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Synthesis of Tin-Tellurium Polyanions: Structure of $(Me_4N)_4Sn_2Te_6$

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The reaction of KSn with Te at high temperature gives congruently melting K_4SnTe_4 (**1**) and Sn. Aqueous extraction and workup of the crude K_4SnTe_4 alloy give nearly quantitative yields of K_4SnTe_4 identified by ^{119}Sn and ^{125}Te NMR, ^{119}Sn Mössbauer, and Raman measurements. Depending on the cation and solvent used, a variety of products can be isolated from solutions of $SnTe_4^{4-}$ including Te_4^{2-} and $Sn_2Te_6^{4-}$. The compound $(Me_4N)_4Sn_2Te_6$ (**2**), which was structurally characterized, is isostructural with B_2H_6 and exhibits effective D_{2h} symmetry. The ditinhexatelluride (4−) anion (**2**) crystallized in the monoclinic space group $P2_1/c$ with lattice constants at −168 °C of $a = 11.229$ (5) Å, $b = 13.590$ (6) Å, $c = 12.67$ (7) Å, and $\beta = 116.96$ (2)° with $Z = 2$. The X-ray data were refined to residuals of $R = 0.0296$ and $R_w = 0.0312$, giving terminal Sn-Te distances of 2.700 (2) and 2.689 (1) Å and bridging Sn-Te distances of 2.794 (1) and 2.804 (1) Å.

Introduction

Compared to the binary and ternary main-group oxides, the heavier chalcogenides of the main-group elements have received relatively little attention. Although the preparation of boron sulfides was reported by Berzelius[1] over 150 years ago, the field has been plagued by preparative and structural inconsistencies until recently. During the last decade the elegant synthetic work of Krebs and co-workers[2] has provided many examples of thio and seleno anions of the group 3 and 4 elements. As expected by analogy to silicate chemistry, the structures of many of these compounds are based on tetrahedral building blocks. Some examples include $Ga_6Se_{14}^{10-}$,[3] $Sn_{10}O_4S_{20}^{8-}$,[4] $B_4S_{10}^{8-}$,[5] $In_4Se_{10}^{8-}$,[6] $Si_4Te_{10}^{4-}$,[7] $Ge_4S_{10}^{4-}$,[8] $Sn_2S_7^{6-}$,[9] $[SnS_3^{2-}]_n$,[10] $Ge_2Se_6^{4-}$,[11] $Sn_2S_6^{4-}$,[12] $GeSe_4^{4-}$,[13] and SnS_4^{4-}.[14] These polyanions have been made either by high-temperature reactions or by using the procedure of Krebs and co-workers, the treatment of the binary main-group sulfides or selenides with HX^- or X^{2-} (X = S, Se) in aqueous solution. Except for a few isolated examples like $Si_4Te_{10}^{4-}$,[7] the tetrahedral main-group tellurides are conspicuous by their absence. For instance, the preparation of tetrahedral main-group tellurides of the group 4 elements Ge or Sn by the aqueous route would be rendered difficult by the reported nonexistence of $GeTe_2$[15] and $SnTe_2$.[16] Another route to tellurium-containing polyanions is by extraction of Zintl phases,[17] which has led to the structural characterization of $Te_3{\cdot}en^{2-}$[18] (en = ethylenediamine), $Te_4^{2-}{\cdot}2CH_3OH$,[19] Te_5^{2-},[20] $Tl_2Te_2^{2-}$,[21] and unusual one-dimensional chains in Cs_2Te_5.[22] Schäfer and co-workers recently structurally characterized the Zintl phase K_2SnTe_5,[23] which contains tetrahedral $SnTe_4$ units bridged together by four-coordinate square-planar tellurium atoms into a one-dimensional array. This unusual tellurium coordination is also observed in Cs_2Te_5.[22] In addition to providing many structurally novel cluster geometries, Zintl type polyanions have recently been used to prepare a large number of novel solids including metalized organic polymers,[24] surface-modified inorganic solids and metals,[25] and a new class of amorphous metallic spin glasses.[26]

In this paper, we report a convenient preparation of water-soluble K_4SnTe_4 (**1**) and the synthesis and structural characterization $(Me_4N)_4Sn_2Te_6$ (**2**) containing the $Sn_2Te_6^{4-}$ anion, which is isostructural with diborane.

