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Bonding in Some Zintl Phases: A Study by Tin-119 Mössbauer Spectroscopy

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The ^{119}Sn Mössbauer parameters for a range of Zintl phase compounds are reported. The compounds containing tetrahedrally coordinated tin of composition M_5SnX_3 (M = Na, K; X = P, As, Sb) have chemical isomer shifts close to that of grey-tin and can be considered to be covalently bonded species. The layer structures of composition $KSnX$ (X = As, Sb) and double-layer compounds MSn_2X_2 (M = Na, Sr; X = As, Sb) have tin in a distorted octahedral environment. The chemical isomer shifts are closer to that of white-tin and can be interpreted in terms of metallic bonding. © 1995 Academic Press, Inc.

INTRODUCTION

Although about three-quarters of all elements are metals or semimetals, the binary and ternary compounds of such elements have not attracted the same degree of attention which chemists have, over many years, given to compounds containing nonmetals. The synthesis of intermetallic compounds of the type A_xB_y, where A is an electropositive metal from Groups I or II and B is a main group IV or V metal or semimetal, initiated by Eduard Zintl during the period 1928 to 1941, gave rise to a range of materials which are now called Zintl phases (1, 2).

Zintl postulated that the stoichiometries and structures of these deeply colored intermetallic phases which sometimes have metallic luster can be interpreted by an ionic concept whereby the electropositive metals A lose their valence electrons to the semimetals B, which gain as many electrons as are necessary to complete their octets. This produces anionic substructures which can be isostructural to the isoelectronic elements. However, a variety of other structures can also be formed, such as clusters with chain-type structures or two- and three-dimensional nets in which the atoms can form different numbers of bonds providing the electron count is satisfied. The structures of ternary phases composed of two semimetals from different Groups and a nonnoble metal often appear as clusters which resemble the complex oxo- or thio-anions such as silicates.

Although the structural properties of many of the binary- and ternary-Zintl phase compounds involving ionic formulations including covalently bonded ionic substructures are now well known, the nature of the bonding remains the subject of some uncertainty (1, 2) and there have been few studies of such materials by Mössbauer spectroscopy (3–5). We report here a study by ^{119}Sn Mössbauer spectroscopy of some Zintl phase compounds of the type M_5SnX_3 (M = Na, K; X = P, As, Sb) with structures based on tetrahedral units; single-layer materials of the type $KSnX$ (X = As, Sb) and structures with double layers of the formula $NaSn_2X_2$ (X = As, Sb), $SrSn_2As_2$, and Sn_4As_3.

EXPERIMENTAL

Compounds of composition M_5SnX_3 (M = Na, K; X = P, As, Sb), $KSnX$ (X = As, Sb), $NaSn_2X_2$ (X = As, Sb), and $SrSn_2As_2$ were prepared by sealing stoichiometric quantities of the elements in evacuated quartz tubes and heating the ampoules in a sand bath gradually increasing the temperature over 4 hr to 973 K (K-compounds), 1073 K (Na-compounds), or 1273 K ($SrSn_2As_2$). The temperature was maintained for 1 hr before quenching the ampoules in liquid nitrogen. The quenched samples were tempered at 523 to 573 K for 8 days. For the synthesis of $Na_5[SnSb_3]$, $K_5[SnSb_3]$, and Sn_4As_3 the ampoules were heated to 1023 K at a rate of 100 K/hr, maintained at this temperature for 1 hr, and then cooled at a rate of 60 K/hr (20 K/hr for Sn_4As_3) to room temperature. The alkali metal compounds, especially compounds of composition M_5SnX_3, are hydrolyzed by moist air within a few minutes. $SrSn_2As_2$ is less reactive. All compounds were handled in an argon-filled glove box. The identity and purity of the compounds was established by X-ray powder diffraction. Samples for Mössbauer spectroscopy were sealed under argon in specially designed brass holders with mylar windows.

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^{119}Sn Mössbauer spectra were recorded at 298 K with a microprocessor controlled Mössbauer spectrometer using a $Ca^{119m}SnO_3$ source. The drive velocity was calibrated with a ^{57}Co–Rh source and a natural iron foil. The spectra were computer fitted by constraining the areas of peaks representing doublets to be equal and the peaks to have equal linewidth. The ^{119}Sn Mössbauer chemical isomer shift data are referred to tin(IV) oxide.

