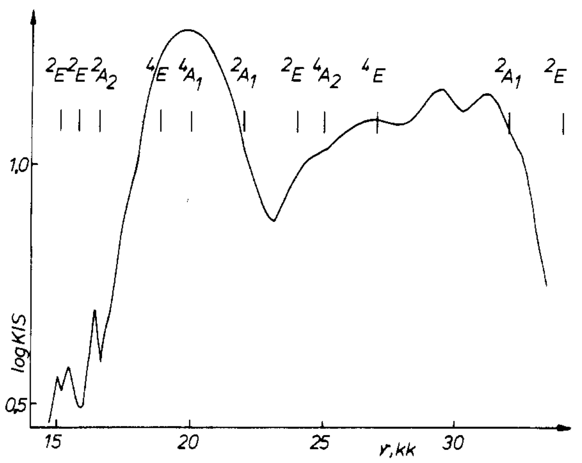

Figure 2. Optical spectrum of $[Cr_2(OH)_3L_2]I_3{\cdot}3H_2O$ at 300 K in the visible and near-UV region in reflection together with the term assignments calculated for the configuration d^3 with a trigonal ligand field.

parameter $\Delta_{oct} \approx 20\,000$ cm^{-1}, which lies between those of the pure Cr^{III}–O_6 and Cr^{III}–N_6 chromophores.[9] The sharp band at 15.0 × 10^3, 15.4 × 10^3 and 16.3 × 10^3 cm^{-1} should then correspond to the first spin-forbidden transitions to the ^2E, $^2T_2(t_2{}^3)$ terms. The broad bands at 25 × 10^3 and 27 × 10^3 cm^{-1} have to be correlated with the second spin-allowed transition to the trigonal-split terms of $^4T_2(t_2{}^2e)$. The higher absorptions at ≃30 × 10^3 cm^{-1} originate possibly from spin-forbidden transitions with high-intensity gain from exchange coupling. For the octahedral case, by calculation in the strong-field coupling scheme with complete d^3 configuration, the Racah parameters $B = 700$ and $C = 3400$ cm^{-1} can be approximated. The trigonal distortion that is indicated in the optical spectra can be specified by use of the EPR spectroscopically determined zero-field splitting of the $^4A_2$ ground state $\Delta E = 2D \approx 1.51$ cm^{-1}. This splitting of the ground level is introduced via second-order spin–orbit coupling and trigonal splitting of the excited states.

From structural information, the C_{3v} symmetry of the CrO_3N_3 entity is known, with the angle $\theta = 48$ and 50° between the C_3 axes and the Cr–O and Cr–N directions, respectively. If we use the concept of the AO model with an averaged σ-bonding parameter e_σ for Cr–O and Cr–N and only a small π-bonding contribution ($e_\pi = 0.1e_\sigma$), we derive a reasonable value of e_σ = 7800 cm^{-1} ($\theta = 54°\,44'$).[10] With the crystallographic angle of $\theta = 48°$, the AOM parameters and the spin–orbit coupling constant of $\zeta = 200$ cm^{-1} from a specific calculation in the d^3 trigonal strong-field coupling scheme,[5] the zero-field splitting $\Delta E = 1.54$ cm^{-1} of the $^4A_2$ ground state results in reasonable agreement with the EPR spectroscopic results. The AOM parameters are transformed to the final traditional parameters $Dq = 1770$, $Dt = 300$, and $Ds = -1260$ cm^{-1} of ref 5. The calculated term sequences are added in Figure 2. The corresponding one-electron configurations of the given trigonal states can easily be correlated to the common octahedral t_2 and e one-electron orbitals. The trigonal distortion characterized above by $\theta = 48°$ splits the octahedral $^4T_2(t_2{}^3)$ and $^4T_1(t_2{}^2e)$ states into essentially two components separated by 1200 and 1800 cm^{-1}, respectively, which seem only resolved in the powder spectra for the latter. As we use the same B and C parameters for different one-electron configurations, the higher doublet states at ≈30 × 10^3 cm^{-1} are not so well fitted to the experimental spectra.

In bis(μ-hydroxo)-bridged Cr(III) dimers, the intensity of their spin-forbidden transitions increases with J,[8] and one should suppose the same trend in our case of much larger exchange coupling. This corresponds to the observed strong unresoled absorption bands in the near-UV region. They should be characteristic for exchange-coupled systems and are much less in intensity for the more weakly coupled bis(μ-hydroxo)-bridged species but appear in both cases at almost the same position. Possibly single-crystal polarized absorption spectra could clear up this weak point in the interpretation of the electron excitations given above.

Acknowledgment. We thank Dr. A. Ozarowski and Prof. D. Reinen for helpful discussions.

Registry No. $[Cr_2(OH)_3L_2]I_3$, 94517-77-8; $[Cr_2(OH)_3L_2]ClO_4$, 94500-15-9.