Experimental Section

All manipulations were performed under an argon atmosphere containing <1 ppm of O_2, and solvents were degassed under vacuum before use. The metals were obtained from Cerac, Inc., Milwaukee, WI. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. NMR measurements were made near 74 MHz for ^{119}Sn and 63 MHz for ^{125}Te. Shifts are reported with respect to external Me_4Sn and Me_2Te ($\delta = 0$) with shifts to lower frequencies assigned negative values. Raman spectra were obtained with excitation from the 647.1-nm line of a Kr^+ laser. Mössbauer data were taken with samples at 77 K and a $CaSnO_3$ source at room temperature. Mössbauer isomer shift (IS) data are relative to $CaSnO_3$, IS ≡ 0 $mm{\cdot}s^{-1}$.

K_4SnTe_4 (1). The compound KSn[27] was prepared by reacting potassium metal (m3n+) with tin metal (m5n+) in a quartz vessel at ~700 °C for 5 min under 1 atm of Ar. The argon atmosphere was vented through a mineral oil bubbler. After cooling, 1 equiv of Te was added and the mixture was remelted and agitated for 5 min, again under a vented argon atmosphere. The alloy was crushed to a fine powder and the precipitated Sn removed for use in the next K_4SnTe_4 preparation. Although the bulk of the precipitated Sn was removed mechanically as a solid metallic plug when the reaction mixture was crushed, the following aqueous extraction step was necessary to obtain an analytically pure product.

The crude K_4SnTe_4 (10 g) was dissolved in water (~40 mL) at 25 °C, and the solution was stirred for 5 min and filtered. The filtrate

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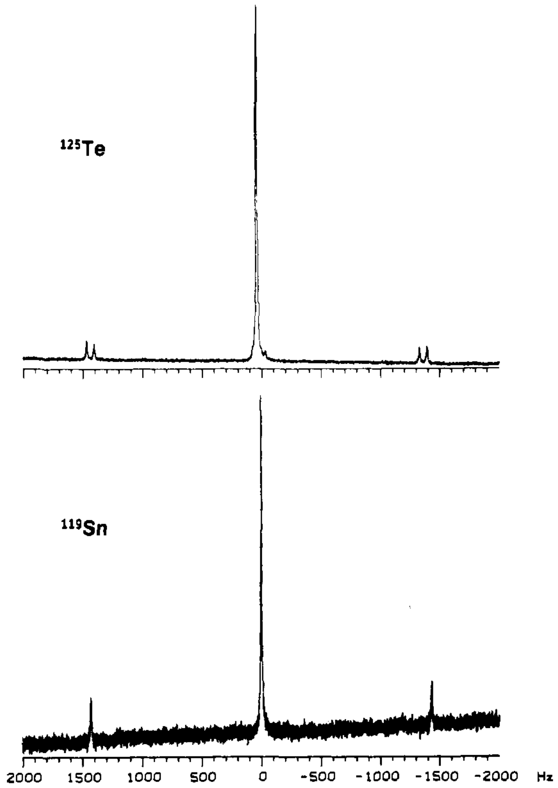

Figure 1. NMR spectra of K_4SnTe_4 in aqueous solution: (A) ^{125}Te; (B) ^{119}Sn.

was evaporated to near dryness and the residue triturated with acetone. Filtration and drying under vacuum at 50 °C for 12 h gave a >90% yield of K_4SnTe_4. Anal. Calcd for K_4SnTe_4: K, 19.87; Sn, 15.16; Te, 64.97. Found: K, 19.56; Sn, 15.43; Te 64.52.

$(Me_4N)_4Sn_2Te_6$ (2). A saturated solution of K_4SnTe_4 in methanol (MeOH) was layered carefully with excess saturated Me_4NBr in MeOH. After the mixture was allowed to stand for 16 h, the resulting well-formed black crystals, were filtered off and washed with MeOH to give a 78% yield of **2** based on K_4SnTe_4. The elemental analysis was unsatisfactory, possibly due to the formation of polytellurides.[21] Anal. Calcd for $C_{16}H_{48}N_4Sn_2Te_6$: C, 14.77; H, 3.69; N, 4.31; Sn, 18.31; Te, 58.89. Found: C, 15.30; H, 3.92; N, 4.76; Sn, 15.02; Te, 60.41. Since the elemental analysis was inconclusive, the structure of **2** was determined by a single-crystal X-ray structure determination as discussed below.