RESULTS AND DISCUSSION

The ^{119}Sn Mössbauer parameters of the compounds are contained in Table 1.

1. Na_5SnP_3, Na_5SnAs_3, and K_5SnSb_3

The isostructural compounds Na_5SnP_3, Na_5SnAs_3, and K_5SnSb_3 contain (6, 7) anionic sublattices which consist of edge-sharing tetrahedral $[Sn_2X_6]^{10-}$ units (X = P, As, Sb) (Fig. 1).

The coordination about tin in these compounds is illustrated by a consideration of the $[Sn_2P_6]^{10-}$ anion (6). The SnP_4 tetrahedron contains two bonds from tin to terminal phosphorus atoms with a length of 250.4 pm approximately equivalent to the sum of the Pauling covalent radii of tin and phosphorus. Although the bonds between the bridging phosphorus atoms and tin are longer (258.0 pm), the tin–phosphorus distances are indicative of predominantly covalent character in the bonding. The internal Sn_2P_2 ring angle P–Sn–P is 96.3°, while other angles vary between 107.3 and 116.1°. The distance of 344.8 pm between tin atoms in each anion is too large to justify a consideration of Sn–Sn bonding interactions.

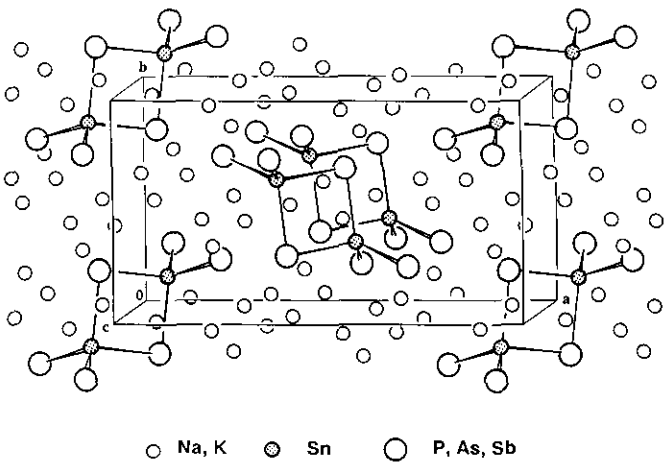

FIG. 1. Edge-sharing tetrahedra in $[Sn_2X_6]^{10-}$ anions (X = P, As, Sb).

The ^{119}Sn Mössbauer spectrum recorded from Na_5SnP_3 was best-fitted to a quadrupole split absorption and a single peak. The single peak can be associated with a small quantity of a tin(II) impurity phase which originated during the recording of the spectrum. The spectra from the compounds Na_5SnAs_3 and K_5SnSb_3 were similar with the doublet components being associated with the asymmetric array of atoms around tin in Na_5SnX_3 and the single peak characteristic of the impurity tin(II) species. The dependence of the ^{119}Sn Mössbauer chemical isomer shift on the Pauling electronegativity of the Group V element is shown in Fig. 2. The approximately linear increase in

TABLE 1
^{119}Sn Mössbauer Parameters of Zintl Phase Compounds Recorded at 298 K

Compound		$\delta \pm 0.05$ (mm sec^{-1})	$\Delta \pm 0.07$ (mm sec^{-1})
Na_5SnP_3		1.54	0.59
	Impurity	2.82	
Na_5SnAs_3		1.79	0.44
	Impurity	0.14	
	Impurity	2.90	
K_5SnSb_3		1.96	0.35
	Impurity	2.87	
Na_5SnSb_3		2.22	0.55
KSnAs		2.33	1.15
KSnSb		2.59	0.96
$NaSn_2As_2$		2.67	0.57
$NaSn_2Sb_2$		2.71	0.48
$SrSn_2As_2$		2.62	0.55
Sn_4As_3	Impurity	−0.09	
		2.68	0.48