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A ^{119}Sn Mössbauer Study of Some Nonclassically (Cluster) and Classically Bonded Zintl Anions

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Received December 12, 1983

Tin-119 Mössbauer spectra have been recorded for the following cluster (i.e., nonclassically) bonded Zintl anions, $[Sn_5]^{2-}$, $[Sn_9]^{4-}$, $[TlSn_8]^{5-}$, and $[Sn_2Bi_2]^{2-}$, and the data interpreted in terms of the known X-ray crystallographic information. Spectra for the following classically bonded Zintl anions, $[SnSe_4]^{4-}$, $[SnTe_4]^{4-}$, and $[SnSe_{3-x}Te_x]_z{}^{2z-}$ (x = 0–3, z = 1, 2), have also been measured. The $[SnSe_4]^{4-}$ and $[SnTe_4]^{4-}$ species are shown to have tin environments slightly distorted from tetrahedral symmetry while $[SnSe_{3-x}Te_x]_z{}^{2z-}$ species are shown to be much more distorted.

Introduction

A number of the heavy main-group elements form intermetallic phases with sodium or potassium that are soluble in liquid ammonia or ethylenediamine (en). About 50 years ago, Zintl and co-workers described electrochemical studies on NH_3 solutions of such sodium alloys and, together with the results of exhaustive alloy extractions, several homopolyatomic anions, namely $Sn_9{}^{4-}$, $Pb_9{}^{4-}$, $Bi_5{}^{3-}$, $Sb_7{}^{3-}$, and $Te_4{}^{2-}$ amongst others, were identified.[1-3] These have become known as Zintl anions. Attempts to isolate the salts of these anions by evaporation of the solvent resulted in the formation of amorphous products or reversion to a known binary alloy phase(s) in each case. However, fairly recently Kummer and Diehl[4] did succeed in isolating crystalline material of composition $Na_4Sn_9{\cdot}6$–$8en$ from ethylenediamine solutions. This was found to be diamagnetic, and ^{119}Sn Mössbauer measurements showed only one broad resonance with an isomer shift of +0.15

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Table I. ^{119}Sn Mössbauer Data for Tin-Alkali-Metal Alloys and Zintl Anions[f]

compd	temp, K	δ, mm s^{-1}	Δ, mm s^{-1}	Γ, mm s^{-1}	% of form
$CaSnO_3$	297	0.0	...	1.16	...
$Na_{1.7}Sn$	77	2.28	...	1.02	63.9
		2.72	...	1.02	36.1
$NaSn_{2.25}$	77	2.04	...	1.19	50.7
		2.72	...	1.19	69.3
$[Na(crypt)]_2[Sn_5]$	77	2.32	...	0.98	79.1
		3.00	...	0.98	20.9
	137	2.31	...	0.89	83.3
		2.85	...	0.89	16.7
	190	2.31	...	0.89	84.5
		2.79	...	0.89	15.5
$[Na(crypt)]_4[Sn_9]$	4.2[a]	2.17	...	1.90	...
	77	2.25	...	0.80	41.6
		2.67	...	0.80	16.8
		2.98	...	0.80	41.6
	165	2.33	...	0.81	50.0
		2.92	...	0.81	50.0
	215	2.34	...	0.77	50.0
		2.90	...	0.77	50.0
Na_5TlSn_8	77	2.19	...	1.35	35.8
		2.63	...	1.35	28.4
		3.05	...	1.35	35.8
$Na_5(en)_2TlSn_8$	77	2.17	...	1.00	43.5
		2.67	...	1.00	13.0
		3.02	...	1.00	43.5
$[K(crypt)]_2[Sn_2Bi_2]\cdot en$	77	2.75	1.07	1.06	...
$[Na(crypt)]_4[SnSe_4]$	77	1.47	0.62	0.95	...
frozen soln	77	1.43	0.95	1.38	...
$[Na(crypt)]_4[SnTe_4]$	77	1.76	0.63	1.03	...
frozen soln	77	1.61	0.97	1.35	...
$K_4[SnTe_4]$[d]	77	1.71 (2)	...	...	...
$[K(crypt)]_{2z}[SnSe_3]_z$	77	1.62	1.20	1.04	...
$[K(crypt)]_{2z}[SnSe_xTe_y]_z$[b]	77	1.59	1.16	0.94	...
$[K(crypt)]_{2z}[SnSe_mTe_n]_z$[c]	77	1.71	1.00	0.94	...
$[K(crypt)]_{2z}[SnTe_3]_z$	77	1.74	1.02	0.98	...
$[(CH_3)_4N]_4[Sn_2Te_6]$[d]	77	~1.80	~0.80[e]	...	...