Results and Discussion

The congruently melting Zintl phase K_4SnTe_4 is conveniently prepared in high yield by the reaction of KSn with Te, which avoids the violent reaction of elemental potassium and tellurium. The crude K_4SnTe_4 is easily purified by aqueous extraction. In contrast to the colorless MX_4^{4-} compounds (M = Ge, Sn; X = S, Se), the tetratellurostannate(4−) anion is deep red-orange. Evaporation of the extremely air-sensitive orange solution and drying of the resulting solid gives analytically pure K_4SnTe_4. The isolated solid was identified by ^{125}Te and ^{119}Sn NMR spectroscopies. The tellurium resonance was located at ~−250 ppm from Me_2Te (Figure 1a) with coupling to ^{119}Sn and ^{117}Sn at 2860 and 2740 Hz, respectively. The ^{119}Sn resonance was observed at ~−1700 ppm from Me_4Sn with the coupling to ^{125}Te easily observable (Figure 1b). The resonance frequencies were found to be solvent and concentration dependent but were in fair agreement with the data reported for en extracts of Na/Sn/Te alloys which were also assigned to $SnTe_4^{4-}$.[28] An en solvate of Na_4SnTe_4 was reported to have been isolated[28] but with no physical data on the solid to support the claim. Raman spectra of solutions of K_4SnTe_4 obtained in en with the red 647.1-nm line of a Kr^+ laser show two peaks at 180 and 130 cm^{-1} (Figure 2), which are assigned to $SnTe_4^{4-}$ on the basis of the close similarity to other tetrahedral species.[29] The ^{119}Sn Mössbauer spectrum of K_4SnTe_4 at 77 K is shown in Figure 3a. The resonance at IS = +1.71 (2) $mm \cdot s^{-1}$ is in the range expected for covalent Sn^{IV}[30] although Sn in many metallic environments also shows isomer shifts in this region.[30] There is no quadrupole interaction evident as expected for a tetrahedral species. The K_4SnTe_4 is extremely air sensitive, and the small resonance at IS = 0 $mm \cdot s^{-1}$ in Figure 3a is an oxidation product. The products formed on exposure of K_4SnTe_4 to air followed by

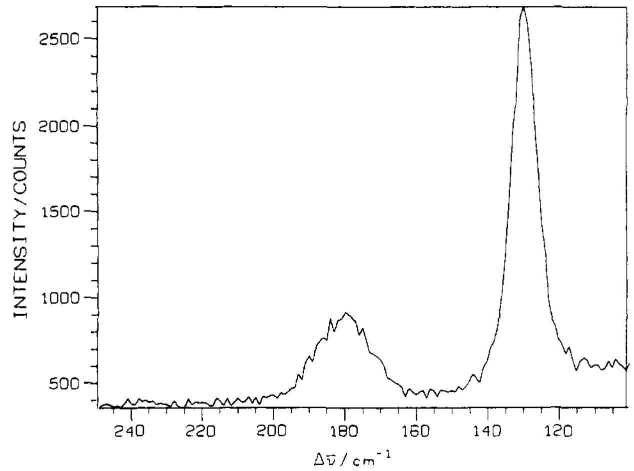

Figure 2. Raman spectrum of an ethylenediamine solution in K_4SnTe_4 with 647.1-nm excitation.

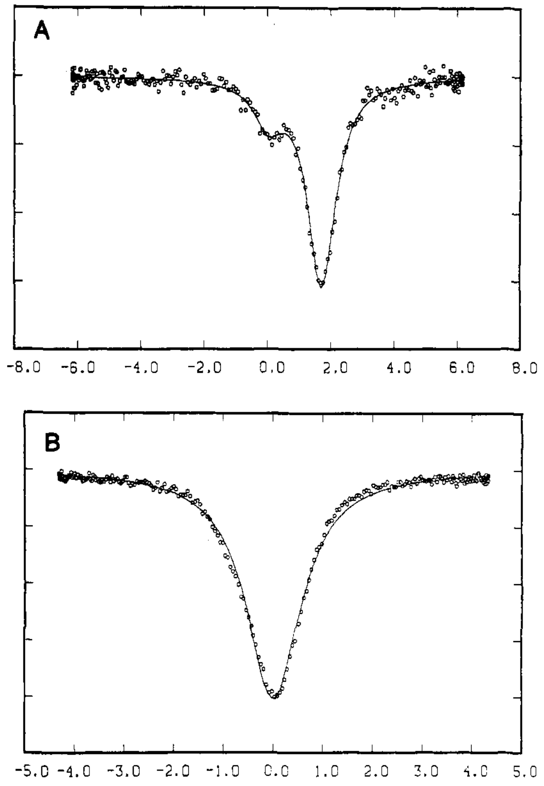

Figure 3. 77 K ^{119}Sn Mössbauer spectra of (A) K_4SnTe_4, IS = +1.71 (2) $mm \cdot s^{-1}$, containing a small amount of oxidized decomposition product, IS = 0.0 $mm \cdot s^{-1}$, and (B) the oxidation/hydrolysis product of K_4SnTe_4, identified as $K_2Sn(OH)_6$, IS = 0.00 (1) $mm \cdot s^{-1}$ (see text).