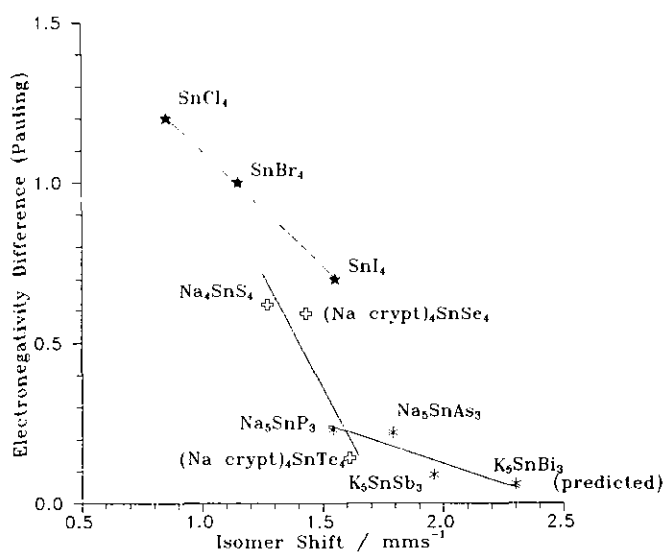

FIG. 2. Variation of ^{119}Sn Mössbauer chemical isomer shift with Pauling electronegativity in some tin-containing compounds.

the chemical isomer shift with decreasing electronegativity of the Group V element reflects the withdrawal of less electron density from tin and resembles the trend previously described for the tetrahedral tin(IV) halides (8). An approximately linear relationship between the ^{119}Sn Mössbauer chemical isomer shift and the electronegativity of the chalcogen atoms in tetrahedral tin chalcogenides is also demonstrated for the first time in Fig. 2 using data taken from the literature (3, 5, 8). Extrapolation of the data for the M_5SnX_3 compounds (X = P, As, Sb) indicates that the chemical isomer shift of K_5SnBi_3 should be ca. 2.3 mm sec^{-1} (the attempted acquisition of the Mössbauer spectrum was precluded by the high nonresonant absorption of γ-rays by bismuth). The chemical isomer shifts of the M_5SnX_3 (X = P, As, Sb) compounds are comparable (8) with those recorded from covalently bonded organotin(IV) halides (e.g., $Bu^n_2SnI_2$, δ 1.80 mm sec^{-1}). This can be contrasted with $SnCl_4$ (where Sn atoms occupy tetrahedral holes in a *ccp* array of highly electronegative halogen atoms), which has a much lower chemical isomer shift (8) of 0.85 mm sec^{-1}. Therefore the chemical isomer shift of 1.96 mm sec^{-1} recorded from the $SnSb_4$ tetrahedra in K_5SnSb_3 is indicative of more covalent character in the bonding and approaches the value of grey-tin (2.00 mm·sec^{-1}) (8), which contains tetrahedrally arranged homonuclear covalent bonds. We therefore suggest that tin in M_5SnX_3 compounds be considered as being sp^3 hybridized and, given the highly positive character of the chemical isomer shift data, to be involved in covalent bonding with the Group V element.

The variation of the quadrupole splitting with Sn–X distances in compounds of the type Na_5SnX_3 (X = P, As, Sb) may also be associated with the electronegativity of the X atom in that the larger and less electronegative X atoms give rise to longer bond lengths resulting in less withdrawal of electron density along the sp^3 hybridized orbitals.

2. Na_5SnSb_3

In the structure of Na_5SnSb_3 an infinite chain of corner-sharing tetrahedra is formed in which the antimony atoms form a distorted tetrahedral array around the tin similar to that found in chain silicates (9). The ^{119}Sn Mössbauer spectrum showed a small quadrupole splitting consistent with the slightly distorted tetrahedral environment around tin. The less positive chemical isomer shift recorded from K_5SnSb_3 which is composed of edge-sharing tetrahedra as compared to that recorded from Na_5SnSb_3 containing an infinite corner-sharing chain suggests that the joining of structural units results in an increase in the withdrawal of *s*-electron density from tin toward the coordinating atoms. This will be the subject of further consideration in subsequent work.