[a] Data for $Na_4Sn_9\cdot6$–8en from ref 4. [b] From alloy $KSnSe_{1.5}Te_{0.5}$. NMR indicated the following solution composition: $SnSe_3^{2-}$, 55%; $SnSe_2Te^{2-}$, 35%; $SnSeTe_2^{2-}$, 10%. [c] From alloy $KSnSe_{0.5}Te_{1.5}$. NMR indicated the following solution composition: $SnSe_2Te^{2-}$, 10%; $SnSeTe_2^{2-}$, 45% $SnTe_3^{2-}$, 45%. [d] Reference 18. Line widths are not quoted. [e] A quadrupole doublet is shown for $[(CH_3)_4N]_4[Sn_2Te_6]$, but no values are given in the paper. [f] δ, Δ, and Γ values are ±0.01 mm s^{-1}.

mm s^{-1} with respect to α-Sn and a width at half-height of 1.90 mm s^{-1}. Attempts to obtain the ^{119}Sn NMR spectrum of this anion in en were unsuccessful. Somewhat later, an incomplete structural report of $Na_4Sn_9\cdot7$en (a corrected composition) appeared, the structure being limited by an inability to resolve the disordered ethylenediamine molecules.[5,6]

With the development of macrobicyclic ligands, such as 2,2,2-crypt,[7] which can be used to complex the alkali-metal cations in solutions of these Zintl phases, it has been possible to obtain stable crystalline "crypt" compounds after removal of the solvent. The X-ray crystal structures of a number of compounds containing novel homopolyatomic anions have now been reported, i.e. the following: $[Sn_9]^{4-}$ (C_{4v});[8] $[Sn_5]^{2-}$, $[Pb_5]^{2-}$ (D_{3h});[9] $[Ge_9]^{2-}$ (D_{3h}), $[Ge_9]^{4-}$ (C_{4v});[10] $[Sb_7]^{3-}$ (C_{3v});[11] $[As_{11}]^{3-}$ (D_3).[12] More recently, mixed-metal anions have been characterized, i.e. the following: $[Tl_2Te_2]^{2-}$;[13] $[TlSn_8]^{3-}$ and $[TlSn_9]^{3-}$;[14] $[Sn_2Bi_2]^{2-}$;[15] $[SnSe_4]^{4-}$, $[SnTe_4]^{4-}$.[16,17] The last anion was characterized by ^{119}Sn and ^{125}Te NMR in ethylenediamine solution.

Apart from that reported by Kummer and Diehl,[4] relatively little Mössbauer spectroscopy has been carried out on these Zintl species in spite of the fact that many of them contain elements that are Mössbauer active. In this paper we report our ^{119}Sn Mössbauer results for a variety of Zintl alloy phases of tin and of some classically and nonclassically bonded Zintl anions. Apart from the earlier $[Sn_9]^{4-}$ work and a recent publication dealing with $[SnTe_4]^{4-}$ and $[Sn_2Te_6]^{4-}$,[18] this is, to the best of our knowledge, the first comprehensive study of these species by Mössbauer spectroscopy. Our data are interpreted in the light of known structural and spectroscopic data.

Experimental Section

Materials and Preparations. Tin (Baker Analyzed, 99.9%), thallium (BDH, 99.999%), selenium (Alfa, 99.9%), and tellurium (Alfa, 99.5%) were used directly as obtained. Freshly cut sections of sodium (BDH, 99.8%) and potassium (MCB) were prepared and handled only in a drybox. Alloys were prepared by fusing together stoichiometric quantities of the appropriate elements in Pyrex or silica tubes. 2,2,2-Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Merck) was also used as received. Ethylenediamine (Fisher) was dried over CaH_2 and then vacuum distilled onto and stored over fresh CaH_2, from which it was vacuum distilled immediately prior to use.

All compounds were prepared according to their reported literature methods,[8,9,15,16] except for those containing $[SnX_3]_z^{2z-}$ and $[SnX_4]^{4-}$ (X

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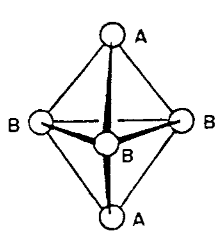
= Se and/or Te), whose preparations are discussed in ref 19. The identity and purity of all samples were verified by ^{119}Sn NMR studies or, if the structure was known, by X-ray powder photography.

Mössbauer Spectra. Mössbauer spectra were recorded on equipment that has already been described, except that a Promeda multichannel analyzer was used.[20] The source was Ca^{119m}SnO$_3$ purchased from Amersham-Searle and was maintained at room temperature throughout while the samples were cooled to low temperatures. The apparatus was periodically calibrated with use of ^{57}Co/Rh and a standard iron foil. Spectra were computer fitted with use of the program of Stone,[21] which has been modified by Dr. D. Grundy of the McMaster University Geology Department.

