shift of Te_b' changes by approximately 480 ppm when going from $^-Te_tTe_b'TeSe^-$ to $^-Se_tTe_b'TeSe^-$, which is similar to the change in the chemical shift of Te_b (450 ppm) when Se_t is substituted for Te_t in the trichalcogenide anions.

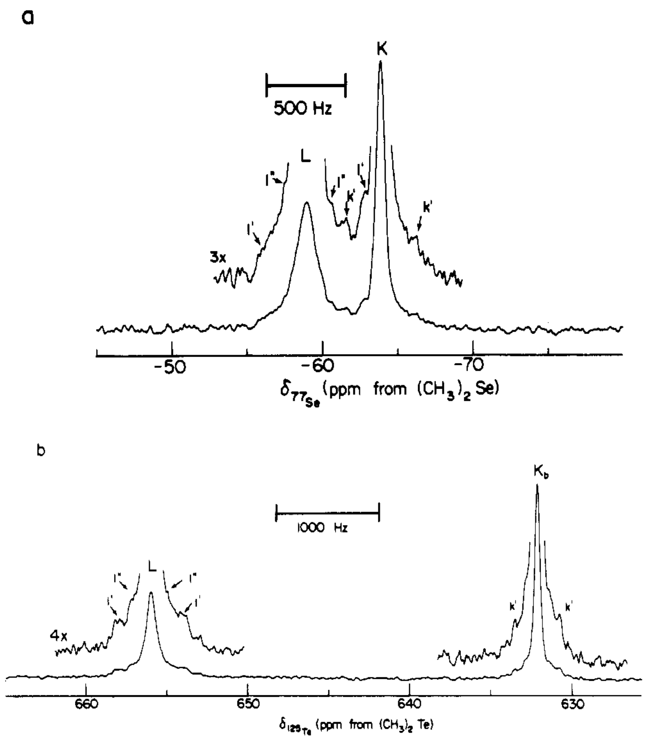


Figure 4. (a) ^{77}Se NMR spectrum (95.383 MHz) and (b) ^{125}Te NMR spectrum (157.792 MHz) of the en solution at 5 °C resulting from the reaction of K_2Se with a 2:1 Te/Se mixture in the presence of 2,2,2-crypt. Peak L is due to $Te_2Se_2^{2-}$, peak K to Te_3Se^{2-}, and peak K_b to Te_b (–$Se_tTe_bTe_b'Te_t$–). Peaks l′ and k′ arise from $^1J(^{77}Se–^{125}Te)$ couplings, and peak l″ is tentatively assigned to the coupling $^2J(^{77}Se–^{125}Te)$.

Cryptated en solutions of either $KTe_{2.00}$ or $KPb_{0.50}Te_{2.50}$ gave only a single broad peak at ~10 ppm, indicating that the Te_t and Te_b environments of Te_4^{2-} (structure V) where undergoing fast chemical exchange on the NMR time scale. The exchange-averaged chemical shift is in good agreement with the average chemical shift value of the Te_b–Te_t^- unit (−5 ppm) in Te_3Se^{2-}. The rate of chemical exchange could not be slowed sufficiently in en at 4 °C, and the solubility of the 2,2,2-crypt-K^+ salt was found to be too low below 0 °C to permit observation in liquid ammonia. Samples of K_2Te/Te (1:3) or K/Te (1:2) in liquid ammonia gave only a single peak at −150 ppm ($\Delta\nu_{1/2}$ = 700 Hz) when recorded at −75 °C, and is probably the result of rapid exchange between an equilibrium mixture of Te_3^{2-} and Te_4^{2-}.

Tetraselenide and Higher Polyselenide Anions, Se_4^{2-} and Se_m^{2-}. The ^{77}Se NMR spectrum of the dark brown solution of Na/Se (1:2) in liquid ammonia solution gave two sharp singlets in a 1:1 ratio (Figure 5a), consistent with a chain structure for Se_4^{2-} ($^-Se_tSe_bSe_bSe_t^-$). The peak at −321 ppm is similar to that of Se_t in Se_3^{2-} and is consequently assigned to the terminal selenium atom of Se_4^{2-}. A set of satellite shoulders (Gaussian line shape) associated with each peak is assigned to the one-bond coupling constant, $^1J(^{77}Se_t–^{77}Se_b)$, of the Se_4^{2-} anion (Figure 5b).