3. *KSnAs and KSnSb*

The compounds KSnAs and KSnSb are isostructural (10, 11) and consist of single-layer-type structures involving puckered nets of alternate tin and arsenic/antimony atoms separated by potassium atoms (Fig. 3). The puckered net is similar to that found in elemental arsenic and antimony. The Sn–As bond length within the [SnAs] net of KSnAs of 271.0 pm is longer than the sum of the Pauling covalent radii (260 pm). The As–Sn–As bond angle of 98.4° is comparable to that in elemental arsenic of 96.7°. In KSnSb the Sn–Sb distances are 288.3 pm compared with the sum of the Pauling covalent radii of 281 pm. The Sb–Sn–Sb bond angle is 97.9°. Band structure calculations (12) have indicated little difference between KSnAs and KSnSb and have associated the compounds with a small band gap with electron transfer from potassium to the tin–arsenic or tin–antimony net.

If the Zintl concept is formally obeyed then the nets can be described as $[SnAs]^-$ and $[SnSb]^-$ and, since they are isoelectronic to elemental arsenic and antimony, the bonding interactions can be considered in terms of an sp^3 hybridized system with tin containing a stereochemically active lone pair. The ^{119}Sn Mössbauer spectra recorded from KSnAs and KSnSb were similar (Fig. 4) and showed quadrupole split absorptions consistent with the distorted environment about tin. Given that the tin–potassium dis-

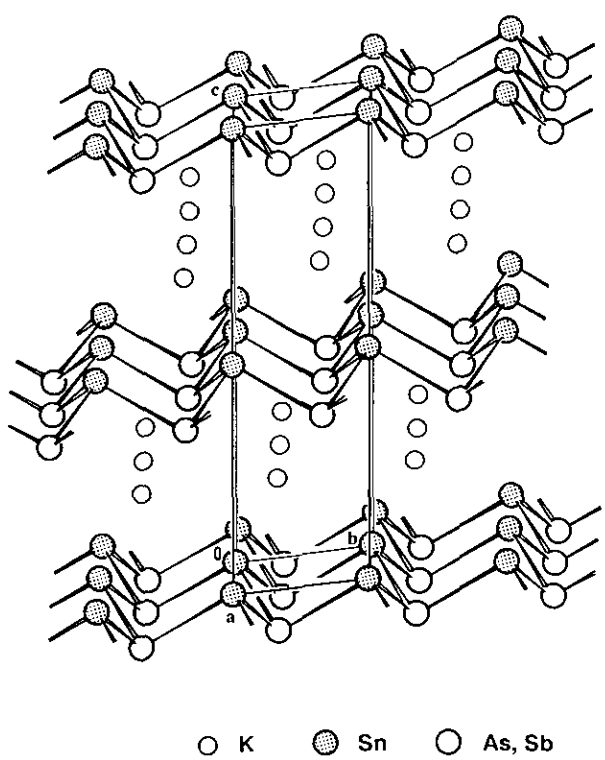

FIG. 3. Single-layer structures of KSnAs and KSnSb.

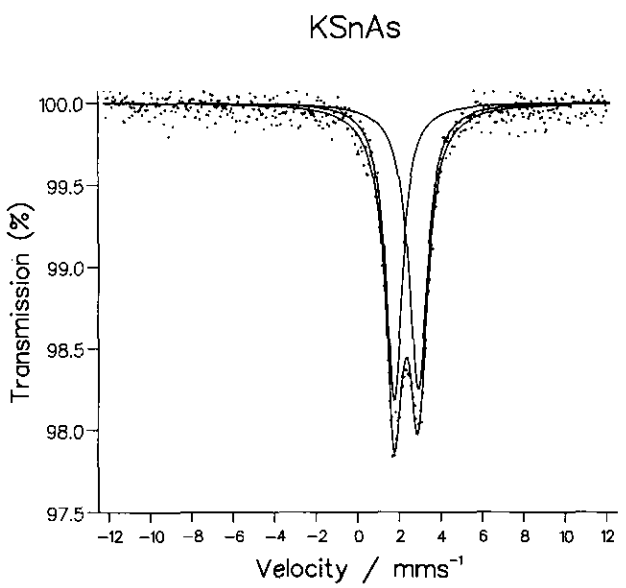

FIG. 4. ^{119}Sn Mössbauer spectrum recorded from KSnAs at 298 K.

tances are similar in both materials, the larger quadrupole splitting in KSnAs may be associated with the higher electronegativity of As and also the shorter tin–arsenic distances which give rise to a more distorted octahedral array around tin of three pnicogen and three potassium neighbors.