Results and Discussion

$[Sn_5]^{2-}$, $[Sn_9]^{4-}$, $[TlSn_8]^{5-}$, and $[Sn_2Bi_2]^{2-}$. Table I contains all of the data that we have recorded together with the literature data for Na$_4$Sn$_9$·6–8en. By way of comparison, two typical binary alloys (nonannealed), Na$_{1.7}$Sn and NaSn$_{2.25}$, were examined since these were the starting alloys from which the $[Sn_5]^{2-}$ and $[Sn_9]^{4-}$ Zintl anions were prepared. Both alloys gave complex spectra which clearly showed that the alloys contained more than one type of tin environment. The spectra were fitted, in each case, to two individual lines having the same width. The isomer shifts obtained from these analyses may not be too accurate because of the lack of resolution, but the lines appear to have values of ~2.1 and 2.7 mm s^{-1}. The former is close to that for α-Sn (2.02 mm s^{-1}), while the latter is similar to the value for β-Sn (2.54 mm s^{-1}),[22] though this may be coincidental. It is clear, however, that as the proportion of tin to sodium is increased the species having the higher isomer shift and hence s-electron density also increases.

Extraction of the Na$_{1.7}$Sn and NaSn$_{2.25}$ alloys with 2,2,2-crypt in ethylenediamine gives solutions from which solids containing the $[Sn_5]^{2-}$ and $[Sn_9]^{4-}$ ions may be isolated. The structures of these two anions have been established by X-ray crystallography,[8,9] and in the solid state these cluster anions have trigonal-bipyramidal (structure I) and monocapped-square-antiprismatic (structure II) geometries, respectively. In solution, however, $[Sn_9]^{4-}$ is known to be fluxional,[23] while all attempts to observe an NMR signal for $[Sn_5]^{2-}$ in solutions from which a solid containing this anion may be obtained have been unsuccessful.[17,24] The ^{119}Sn Mössbauer spectra of [Na(crypt)]$_2$[Sn$_5$] and [Na(crypt)]$_4$[Sn$_9$] were recorded at several temperatures, and the data are summarized in Table I. The spectrum for the $[Sn_5]^{2-}$ species at 77 K is shown in Figure 1a and consists of a quite asymmetric single line. This we have fitted to two peaks whose line widths we have constrained to be equal, allowing their positions and areas to vary. The isomer shifts obtained are 2.32 and 3.00 mm s^{-1}, and the two components are in the ratio 3.78:1. The structure of this anion, as determined by X-ray crystallography,[9] is that of a trigonal bipyramid with three equatorial tin atoms and two axial tin atoms. We might therefore have expected the Mössbauer analysis to show peaks in the ratio of 3:2 rather than the 3.78:1 actually found. Raising the temperature results in the peak ratio increasing to 5.45:1, indicating that the smaller peak corresponds to a tin atom with a lower Debye temperature than the other type of tin. On this basis we assign the more intense peak to the equatorial tin atoms, which have four nearest-neighbor tin atoms, while the axial tin atoms, with only three neighbors and therefore perhaps less rigidly bound, can be assigned to the smaller peak.[25] From the isomer shifts it is apparent that the axial tin atoms have the highest s-electron density. It is interesting to compare these data with those from the starting alloy Na$_{1.7}$Sn, where the s-electron densities for both tin sites have increased after the cation has been complexed by the crypt. We are not, however, suggesting that the $[Sn_5]^{2-}$ anion is present in the starting alloy.



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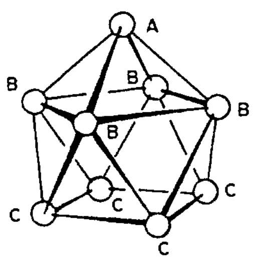

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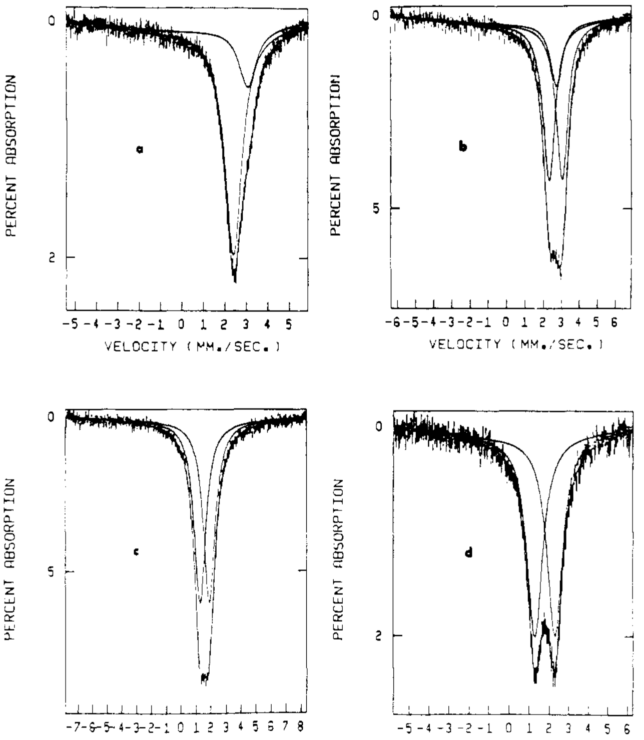

Figure 1. ^{119}Sn Mössbauer spectra at 77 K of (a) [Na(2,2,2-crypt)]$_2$[Sn$_5$], (b) [Na(2,2,2-crypt)]$_4$[Sn$_9$], (c) [Na(2,2,2-crypt)]$_4$[SnSe$_4$], and (d) [K(2,2,2-crypt)]$_{2z}$[SnSe$_m$Te$_n$]$_z$ obtained from the KSnSe$_{0.5}$Te$_{1.5}$ alloy.