The dark brown en solution of K_2Se/Se (1:3) turned dark green with the accompanying formation of black crystalline material

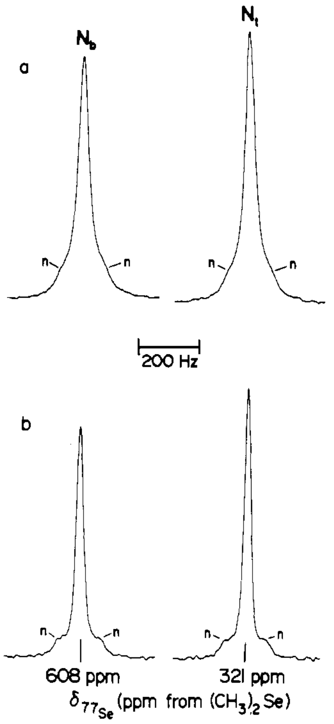


Figure 5. ^{77}Se NMR spectra (47.704 MHz) of $2Na^+ + Se_4^{2-}$ in NH_3(l) at −75 °C with (a) Lorentzian and (b) Gaussian line shapes. Peaks N_t and N_b denote the bridging and terminal environments of Se_4^{2-}, respectively. Peaks labeled n are assigned to the spin–spin coupling $^1J(^{77}Se_t-^{77}Se_b)$.

when 2,2,2-crypt was added. Only the Se_3^{2-} anion was observed in the ^{77}Se NMR spectrum. Evidently the Se_4^{2-} anion disproportionates in the cryptated solution to Se_3^{2-} and higher polyselenide anions, as exemplified in eq 5, even though the 2,2,2-crypt-Ba^{2+} salt of Se_4^{2-} has been isolated from en solutions by other workers.[3] Large quantities of black crystalline material also precipitated when the brown K_2Se/Se (1:4) and dark green K_2Se/Se (1:5) en solutions were cryptated. The crystalline material was presumed to be the 2,2,2-crypt-K^+ salt of Se_6^{2-}. The ^{77}Se spectrum was difficult to observe owing to the low solubility of $(2,2,2\text{-crypt-}K^+)_2Se_6^{2-}$ and exchange broadening of the lines. Only a single broad peak at 700 ppm ($\Delta\nu_{1/2}$ = 1400 Hz) was observed in the ^{77}Se NMR spectrum of the latter solution.

$$3Se_4^{2-} \rightarrow 2Se_3^{2-} + Se_6^{2-} \qquad (5)$$

These results suggest that complex equilibria occur for the higher polyselenide anions, Se_n^{2-} ($n > 3$), in which the total number of Se_b-Se_t and Se_b-Se_b bonds remain constant. Consequently, the presence of each type of anion is dependent on the solubility of its salt as well as on its relative stability in different solvents.

Chemical Exchange. An intermolecular rather than intramolecular exchange is believed to take place between the terminal and bridging tellurium environments of Te_3^{2-} in uncryptated solutions as no reasonable intermediate can be invoked that involves K^+ cations in the latter mechanism. The existence of solvated cations in solution may simply serve to lower the activation energy barrier for two Te_3^{2-} anions coming in contact with one another, or the cation may stabilize the formation of an intermediate by strong ion-pair formation. Similarly, even though two possible intermediates for an intramolecular exchange can be invoked for open-chain tetrachalcogenide anions—i.e., a planar Ch_4^{2-} species, isovalent with the I_4^{2+} cation,[28] or a pyramidal Ch_4^{2-} anion, isovalent with the $TeSe_3^{2-}$ anion—exchange broadening of their NMR resonances was found to be dependent on the relative concentrations of the species in solution, suggesting an intermolecular exchange process.

The present study shows that chemical exchange rates generally increase with increasing chalcogen anion chain length and as the number of tellurium atoms in a chain increases. Böttcher et al.[29,30] have previously noted that a high degree of association is found in the solid state for the longer chain length polytelluride anions when the negatively charged terminal atoms coordinate to a two-coordinate atom in the chain. A similar type of association can account for the nonlinear chain geometry of the recently reported Se_{11}^{2-} anion.[30,31] However, association between polytelluride anions should be more common owing to the high polarizability of tellurium. It is likely that similar types of association are responsible for the increase in exchange rate resulting as the number of tellurium atoms and the chain length increase. Although the detailed mechanism for the intermolecular exchange cannot be deduced from this study, it should be noted that an intermolecular exchange mechanism involving the association of terminal atoms cannot be excluded as is evident for the Te_5^{4-} anion in $NaTe_2$[9] and for the polymeric Te_6^{2-} anion in $LiTe_3$.[32]