The transition from tetrahedrally coordinated tin in Na_5SnAs_3 and K_5SnSb_3 (*vide supra*) to the trigonal pyramidal coordination of tin in KSnAs and KSnSb can be envisaged as involving increasing *p*-character in the covalent tin–arsenic and tin–antimony bonds. The consequent deshielding of the 5*s* electron orbital results in higher chemical isomer shifts for KSnAs and KSnSb. The larger chemical isomer shift for KSnSb can be associated with the lower electronegativity of antimony as compared to arsenic and is in accord with the trend observed in the tetrahedral compounds (*vide supra*).

The value of δ for KSnAs (2.33 mm sec^{-1}) lies between that reported (8) for grey- and white-tin (2.00 and 2.56 mm sec^{-1}, respectively) whereas in KSnSb, the chemical isomer shift (δ 2.59 mm sec^{-1}, is closer to that of white-tin, suggesting that the bonding is more metallic in character. The band structure calculations (12) indicate an electron transfer to the [SnAs] or [SnSb] net with the transferred charge being delocalized over the atoms within the net. The larger ^{119}Sn Mössbauer chemical isomer shifts are consistent with this and are indicative of metallic character in the bonding in these phases. The sensitivity of the chemical isomer shift to the presence of arsenic or antimony reflects the more metallic nature of the antimony-containing analogue.

4. *$NaSn_2As_2$ and $NaSn_2Sb_2$*

The structures (13) of the compounds $NaSn_2As_2$ and $NaSn_2Sb_2$ contain puckered nets analogous to those in KSnAs and KSnSb but with a different stacking arrangement and a different coordination about tin. The nets are stacked so that every second layer is separated by sodium atoms and are oriented such that the tin has distorted trigonal antiprismatic coordination formed by three Group V atoms within the same net and three tin atoms in the neighboring net (Fig. 5). A sequence of three double layers is observed in $NaSn_2As_2$ (Fig. 5) and of two in $NaSn_2Sb_2$ while retaining a common environment about tin. The bond distances within the net (Sn–As 267.8 pm and Sn–Sb 289.3 pm) are slightly larger than the sum of the Pauling covalent radii (260 and 280 pm, respectively). The tin–tin interlayer distances in both compounds (333.3 and 333.7 pm) are indicative of weak bonding interactions.

These compounds cannot be treated as classical Zintl phases since, according to the Zintl concept, two electrons would need to be donated to the anionic sublattice and in these compounds sodium can only contribute one

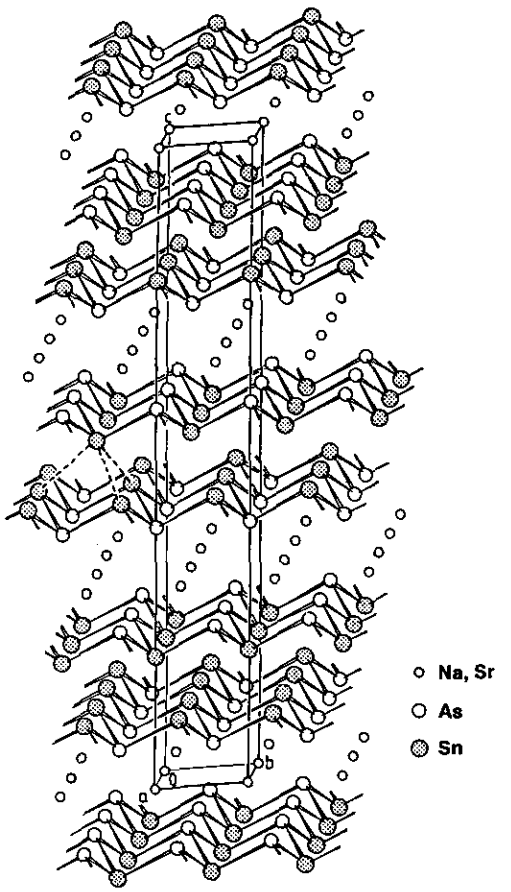

FIG. 5. $^{2}_{\infty}[Sn_2As_2]$ and $^{2}_{\infty}[Sn_2Sb_2]$ double layers in $SrSn_2As_2$ and $NaSn_2Sb_2$. The dotted lines indicate the local coordination of tin.

electron. Band structure calculations (12) for $SrSn_2As_2$, which conforms to the Zintl concept and which is isostructural with $NaSn_2As_2$, indicate a very small band gap and also infer only partial electron transfer from strontium to the net. It would appear that the additional weak tin–tin interactions have a stabilizing effect which compensate for the electron deficiency in these double-layer compounds.