A ^{119}Sn Mössbauer spectrum of Na$_4$Sn$_9$·6–8en has been measured[4] at 4.2 K and consists of one line with an isomer shift of +0.15 mm s^{-1} with respect to α-Sn. We have added 2.02 mm s^{-1} to this value as being the accepted conversion from α-Sn to CaSnO$_3$,[22] in order that we can compare this shift with our values. This introduces an unknown error into the isomer shift that we have reported in Table I, but this error is not likely to be serious. Of concern to us, however, is the reported line width of 1.90 mm s^{-1}, which is twice that expected from an unsplit absorption. This value is, in fact, larger than the overall width at half-height of the spectrum of [Na(crypt)]$_4$[Sn$_9$] that we have recorded at 77 K and that is shown in Figure 1b. This spectrum clearly does not arise from a single tin atom in a cubic environment. We attempted to fit this spectrum in a variety of ways, and the most

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(25) Note that there is some positional disorder at the $[Sn_5]^{2-}$ anionic sites with major (86%) and minor (14%) components, the latter being a rotation of about 60° around the threefold axis of the trigonal bipyramid together with a slight displacement (0.25 Å) along this axis, with respect to the major component. It is not felt that this disorder is the cause of the asymmetric single line for $[Sn_5]^{2-}$ as the ratio of 86:14 (6.14:1) is very different from the observed ratio of the areas (3.78:1) and would imply that the isomer shifts of the two environments of the trigonal bipyramid are the same. Furthermore, such a model would require that the relative areas show little or no change with temperature, as was clearly not the case (see Table I).

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Table II. Charge Calculations for the $[Sn_5]^{2-}$ and $[Sn_9]^{4-}$ Anions[a]

$[Sn_5]^{2-}$

	site[b]	
	A	B
extended Hückel	−0.49	−0.34
relativistic extended Hückel	−0.32	−0.45
SCF-CNDO	−0.53	−0.31

$[Sn_9]^{4-}$

	site[b]		
	A	B	C
extended Hückel	−0.58	−0.26	−0.60
relativistic extended Hückel	−0.45	−0.32	−0.57
SCF-CNDO	−0.75	−0.25	−0.55

[a] Data taken from ref 8, 26, and 27. [b] For a definition of these sites,see structures I and II.

satisfactory fit is the one shown. This was a fit of two lines of equal intensity plus a third, less intense, line; all three lines were constrained to be of equal width. This choice was, not surprisingly, influenced by the known geometry of the $[Sn_9]^{4-}$ anion, which has been reported by Corbett and Edwards.[8] This anion has the monocapped-square-antiprismatic configuration, like the appropriate (but presently unknown) *nido*-borane, with the tin atoms being held together by $2n + 4$ (=22) skeletal electrons. In the structure there are three types of tin atoms in the ratio 1:4:4, and if one bears in mind the constraints placed on the fitting procedure, our spectrum is in good agreement with this. The fact that earlier workers[4] obtained only one very broad resonance with a quite different isomer shift suggests that perhaps their sample was impure, although the broadness may be attributable, in part, to the somewhat distorted geometry of the anion in this compound (described as a distorted, tricapped trigonal prism[5,6]), with many of the atoms to one side of the anion having large thermal ellipsoids suggestive of positional disorder.[8] Also, the absence of a crypting agent for the sodium would result in stronger cation–anion interactions and further complicate the spectrum.

While assignment of the two resonances observed for the $[Sn_5]^{2-}$ anion was straightforward and was based upon the relative areas of the two peaks as discussed earlier, it is not immediately obvious how the assignment should be made for $[Sn_9]^{4-}$. Clearly the peak of the lowest intensity should be assigned as tin atom A in structure II. In $[Sn_5]^{2-}$ (structure I), the apical tin atoms A have a higher s-electron density than the equatorial B atoms. Extended-Hückel and SCF–CNDO calculations show that there is a higher negative charge at A than at B, though a relativistic extended-Hückel calculation shows the opposite trend (Table II). For $[Sn_9]^{4-}$ (structure II) all three types of calculations put the smallest negative charge on atoms B and all but the SCF–CNDO calculation place the highest charge on C. We have therefore assigned the peak at 2.25 mm s^{-1} to Sn_B, that at 2.67 mm s^{-1} to Sn_A, and the remaining peak at 2.98 mm s^{-1} to Sn_C.