Structural Relationships and NMR Parameters of Ch_n^{2-}. Structural Correlations. The structures of the polychalcogenide anions reported here can be rationalized by considerations of the electronegativity difference between Se and Te and the topological charge stabilization rule (TCSR).[33] 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. When the substitution of a tellurium atom by the more electronegative selenium atom is considered, the latter atom goes to the position with the highest electron density, i.e., the terminal position. Therefore, by successive substitution of a Te with a Se atom, starting with Te_3^{2-}, one arrives at the series of anions shown in Scheme I. The structures are identical with those observed in solution. The same pattern is obtained after two successive substitutions of Te_4^{2-} (Scheme II); i.e., the selenium atoms go to the positions with the highest negative charges. However, the substitution of a third selenium atom does not give the open-chain structure expected from the TCSR for the $TeSe_3^{2-}$ anion, but the pyramidal shaped (C_{3v}) structure. Evidently higher order terms become important for the perturbation Hamiltonian, with the chain structure becoming less stable as Se atoms are substituted in Scheme II with the three Se_t-Te_c bonds of the pyramid being more stable than the Se_t-Te_b, Se_b-Te_b, and Se_t-Se_b bonds of the alternative open-chain structure. Furthermore, the Se_t-Te_c bonds of the pyramid have a higher bond order resulting from π back-bonding and are expected to be stronger than single bonds. The presence of $TeSe_3^{2-}$ in all the solutions of the mixed Se/Te tri- and tetraheterochalcogenide anions studied in the present work is consistent with the proposed high stability of this anion.

Correlation of Se and Te Chemical Shifts. 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.[34] A similar linear relationship was found for the corresponding isostructural environments of selenium and tellurium in the polychalcogenide anions (Figure 6). The parameters for the best line fit were obtained by least-squares analysis (R = 0.999) and are given by eq 6. The slope (2.10) is larger than the slopes reported for the organochalcogenides (1.6–1.8).[34-37] McFarlane

$$\delta(^{125}Te)_{ppm} = 2.10\delta(^{77}Se)_{ppm} - 47 \text{ ppm} \qquad (6)$$

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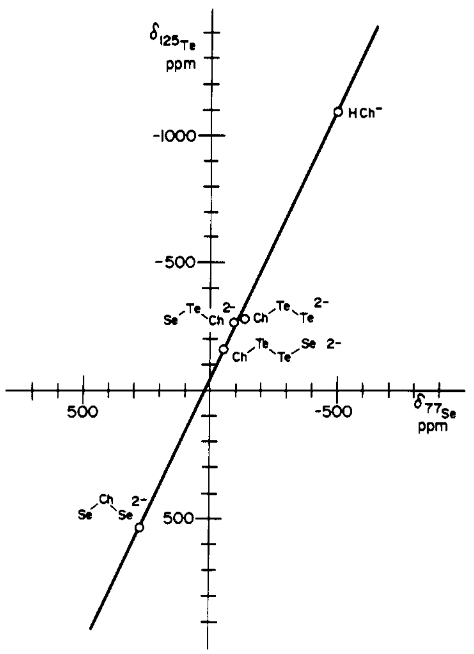

Figure 6. Correlation of the ^{125}Te and ^{77}Se chemical shifts for isostructural environments of the polychalcogenide anions (Ch = Se/Te).

Table II. Reduced Coupling Constants, ^1K, and Relativistically Corrected Reduced Coupling Constants, $^1K_{RC}$, for the Polychalcogenide Anions[a]

	^1K, 10^{20} N A^{-2} m^{-3}			$^1K_{RC}$, 10^{20} N A^{-2} m^{-3}		
anion	Se–Se	Te–Se	Te–Te	Se–Se	Te–Se	Te–Te
Te_2^{2-}			366			177
Se_3^{2-}	61			45		
$TeSe_2^{2-}$		92.7			55.7	
Te_2Se^{2-}		86.9	187		52.3	90.1
Te_3^{2-}			181			87.6
Se_4^{2-}	30			22		
$Te_2Se_2^{2-}$		87			52	
Te_3Se^{2-}		59			36	
$TeSe_3^{2-}$		29.0			17.5	

[a] The one-bond coupling constants are between the Ch_t–Ch_t and Ch_t–Ch_b environments of the anions as measured in en and liquid ammonia (see Table I).