The ^{119}Sn Mössbauer spectra recorded from $NaSn_2As_2$ and $NaSn_2Sb_2$ were fitted to quadrupole split absorptions consistent with the distorted trigonal antiprismatic coordination about the tin. The tin–tin interactions result in the coordination being more symmetric than the materials with a single-layer structure and give rise to a smaller quadrupole splitting.

The chemical isomer shifts of the double-layer compounds $NaSn_2As_2$ (δ 2.67 mm sec^{-1}) and $NaSn_2Sb_2$ (δ 2.71 mm sec^{-1}) are larger than that of white-tin (δ 2.56 mm sec^{-1}) (8). This observation suggests that the change in coordination about tin involves an increase in *p*-character of the bonds and a concomitant decrease in the shielding of the 5*s* electrons of tin: here a tin atom is coordinated by three Group V atoms and three Sn atoms instead of three K^+ cations as in KSnAs. The deshielding effect is enhanced by an increase in the number of electronegative ligands in the coordination sphere of the tin. The more positive chemical isomer shift of $NaSn_2Sb_2$ as compared to that of $NaSn_2As_2$ reflects the difference in the electronegativity of the Group V element (*vide supra*).

5. $SrSn_2As_2$

$SrSn_2As_2$ is isostructural (11) with $NaSn_2As_2$, in which each tin is bonded to three other tin species and to three arsenic species (Sn–As 278.4 pm, Sn–Sn 329.9 pm). The similarity of the environment about tin in these materials and in $NaSn_2Sb_2$ is reflected by the similarity of the ^{119}Sn Mössbauer parameters (Table 1).

$SrSn_2As_2$ can be envisaged in terms of the Zintl concept if valence electrons from strontium are transferred to the tin atoms to produce anionic sublattices of $^2_\infty[SnAs]^-$ in which the elements obey the octet rule. Band theory calculations (12) suggest that this simple model is not obeyed and that only partial electron transfer from strontium is likely to occur. The similarity of the Mössbauer parameters recorded from $SrSn_2As_2$, $NaSn_2As_2$, and $NaSn_2Sb_2$ are consistent with this.

6. Sn_4As_3

The compound Sn_4As_3 has no Group I or II metal and is not a Zintl phase compound (14) although its structure shows a strong relationship to that of $SrSn_2As_2$ and can be described as a sequence of double layers $[Sn_2As_2]$ as in $SrSn_2As_2$ and $NaSn_2As_2$, followed by a sheet of $[AsSn_2]$ edge-sharing octahedra, $[AsSn_6]$. There are two different tin sites, one in which tin is surrounded by six arsenic atoms in a distorted octahedral array (three Sn–As at 285.3 pm and three at 301.8 pm) and the other in which tin is coordinated to three arsenic and three tin atoms also in distorted octahedral coordination (three Sn–As at 275.3 pm and three Sn–Sn at 324.5 pm), similar to the coordination of tin in the double-layer structures.

The ^{119}Sn Mössbauer spectrum showed a single peak at δ −0.09 mm sec^{-1}, which can be assigned to a tin(IV) oxide impurity phase, and a doublet δ 2.68 mm sec^{-1}, Δ 0.48 mm sec^{-1}. The similarity of the chemical isomer shift of the doublet with that of white-tin suggests that bonding in Sn_4As_3 has metallic character. The shift is similar to those recorded from the double-layer Zintl phase compounds and reflects a comparable electron density around tin in both types of materials. This result supports the suggestion above that there is only limited electron transfer from alkali- or alkaline-earth-metals to the net in the double layer Zintl phase compounds.

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