Replacement of a tin atom in $[Sn_9]^{4-}$ by thallium, with retention of the 40-valence-electron count (22 skeletal electrons), gives the $[TlSn_8]^{5-}$ anion, which has been identified by Rudolph and coworkers using ^{119}Sn NMR.[17] This anion is fluxional in solution, but in the solid state, it is expected to possess the monocapped-square-antiprismatic configuration (like structure II). Assuming that the thallium atom occupies the unique capping position as is found from the structural characterization of the related $TlSn_9^{3-}$ and $TlSn_8^{3-}$ anions,[14] then there would be only two types of tin atoms and by analogy with the other tin polyanions there should be two Mössbauer resonances of equal area, assuming equal recoil-free fractions. However, should the thallium atom occupy a capped or basal position as predicted from relativistic extended-Hückel calculations[27] (although the energy differences between the various alternatives are small), then the Mössbauer spectrum would be considerably more complicated.

Attempts to obtain $[TlSn_8]^{5-}$ as a crypt compound were unsuccessful; extraction of $NaSnTl_{1.5}$ in ethylenediamine in the presence of 2,2,2-crypt gave several products identical with those formed by extraction of KTlSn under the same conditions,[14] but no evidence for $[TlSn_8]^{5-}$. We therefore decided to extract only with ethylenediamine since Rudolph and co-workers[17] had identified $[TlSn_8]^{5-}$ by ^{119}Sn NMR in this solvent in the absence of 2,2,2-crypt[28] and also were able to isolate a solid of composition $[Na_5(en)_2(TlSn_8)]$ from such solutions. Slow evaporation yielded a red-brown solid whose Mössbauer spectrum was recorded. The spectrum obtained was very similar to that shown in Figure 1b, and the data (Table I) are very similar to those obtained for $[Na(crypt)]_4[Sn_9]$. It would appear either that the fluxional (in solution) $[TlSn_8]^{5-}$ crystallizes in a disordered manner, as found for the $[Sn_9]^{4-}$ anion in $Na_4Sn_9{\cdot}7en$, to give at least three tin environments or that the thallium atom does not occupy the expected capping position. We also prepared an alloy of composition Na_5TlSn_8, since an alloy of this overall composition would result on complete loss of ethylenediamine from $[Na_5(en)_2(TlSn_8)]$. The Mössbauer spectrum of this alloy (nonannealed) appeared as a broad, almost featureless resonance, having an isomer shift of 2.68 mm s^{-1} and a line width of 1.85 mm s^{-1}. Fitting this spectrum to three overlapping lines does give a better fit, and these data are reported in Table I. The isomer shifts are comparable to those of the binary Na–Sn alloys. Also, they are similar to those of $[Na_5(en)_2(TlSn_8)]$, suggesting strong cation–anion interactions are present in the latter, as certainly must be the case in view of the low ratio of ethylenediamine molecules to sodium cations in this compound compared to that in the case of $Na_4Sn_9{\cdot}7en$.

We have also attempted to isolate pure samples of $[Sn_9]^{3-}$ by extraction of KSn_2 (or KSn_3) in ethylenediamine in the presence of 2,2,2-crypt.[29] Unfortunately, the NMR spectra of these solutions always showed evidence for considerable quantities of the $[Sn_9]^{4-}$ species. The NMR spectra exhibited broad signals ($\Delta\nu_{1/2}$ = 1100 Hz) with chemical shifts corresponding to $[Sn_9]^{4-}$, the broadening probably resulting from relaxation by the paramagnetic $[Sn_9]^{3-}$ anion. It was difficult to estimate the relative amounts of $[Sn_9]^{3-}$ and $[Sn_9]^{4-}$ present at any one time in solution. Hence, it was not surprising to us that the solids isolated from these solutions gave ^{119}Sn Mössbauer spectra that were similar in appearance to those of $[Sn_9]^{4-}$. Further analyses of these solids were not pursued.

It should be pointed out that, for all of the anions discussed above, none of them have any tin atoms in cubic environments. Because of this, one might have expected that each tin environment would then give rise to a quadrupole doublet rather than a single line. However, the observation of only a single resonance line from a compound containing tin in a noncubic environment is certainly not unprecedented. Numerous examples exist in the literature, and some of these have been tabulated by Greenwood and Gibb.[30] One would, however, need to examine these earlier data rather carefully in order to establish that a quadrupole splitting had not gone undetected through the use of a broadened source or thick absorbers. Our line widths are generally quite narrow, and we are therefore confident that there are no unresolved quadrupole splittings in the absorption envelopes of the compounds discussed above.

The situation is, however, different for the mixed tin–bismuth cluster anion $[Sn_2Bi_2]^{2-}$. The geometry of this anion is based on a tetrahedron with tin and bismuth atoms at the apices with both elements exhibiting a 50% occupancy at each apex (the site symmetry of the anion is C_1).[15] Irrespective of this occupational disorder, the tin atoms are equivalent, each having one tin and two bismuth neighbors, and hence the symmetry at tin is far from

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[27] Lohr, L. L., Jr. *Inorg. Chem.* **1981**, *20*, 4229.

[28] Our studies indicate that there is about 3% $[Sn_9]^{4-}$ impurity formed on extraction under these conditions, based on ^{119}Sn NMR integrated intensities of both species.

[29] Critchlow, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 5715.