et al.[34] have based this rationalization of the linear relationship between selenium and tellurium chemical shifts upon the paramagnetic shielding term, σ^p (eq 3), as it makes the dominant contribution to the observed chemical shift ranges of the heavy nuclei.[38]

Coupling Constants (^1J, ^1K, and $^1K_{RC}$). Among the most significant findings resulting from the present solution NMR study are the large one-bond spin–spin coupling constants found for the Te_2^{2-} anion and Ch_b–Ch_t^- units in general (Table I). In order to compare the coupling constants of the Ch_n^{2-} anions with other systems, the reduced coupling constants, ^1K, have been calculated and are listed in Table II. The reduced one-bond spin–spin coupling constant is usually believed to be dominated by the Fermi contact mechanism where the spin–spin coupling between heavy elements has, in turn, been shown to reflect the s character of the bond.[39–41] The Fermi contact term can become very large for coupling constants involving the heavier elements owing to large relativistic effects.[41] Consequently, the relativistically corrected reduced coupling constants, $^1K_{RC}$, have been calculated for the polychalcogenide anions by a method described previously[15] and are listed in Table II.

Table III. Linear Relationship between the One-Bond M–Se and M–Te Reduced Coupling Constants, ^1K, and the Relativistically Corrected Reduced Coupling Constants, $^1K_{RC}$, of $M_rSe_nTe_{m-n}{}^{k-}$ and the Number of Se Atoms, n

	reduced coupling constants[a]			
	M–Se bond		M–Te bond	
Series[b] $M_rSe_nTe_m{}^{k-}$	^1K	$^1K_{RC}$	^1K	$^1K_{RC}$
$HgSe_nTe_{2-n}{}^{2-}$ [c,d] (sp)	$559 - 2.9n$	$154 - 0.8n$	$961 - 4.4n$	$213 - 1.0n$
$TlSe_nTe_{3-n}{}^{3-}$ [c] (sp^2)	$501 + 15.7n$	$142 + 4.5n$	$740 + 35.0n$	$168 + 8.0n$
$SnSe_nTe_{3-n}{}^{2-}$ [c] (sp^2)	$217 + 8.0n$	$132 + 4.8n$	$321 + 17.7n$	$156 + 8.6n$
$SnSe_nTe_{4-n}{}^{4-}$ [c] (sp^3)	$140 + 7.7n$	$85 + 4.7n$	$202 + 17.0n$	$98 + 8.3n$
$TeSe_nTe_{2-n}{}^{2-}$ [d] (sp^3)	$83 + 4.8n$	$50 + 2.9n$	$181 + 5.3n$	$88 + 2.5n$
$Pb_2Se_nTe_{3-n}{}^{2-}$ [e] (p)	$56 - 8.1n$	$16 - 2.3n$	$135 - 9.8n$	$30 - 2.2n$

[a] Values in $10^{20} \times$ N A^{-2} m^{-3}. [b] Formal hybridization of the central metal atom, M, is given in parentheses. [c] Reference 15. [d] Line defined by only two points. [e] Reference 16.

The one-bond ^{77}Se–^{77}Se coupling constants reported for a large number of diselenides,[42,43] organopolyselenides,[44] and Se_nS_{8-n} species[45] are, in general, small, i.e., 4–55 Hz ((1–13) × 10^{20} N A^{-2} m^{-3}). Similar small values for the coupling constants are observed in diaryl ditellurides,[46] 213–369 Hz ((21.2–26.8) × 10^{20} N A^{-2} m^{-3}) and 170–207 Hz ((14.0–17.1) × 10^{20} N A^{-2} m^{-3}) for $^1J(^{123}Te–^{125}Te)$ and $^1J(^{125}Te–^{125}Te)$, respectively, and, for MeSeTeMe,[47] 169 Hz (23.2 × 10^{20} N A^{-2} m^{-3}). However, coupling constants of the same magnitude as those reported here have been observed between chalcogen atoms of organodichalcogenide anions, $RChCh^-$ (Ch = Se/Te), i.e., 267–323 Hz ((61.1–74.0) × 10^{20} N A^{-2} m^{-3}) for Se_b–Se_t, 1637–2186 Hz ((135.1–180.3) × 10^{20} N A^{-2} m^{-3}) for Te_b–Te_t, and 481–738 Hz ((66.1–101) × 10^{20} N A^{-2} m^{-3}) for Te_b–Se_t.[48] Evidently, the nature of Ch_b–Ch_t^- anion bonds is significantly different from that of Ch_b–Ch_b bonds in neutral species.