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Table I. Crystal Data for $(Me_4N)_4Sn_2Te_6$ (**2**)

empirical formula	$C_{16}H_{48}N_4Sn_2Te_6$
M_r	1299.56
color of cryst	black
cryst dimens	0.048 × 0.046 × 0.056 mm
space group	$P2_1/c$
cell dimens	$a = 11.229$ (5) Å; $b = 13.590$ (6) Å; $c = 12.671$ (7) Å; $\beta = 116.96$ (2)°
Z	2
vol	1723.4 Å^3
d(calcd)	2.50 g·cm^{-3}
X-ray λ	0.710 69 Å, Mo Kα
abs coeff	64.624 cm^{-1}
θ_{min}, θ_{max}	6°, 50°
scan type	moving cryst, moving detector
no. of reflcns collcd	5700
no. with $F > 2.33\sigma(F)$	2643
R	0.0296
R_w	0.0312
GOF for last cycle	1.009
max Δ/σ for last cycle	0.03

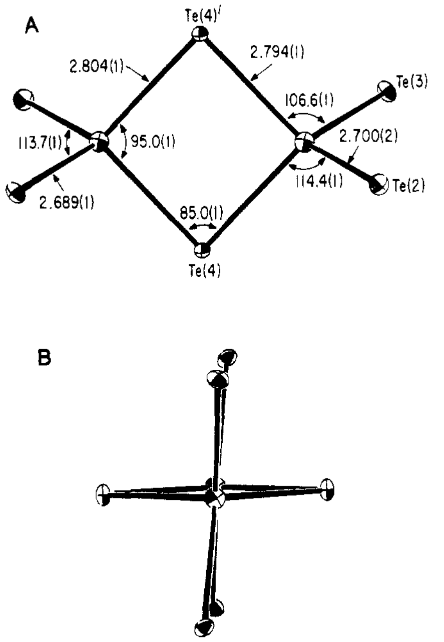

Figure 4. (A) $Sn_2Te_6^{4-}$ anion showing the atom-labeling scheme, distances (Å), and angles (deg). (B) End-on view of the anion.

Table II. Fractional Coordinates for **2**[a]

atom	x	y	z	B_{iso}, Å^2
Sn(1)[b]	1422.2 (5)	452.3 (3)	6426.3 (4)	12
Te(2)[b]	4006.3 (5)	445.5 (4)	6852.0 (4)	12
Te(3)[b]	992.7 (5)	1267.2 (4)	8157.5 (4)	10
Te(4)[b]	−280.8 (5)	1411.4 (3)	4329.4 (4)	9
N(5)[b]	6135 (6)	2203 (5)	606 (5)	15
C(6)[b]	6651 (11)	2460 (8)	1886 (8)	28
C(7)[b]	6943 (14)	1407 (11)	452 (12)	42
C(8)[b]	4727 (9)	1861 (7)	149 (8)	23
C(9)[b]	6157 (10)	3108 (8)	−75 (10)	31
N(10)[b]	1983 (6)	893 (5)	1991 (5)	12
C(11)[b]	555 (8)	1233 (6)	1398 (7)	16
C(12)[b]	2409 (8)	683 (6)	3277 (7)	16
C(13)[b]	2873 (8)	1673 (6)	1884 (8)	17
C(14)[b]	2101 (8)	−28 (6)	1394 (7)	16
H(1)	734 (10)	275 (7)	217 (8)	18 (20)
H(2)	609 (9)	303 (7)	198 (8)	25 (19)
H(3)	684 (8)	184 (6)	244 (7)	10 (16)
H(4)	652 (8)	136 (6)	−50 (8)	19 (18)
H(5)	773 (13)	160 (10)	91 (12)	52 (35)
H(6)	700 (7)	90 (6)	79 (7)	0 (15)
H(7)	421 (9)	246 (7)	20 (8)	20 (18)
H(8)	437 (8)	165 (6)	−69 (7)	11 (15)
H(9)	464 (8)	140 (6)	60 (7)	10 (16)
H(10)	724 (12)	332 (9)	19 (10)	53 (29)
H(11)	579 (8)	288 (6)	−89 (8)	16 (17)
H(12)	570 (8)	370 (6)	16 (7)	11 (16)
H(13)	26 (11)	140 (8)	40 (10)	46 (27)
H(14)	−2 (8)	62 (6)	150 (7)	17 (17)
H(15)	46 (8)	180 (6)	168 (7)	10 (15)
H(16)	183 (7)	16 (5)	341 (6)	3 (13)
H(17)	342 (9)	56 (6)	369 (8)	20 (18)
H(18)	229 (8)	128 (6)	366 (7)	12 (16)
H(19)	391 (7)	141 (5)	236 (6)	6 (14)
H(20)	260 (9)	184 (7)	109 (8)	20 (18)
H(21)	288 (7)	223 (5)	227 (6)	0 (13)
H(22)	188 (6)	19 (5)	44 (6)	0 (12)
H(23)	306 (10)	−21 (7)	182 (8)	30 (20)
H(24)	157 (8)	−43 (6)	142 (7)	6 (16)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. [b] Isotropic values for these atoms, which were refined anisotropically, were calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609.