[30] Greenwood, N. N.; Gibb, T. C. "Mössbauer Spectroscopy"; Chapman and Hall: London, 1971; p 371.

cubic. One would therefore expect to obtain a quadrupole split absorption for this anion. This is indeed observed; the isomer shift is 2.75 mm s^{-1}, and the quadrupole splitting is 1.07 mm s^{-1}. Note that the isomer shift is very similar to those of the other nonclassically bonded Zintl anions even though this anion is isovalent with P_4 (20 valence electrons) and can be represented by a single valence bond structure involving six two-center–two-electron bonds and perhaps should be considered classically bonded.

$[SnX_4]^{4-}$ and $[SnX_3]_z^{2z-}$ = Se and/or Te). Zintl anions having classical structures where the tin is bonded by formal two-electron bonds to other nuclei are known. The X-ray crystal structure of the $[SnSe_4]^{4-}$ anion in $Na_4SnSe_4{\cdot}16H_2O$ has been reported,[16] and there is NMR evidence for a $[SnTe_4]^{4-}$ anion.[17] These two anions are described as having a tetrahedral arrangement of selenium or tellurium atoms about the central tin atom. In solution, the evidence[17,19] appears to be in favor of such a regular tetrahedral arrangement, although in the solid state in $Na_4SnSe_4{\cdot}16H_2O$ the $[SnSe_4]^{4-}$ anion has a symmetry lower than T_d (it is C_s) since all Sn–Se bonds are not equal in length (2.504 (2)–2.527 (2) Å) nor are all Se–Sn–Se angles of the tetrahedral value but vary from 106.6 (1) to 111.1 (1)°.[16] Table I contains our ^{119}Sn Mössbauer data for the two $[SnX_4]^{4-}$ species. The isomer shifts are significantly smaller than those for the cluster Zintl anions, indicating that s-electron density has been removed from the tin (with formal sp^3 character) presumably via covalent bonds to the chalcogen ligands. The more electronegative selenium is more effective in this regard, and as a result, the isomer shift of $[SnSe_4]^{4-}$ is found to be less positive than that of $[SnTe_4]^{4-}$, whose isomer shift is close to that reported by Huffman et al.[18] Analysis of either spectrum as a single resonance arising from an anion with T_d symmetry was not satisfactory, and better fits were obtained when two lines of equal intensity were used for the simulations in each case (Figure 1c). In other words, each resonance was a closely spaced quadrupole doublet having a separation of 0.62 mm s^{-1} in the case of $[SnSe_4]^{4-}$ and 0.63 mm s^{-1} for $[SnTe_4]^{4-}$. Huffman and co-workers[18] report only a single absorption for their K_4SnTe_4, and they conclude that $[SnTe_4]^{4-}$ is tetrahedral. We conclude that both anions are distorted in the solid state in our compounds, as has been observed for the $[SnSe_4]^{4-}$ anions in $Na_4SnSe_4{\cdot}16H_2O$. Frozen-solution spectra of these species in ethylenediamine gave similar results, though the quality of the spectra were not as good. Although the tin in $[SnX_4]^{4-}$ (X = Se, Te) may have T_d symmetry in the liquid solution, the frozen-solution spectra show noncubic tin environments. However, these distortions could be imposed by freezing of the solvent. NMR, being a relatively "slow" technique on the spectroscopic time scale, could not be expected to detect such small time-averaged distortions.

Since both the $[SnSe_4]^{4-}$ and $[SnTe_4]^{4-}$ anions had been characterized, it seemed reasonable that the mixed species $[SnSe_{4-x}Te_x]^{4-}$ should exist. With the idea of obtaining such species, alloys of composition $KSnSe_{1.5}Te_{0.5}$ and $KSnSe_{0.5}Te_{1.5}$ were extracted with ethylenediamine in the presence of 2,2,2-crypt. Examination of these solutions by ^{119}Sn, ^{125}Te, and ^{77}Se NMR showed that no $[SnX_4]^{4-}$ anions were present, but evidence for a new series of species was obtained.[31] The following new anions were identified from their NMR spectra: $[SnSe_3]^{x-}$, $[SnSe_2Te]^{x-}$, $[SnSeTe_2]^{x-}$, and $[SnTe_3]^{x-}$, where x would be 2 or 4 depending upon whether the tin is in a formal oxidation state of IV or II, respectively. These anions could either be planar or pyramidal, again depending upon the formal oxidation state of the tin and provided that the coordination number of the tin remains 3. NMR data indicated that the solution obtained from the $KSnSe_{1.5}Te_{0.5}$ alloy contained $[SnX_3]^{x-}$ species in the following proportions: $[SnSe_3]^{x-}$, 55%; $[SnSe_2Te]^{x-}$, 35%; $[SnSeTe_2]^{x-}$, 10%. The $KSnSe_{0.5}Te_{1.5}$ alloy gave the following proportions: $[SnTe_3]^{x-}$, 45%; $[SnSeTe_2]^{x-}$, 45%; $[SnSe_2Te]^{x-}$, 10%. Tin-119 Mössbauer spectra of the products obtained after evaporation of the solvent from these solutions were recorded, and the data are summarized in Table I, together with data for samples obtained from solutions of $[SnSe_3]^{x-}$ and $[SnTe_3]^{x-}$. These last samples were obtained, not unexpectedly, by removal of the solvent from extractions of the ternary alloys $KSnSe_2$ and $KSnTe_2$ with ethylenediamine in the presence of 2,2,2-crypt.