Previous multi-NMR studies of the main-group-metal chalcogenide anions $HgCh_2^{2-}$, $TlCh_3^{3-}$, $SnCh_3^{2-}$, $SnCh_4^{4-}$, and $Pb_2Ch_3^{2-}$ have shown that the one-bond coupling constants can be correlated with the formal hybridization of the central metal atom; i.e., the coupling constant is greater when the s character of the metal atomic bonding hybrid orbital is larger.[15,16] The values of ^1K(M–Se), ^1K(M–Te), $^1K_{RC}$(M–Se), and $^1K_{RC}$(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, and are given in Table III for comparison. From Table III, it is noted that $^1K(Te_b–Se_t)$ and $^1K(Te_b–Te_t)$ for the $TeCh_2^{2-}$ anions are roughly midway between the corresponding values for the $SnCh_4^{4-}$ and $Pb_2Ch_3^{2-}$ series. A similar correlation is also evident for $^1K_{RC}(M–Se_t)$ and $^1K_{RC}(M–Te_t)$ except the $^1K_{RC}(M–Te_t)$ values for the $SnCh_4^{4-}$ and $TeCh_2^{2-}$ series are very similar whereas the $^1K_{RC}(Te_b–Se_t)$ values for the $TeCh_2^{2-}$ anions are midway between the $^1K_{RC}$(M–Se) values for the $SnCh_4^{4-}$ and $Pb_2Ch_3^{2-}$ anions. This trend suggests a relatively high formal s character for the atomic hybrid orbitals of Te_b in the Te_b–Ch_t bonds of the $TeCh_2^{2-}$ anions. A high formal s character for the bridging chalcogen atom would be consistent with diffuse bond

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pairs in the valence shell of Te_b (AX_2E_2)[49–51] and, consequently, the relatively large bond angles observed for Te_3^{2-} (113°)[11] and $TeSe_2^{2-}$ (110°).[27] A higher formal s character of the Ch_b atomic hybrid would render it more electronegative and would result in the bridging atom of the Ch_t–Ch_b bond bearing some of the negative charge of the anion. Although this partial "delocalization" of the negative charge would presumably be relatively small, it could be responsible for the unexpected higher shielding of Ch_b relative to Ch_t in the Se_3^{2-} and Te_3^{2-} anions owing to a decrease in the electron imbalance term of Ch_b relative to that of Ch_t.[38] However, a more detailed theoretical analysis of these systems is needed in order to more fully account for the relationships that have been noted in the preceeding discussion.

Experimental Section

The compounds prepared during the course of this work were all air-sensitive. Consequently, all manipulations were carried out under anhydrous conditions and in the absence of oxygen on grease-free glass vacuum lines or in a nitrogen-atmosphere drybox (Vacuum Atmospheres Model DLX) or a glovebag. The drybox moisture and oxygen levels were routinely less than 0.1 ppm. The glovebag was flushed with dry nitrogen gas (moisture level less than 0.1 ppm) or argon gas (Matheson; $O_2 < 1$ ppm), when handling lithium metal, for several hours prior to use.

Potassium (MCB) and sodium (BDH Chemicals, 99.98%) were used as received, and freshly cut samples were handled only in the drybox. Selenium metal powder (Alfa Inorganics, 99.9%), tellurium metal powder (Alfa Inorganics, 99.5%), and lead shot (BDH, 99.9%) and the complexing ligands 2,2,2 crypt (Merck) and 12-crown-4 (Aldrich Chemical Co.) were 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 additional week prior to use. Liquid ammonia (Canadian Liquid Air) was stored over sodium at −78 °C for at least 1 week prior to use. Absolute ethanol (Consolidated Alcohols Ltd.) was dried by storing over molecular sieves (Fisher Scientific Co., Type 4A) for at least 2 weeks prior to use.