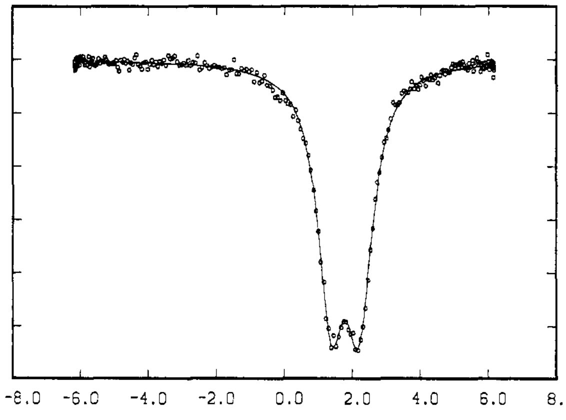

Figure 5. 77 K ^{119}Sn Mossbauer spectrum of $(Me_4N)_4Sn_2Te_6$.

drying at 100 °C are $K_2Sn(OH)_6$ and Te metal. This was determined from examination of the powder X-ray diffraction pattern of the oxidized material as well as the Mössbauer spectrum of the oxidation product (Figure 3b), which shows complete conversion to a species with IS = 0 mm·s^{-1}, consistent with the IS of $K_2Sn(OH)_6$.[30]

A variety of products can be obtained from solutions of K_4SnTe_4 by treatment with various cations. We recently isolated and structurally characterized $(PPh_4)_2Te_4{\cdot}2CH_3OH$,[19] which was prepared from K_2SnTe_4 and contained tetratelluride(4−) chains with methanol molecules hydrogen bonded to the terminal tellurium atoms. The reaction of $SnTe_4^{4-}$ with transition-metal cations has led to a novel family of amorphous metallic spin glasses,[26] and (**1**) has also been used as an electron-transfer reagent in the reduction and intercalation of certain organic polymers.[24]

Treatment of **1** with Me_4NBr in MeOH gives high yields of $(Me_4N)_4Sn_2Te_6$. The anion $Sn_2Te_6^{4-}$ has also been isolated at its bis(tetraphenylphosphonium) salt. A possible mechanism for the formation of $Sn_2Te_6^{4-}$ is shown in Scheme I. This mechanism is supported by several qualitative observations: (1) the reaction forming $Sn_2Te_6^{4-}$ from $SnTe_4^{4-}$ does not proceed at an appreciable rate when Me_4NPF_6 is used in place of Me_4NBr; (2) similar species to the proposed corner-sharing tetrahedral intermediate in Scheme I have been isolated, i.e., $Sn_2Se_7^{6-}$;[9] (3) the nearly colorless filtrate from the reaction of K_4SnTe_4 and Me_4NBr gives a positive test for the presence of telluride ions.