It is clear from the isomer shifts that these species do not contain Sn(II) since the isomer shifts are smaller than that for α-Sn. The values (~1.6–1.8 mm s^{-1}) are similar to those found for $[SnSe_4]^{4-}$ and $[SnTe_4]^{4-}$, 1.47 and 1.76 mm s^{-1}, respectively. The same trends are found in this series as in the $[SnX_4]^{4-}$ series in that the selenium analogue has the lower isomer shift, at least for the end members. One might have expected the Mössbauer spectra obtained from the solids isolated from the mixed selenium–tellurium alloy extractions to show peaks corresponding to the individual compounds which are known to be present in solution. However, the spectra are quite clean and all appear as well-resolved quadrupole doublets with no evidence of any line asymmetry (Figure 1d). Since the parameters for the end members do not vary by more than 0.2 mm s^{-1}, detection of the intermediate species in a mixture containing three components would be virtually impossible by Mössbauer spectroscopy.

The isomer shift of the solid obtained from solutions of the $[SnTe_3]^{2-}$ anion is very similar to the shifts of K_4SnTe_4 (1.71 (2) mm s^{-1}),[18] $[SnTe_4]^{4-}$ (1.76 mm s^{-1}, this work), and $[(CH_3)_4N]_4[Sn_2Te_6]$ (~1.80 mm s^{-1}),[18] indicating the same s-electron density on tin. This suggests that the bonding pattern in these three anions is similar and throws doubt on the likelihood that the $[SnTe_3]^{2-}$ anion has a trigonal-planar structure in the solid state. The quadrupole splitting for the solid product obtained from the solution of $[SnTe_3]^{2-}$ salts is larger than that reported by Huffman et al.[18] These workers report a quadrupole splitting value of ~0.8 mm s^{-1} for $[(CH_3)_4N]_4[Sn_2Te_6]$ while we find a splitting of 1.02 mm s^{-1} for $[K(crypt)]_{2z}[SnTe_3]_z$ indicating that the salt, in which the cation is crypted, contains a tin atom in a more distorted environment than that found for $[(CH_3)_4N]_4[Sn_2Te_6]$.[18] Whether this difference in quadrupole splitting between $[(CH_3)_4N]_4[Sn_2Te_6]$ and $[K(crypt)]_{2z}[SnTe_3]_z$ reflects the difference between a distorted-tetrahedral structure and a trigonal-planar arrangement with $z = 1$ is difficult to say. If $z = 2$ and $[SnTe_3]^{2-}$ has dimerized on removal of solvent, then the arrangement about the tin is much more distorted than that found by Huffman.[18] Such an increased distortion then could arise because of the reduced cation–anion contacts as a result of using the much larger cation $[K(2,2,2\text{-crypt})]^+$. We are attempting to obtain supporting evidence for one or the other of these structures.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. We also wish to thank one of the reviewers for helpful suggestions and discussion and for making available his data on $[Sn_2Te_6]^{4-}$ in advance of publication.

Registry No. $CaSnO_3$, 12013-46-6; $Na_{1.7}Sn$, 94781-06-3; $NaSn_{2.25}$, 74846-76-7; $[Na(crypt)]_2[Sn_5]$, 61665-35-8; $[Na(crypt)]_2[Sn_9]$, 58787-49-8; Na_5TlSn_8, 89680-10-4; $[K(crypt)]_2[Sn_2Bi_2]{\cdot}en$, 82167-47-3; $[Na(crypt)]_4[SnSe_4]$, 94781-08-5; $[Na(crypt)]_4[SnTe_4]$, 94781-09-6; $K_4[SnTe_4]$, 85533-99-9; $[K(crypt)]_{2z}[SnSe_3]_z$, 94800-02-9; $[K(crypt)]_{2z}[SnSeTe_2]_z$, 94800-04-1; $[K(crypt)]_{2z}[SnSe_2Te]_z$, 94800-06-3; $[K(crypt)]_{2z}[SnTe_3]_z$, 94800-07-4; $[(CH_3)_4N]_4[Sn_2Te_6]$, 94781-11-0.

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(31) The mixed $[SnSe_{4-x}Te_x]^{4-}$ (x = 1–3) anions were subsequently obtained by extraction of the alloys $NaSnSe_{0.33}Te_{0.67}$ and $NaSnSe_{0.67}Te_{0.33}$ with en in the presence of 2,2,2-crypt and identified by ^{119}Sn, ^{77}Se, and ^{125}Te NMR.[19]