Potassium Monochalcogenides. In a typical preparation, potassium metal (1.5–2.6 g) and the necessary amount of chalcogen metal (1.5 g of Se and 2.1 g of Te) were placed in separate arms of an H-shaped, thick-walled glass reaction vessel equipped with a Teflon Rotaflo valve. The potassium metal was kept in 15–20% excess as some ammonolysis of the metal always occurred. After liquid ammonia had been condensed at −78 °C onto the potassium metal, the vessel was flame sealed from the Rotaflo valve and the potassium metal/ammonia solution was poured, in small quantities, onto the chalcogen metal powder. The solution was kept at −78 to −50 °C until all the chalcogen metal had reacted in order to minimize amide formation. When the reaction was complete, the solution was allowed to warm to room temperature, and the solid white K_2Ch was collected into one arm of the vessel and washed several times by statically distilling the ammonia onto the solid and decanting the solution off the solid. Residual ammonia was removed from K_2Ch by cooling the branch of the reaction vessel containing ammonia and KNH_2 to −196 °C. The tube containing K_2Ch was flame sealed from the remaining arm of the H-shaped reaction vessel, which had been cooled to −196 °C and contained the ammonia and KNH_2. *Caution!* Owing to ammonolysis, a sufficiently high hydrogen gas pressure may develop inside the reaction vessel, causing it to explode. The reaction vessel should always be kept in a well-shielded area, particularly when the solution is warmed to room temperature.

Preparation of Alloys. The alloys $LiPbSe_{0.33}Te_{0.67}$, $KPb_{0.50}Se_{2.00}$, $KPb_{0.50}Te_{2.50}$, and $KTe_{2.00}$ were prepared in thick-walled Pyrex glass vessels by a procedure similar to that described in refs 15 and 16. Extraction of these alloys in en solvent followed by the addition of a stoichiometric amount of 2,2,2-crypt (12-crown-4 in the case of $LiPbSe_{0.33}Te_{0.67}$) gave rise to the HTe^-, Se_3^{2-}, and Te_4^{2-} anions.

Preparation of Polychalcogenide Anions and NMR Samples. The desired stoichiometric amounts of K_2Ch, chalcogen metal powder, and, when appropriate, 2,2,2-crypt were thoroughly mixed in a glass ampule. The amount of 2,2,2,-crypt used was usually kept in 3–6% excess relative to the total amount of alkali metal in order to ensure that all the alkali-metal cations were complexed in solution. In order to compensate for the possibility that small amounts of the polychalcogen anions may be oxidized in solution, the monochalcogenides were always in 2–5% excess relative to the chalcogen metals. After approximately 10 mL of en had been vacuum distilled onto the mixture of 0 °C, nearly every solution became immediately colored. The solutions were allowed to react for a further 2 days to 3 weeks at room temperature. For most of the preparations, and particularly those involving K_2Te, the 2,2,2-crypt was not added to the solution until all of the monochalcogenide had reacted in order to avoid reduction of 2,2,2-crypt by the monochalcogenide. The solutions were then cooled in an ice bath, and a stoichiometric amount of 2,2,2-crypt was decanted in small portions into the polychalcogenide solution.

Samples for NMR studies were prepared by allowing the undissolved materials to settle prior to decantation of the clear solutions into precision thin-walled 10-mm-o.d. NMR tubes (Wilmad) that had been glassblown onto the Pyrex reaction vessels. The solutions were concentrated to 2–4 mL as described in ref 15. The concentrations of the anions in the NMR samples often cannot be specified owing to large amounts of crystalline solid that had formed upon concentration of the NMR sample solutions. When solid formation occurred, the material was collected into the top of the sealed inverted glass NMR tube prior to obtaining NMR spectra.

In typical preparations of the homo- and heteropolychalcogenide anions in en solvent, the following amounts of reagents were used: for Se^{2-}, K_2Se (46.8 mg, 0.298 mmol) and 2,2,2-crypt (233 mg, 0.618 mmol); for Te^{2-}, K_2Te (64.0 mg, 0.311 mmol) and 2,2,2-crypt (239 mg, 0.633 mmol); for Te_3^{2-}, K_2Te (29.3 mg, 0.142 mmol), Te (34.1 mg, 0.267 mmol), and 2,2,2-crypt (112 mg, 0.297 mmol); for $TeSe_2^{2-}$, K_2Te (63.0 mg, 0.306 mmol), Se (50.1 mg, 0.634 mmol), and 2,2,2-crypt (252 mg, 0.669 mmol); for Te_2Se^{2-}, K_2Se (59.4 mg, 0.378 mmol), Te (96.4 mg, 0.755 mmol), and 2,2,2-crypt (290 mg, 0.771 mmol); for Te_3Se^{2-}, K_2Se (58.8 mg, 0.374 mmol), Te (143 mg, 1.121 mmol), and 2,2,2-crypt (289 mg, 0.767 mmol); for $Te_2Se_2^{2-}$, K_2Se (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); for $TeSe_3^{2-}$, K_2Te (52.3 mg, 0.254 mmol) and Se (60.6 mg, 0.767 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 obtained, in particular for the tri- and tetraheterochalcogenide anions.

Alternative preparations of some polyselenide and polytelluride anions involved the extraction of the alloys $KPb_{0.50}Se_{2.00}$, $KPb_{0.50}Se_{3.00}$, $KPb_{0,50}Te_{2,50}$, and KTe_2 in en solvent in the presence of 2,2,2-crypt as described in ref 15.

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 Pyrex glass reaction vessel. For each preparation, a mixture of the alkali metal and a stoichiometric amount of the chalcogen metal powder were allowed to react at −78 °C until the alkali metal had completely dissolved. 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 for NMR sample preparation was not decanted from the solid residue for at least another 2–5 weeks. In typical preparations, the following amounts of alkali and chalcogen metals were used: for K/Te, 143 mg (3.66 mmol) of K and 445 mg (3.49 mmol) of Te; for K/2Te (1:2) 276 mg (7.06 mmol) of K and 1799 mg (14.10 mmol) of Te; for Na/2Se (1:2) 51 mg (2.2 mmol) of Na and 354 mg (4.48 mmol) of Se.

Preparation of HCh^- (Ch = Se, Te). Solution samples of HSe^- were prepared by dissolving Na^+HSe^-, prepared as described in ref 52, in dry C_2H_5OH and concentrating the final solutions in Pyrex glass NMR tubes (10 mm o.d. for ^{77}Se NMR spectroscopy and 5 mm o.d. (Wilmad) for ^1H NMR spectroscopy).

When the alloy $LiPbTe_{0.67}Se_{0.33}$ (1.187 g, 3.65 mmol) and 12-crown-4 (0.642 g, 3.65 mmol) were added to a reaction vessel, a violet solution in 12-crown-4 immediately formed. Ethylenediamine was then condensed onto the mixture as described above to give an intense violet-colored solution, which was decanted into a 10-mm NMR tube and shown by ^1H and ^{125}Te NMR spectroscopy to contain a high concentration of the HTe^- anion.

Multinuclear Magnetic Resonance Spectroscopy. All ^1H, ^{77}Se, ^{123}Te, and ^{125}Te NMR spectra were recorded on Bruker WM-250 and/or AM-500 pulse spectrometers at field strengths of 5.8719 and 11.745 T, respectively. Spectra were routinely obtained without locking (field drift < 0.1 Hz/h). The 10-mm multinuclear probes used to record ^{77}Se, ^{123}Te, and ^{125}Te spectra were broad-banded over the frequency ranges 23–103, 12–101, and 23–202 MHz. The ^1H NMR spectrum of the HSe^- anion was recorded by using a normal 5-mm ^1H probe on the AM-500 spectrometer whereas the ^1H NMR spectrum of the HTe^- anion was recorded through the ^1H-decoupling coils of the 10-mm probe of the WM-250

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spectrometer. The observing frequencies were 250.161 (^1H), 47.704 (^{77}Se), and 78.917 MHz (^{125}Te) on the WM-250 spectrometer and 500.138 (^1H), 95.383 (^{77}Se), 130.885 (^{123}Te), and 157.792 MHz (^{125}Te) on the AM-500 spectrometer. Free induction decays were typically accumulated in 16 K or 32K memories. Spectral width settings of 25–100 kHz were employed, yielding data point resolutions of 3.0–6.1 Hz and acquisition times of 0.328–0.655 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 10 000–300 000 scans being typical for these samples. Pulse widths for bulk magnetization tip angles corresponding to 90° were 2 (^1H), 20 (^{77}Se), and 25 μs (^{125}Te) on the WM-250 spectrometer and 2 (^1H), 12 (^{77}Se), 26 (^{123}Te), and 10–18 μs (^{125}Te) on the AM-500 spectrometer. Line-broadening parameters used in the exponential multiplication of the free-induction decays were 5–20 Hz for the heavier isotopes; however, values on the order of 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 Hz and a line broadening greater than or equal to the negative of the data point resolution were applied.

The respective nuclei were referenced to neat samples of $(CH_3)_2Se$ (^{77}Se), $(CH_3)_2Te$ (^{123}Te and ^{125}Te), and $(CH_3)_4Si$ (^1H) at 24 °C. The chemical shift convention used is that a positive (negative) sign signifies a chemical shift to high (low) frequency of the reference compound.

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Three-Coordinate Iron Complexes: X-ray Structural Characterization of the Amide-Bridged Dimers $[Fe(NR_2)_2]_2$ (R = $SiMe_3$, C_6H_5) and the Adduct $Fe[N(SiMe_3)_2]_2(THF)$ and Determination of the Association Energy of the Monomer $Fe\{N(SiMe_3)_2\}_2$ in Solution

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The X-ray structural characterization of the iron(II) amides $[Fe\{N(SiMe_3)_2\}_2]_2$ (**1**) and $[Fe(NPh_2)_2]_2$ (**2**) and the Lewis base adduct $Fe[N(SiMe_3)_2]_2(THF)$ (**3**), as well as the syntheses of the last two compounds, is described. These complexes are rare examples of the coordination number 3 for iron. Compounds **1** and **2** are both dimeric in the solid state, with each trigonal-planar ion bound to one terminal and two bridging amides. They closely resemble the corresponding Mn(II) and Co(II) compounds. Compound **3** is monomeric in the solid state, with one THF and two amides arranged in a trigonal-planar fashion. The terminal Fe–N bond lengths in **1**–**3** are similar to those reported for two-coordinate iron(II) amides. The Fe–N bonds in **1** are somewhat longer than those in **2**, indicating weaker association in **1**. This is borne out in the solution behavior of the two compounds. Thus **1**, which was studied by variable-temperature ^1H NMR spectroscopy, was seen to be a monomer in solution at 30 °C. Increasing amounts of the dimer were observed at lower temperature, and calculations based on the monomer–dimer equilibrium indicate an association energy of ~+3 kcal mol^{-1} for $[Fe\{N(SiMe_3)_2\}_2]_2$. Crystal data with Mo Kα (λ = 0.710 69 Å) radiation at 130 K: **1**, $C_{24}H_{72}Fe_2N_4Si_8$, $a = 17.978$ (4) Å, $b = 14.691$ (4) Å, $c = 18.564$ (5) Å, $\beta = 120.15$ (2)°, $Z = 4$, monoclinic, space group $C2/c$, $R = 0.031$; **2**, $C_{48}H_{40}Fe_2N_4$, $a = 9.579$ (5) Å, $b = 10.264$ (5) Å, $c = 10.482$ (6) Å, $\alpha = 91.78$ (4)°, $\beta = 110.68$ (4)°, $\gamma = 85.67$ (4)°, $Z = 1$, triclinic space group $P\bar{1}$, $R = 0.039$; **3**, $C_{16}H_{44}FeN_2OSi_4$, $a = 11.225$ (5) Å, $b = 13.391$ (5) Å, $c = 17.903$ (8) Å, $Z = 4$, orthorhombic, space group $Pcan$, $R = 0.061$.

Introduction

The use of bulky amide ligands to synthesize low-coordinate transition-metal complexes originated with two seminal[1,2] papers in the early 1960s that described the use of the $-N(SiMe_3)_2$ group to synthesize transition-metal compounds of the formula $M[N(SiMe_3)_2]_n$ (M = Cu[2] $n = 1$; M = Mn,[2] Co,[1] Ni,[2] $n = 2$; M = Cr,[2] Fe,[1] $n = 3$). This work was later extended to include further tris(amido) derivatives $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, or V[3] and the lanthanides[4]). In addition, their chemistry and some aspects of the chemistry of the divalent transition-metal[3,5,6] and lanthanide amides[7] were explored. Structural data have appeared for many of these, including $[M\{N(SiMe_3)_2\}_2]_2$ (M = Mn,[8,9] Co[9]) and, in addition, the three-coordinate Lewis base adducts $Mn[N(SiMe_3)_2]_2(THF)$,[5] $Co[N(SiMe_3)_2]_2(PPh_3)$,[6] and $M[N(SiMe_3)_2](PPh_3)_2$ (M = Co, Ni).[6] Many of these compounds were among the earliest well-characterized three-coordinate transition-metal complexes. Until recently, hardly any data had appeared on iron(II) amides.[10,11] The synthesis of $Fe[N(SiMe_3)_2]_2$[11] was not reported until 1988, and it was shown that both it and its manganese and cobalt analogues were two-coordinate in the gas phase by electron diffraction. Magnetic data and PES data for all three compounds were also reported.[11]

Investigation of transition-metal amides in this laboratory stems in part from a general interest in the structures and reactivity of

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