Scheme I

$$SnTe_4^{4-} + Br^- \rightleftarrows SnTe_3Br^{3-} + Te^{2-}$$

$$SnTe_3Br^{3-} + SnTe_4^{4-} \rightleftarrows Sn_2Te_7^{6-} + Br^-$$

$$Sn_2Te_7^{6-} \rightarrow Te^2 + Sn_2Te_6^{4-}$$

Table III. Bond Angles and Distances for **2**

A	B	C	angle, deg
Te(2)	Sn(1)	Te(3)	114.4 (0)
Te(2)	Sn(1)	Te(4)	113.7 (0)
Te(3)	Sn(1)	Te(4)	106.6 (0)
Te(4)	Sn(1)	Te(4)	95.0 (0)
Sn(1)	Te(4)	Sn(1)	85.0 (0)
C(6)	N(5)	C(7)	110.7 (8)
C(6)	N(5)	C(8)	108.4 (7)
C(6)	N(5)	C(9)	109.3 (7)
C(7)	N(5)	C(8)	109.0 (9)
C(7)	N(5)	C(9)	110.5 (9)
C(8)	N(5)	C(9)	108.8 (6)
C(11)	N(10)	C(12)	110.1 (6)
C(11)	N(10)	C(13)	109.8 (6)
C(11)	N(10)	C(14)	108.9 (6)
C(12)	N(10)	C(13)	109.5 (6)
C(12)	N(10)	C(14)	109.4 (6)
C(13)	N(10)	C(14)	109.2 (6)

A	B	dist, Å	A	B	dist, Å
Sn(1)	Te(2)	2.700 (2)	N(5)	C(8)	1.490 (10)
Sn(1)	Te(3)	2.689 (1)	N(5)	C(9)	1.509 (11)
Sn(1)	Te(4)	2.794 (1)	N(10)	C(11)	1.502 (9)
Sn(1)	Te(4)	2.804 (1)	N(10)	C(12)	1.502 (9)
N(5)	C(6)	1.495 (11)	N(10)	C(13)	1.506 (10)
N(5)	C(7)	1.481 (11)	N(10)	C(14)	1.499 (10)

We have determined the structure of $(Me_4N)_4Sn_2Te_6$ from single-crystal X-ray data. A sample was transferred anaerobically to the goniostat and cooled to −168 °C, at which temperature all data were collected. Table I shows the crystal data for **2**. The unit cell parameters were obtained from 44 reflections at −168 °C. The structure was solved by using direct methods and standard Fourier techniques, and all hydrogens were located and refined isotropically. All non-hydrogen atoms were refined anisotropically. The data were corrected for absorption by using an analytical technique. A final difference Fourier was featureless, the largest peak being 0.45 e·$Å^{-3}$. The atomic coordinates and bond lengths and angles for non-hydrogen atoms are given in Tables II and III, respectively. A view of the $Sn_2Te_6^{4-}$ anion, including the atom-labeling scheme and important distances and angles, is shown in Figure 4. Although the anion is required to have only a crystallographic center of inversion, it has effective D_{2h} symmetry. This geometry has been observed in many compounds including B_2H_6, $Rb_6In_2S_6$,[31] $Ge_2Se_6^{4-}$,[11] and $C_2S_2Cl_4$.[32]

Unlike that **1**, of the ^{119}Sn Mössbauer spectrum of **2** (Figure 5) shows a quadrupole interaction due to the lifting of rigorous T_d symmetry at the Sn site.

Summary and Conclusions

The extraction of Zintl phases to obtain tetrahedral main-group polyanions provides an alternative method of preparation to the well-known basic degradation of binary main-group chalcogenides in aqueous solution. Both methods, however, rely on protic solvents, so hydrolytically unstable species such as boron chalcogenides or silicon chalcogenides will be difficult to access by either method. For example, we recently showed that the extraction of certain K/Si/Te alloys with ethylenediamine gave the TeH^- anion instead of anionic silicon tellurides.[19]

By use of high-temperature reactions, Kreb's aqueous route, or the Zintl phase extractions used here, the preparation of a large number of structural analogues of the silicates containing heavier main-group elements should be possible.

Acknowledgment. We thank A. Kostka for the NMR measurements and the Division of Materials Science, U.S. Department of Energy, for generous financial support under Contract W-31-109-ENG-38.

Registry No. 1, 85533-99-9; 2, 90388-59-3; KSn, 89871-27-2; Te, 13494-80-9.

Supplementary Material Available: Listings of anisotropic thermal parameters, bond distances and angles, and observed and calculated structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

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Zn^{2+}-Catalyzed Decomposition of a Tris(imidazol-2-yl)phosphine. Crystal and Molecular Structure of [Bis(4,5-diisopropylimidazol-2-yl)phosphinic acid]dichlorozinc Hydrate

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The reaction of an ethanolic solution of bis(4,5-diisopropylimidazol-2-yl)(imidazol-2-yl)phosphine with aqueous $ZnCl_2$ results in the formation of the title complex, $C_{18}H_{33}Cl_2N_4O_3PZn$, which was characterized by X-ray crystallography. The complex crystallizes in the space group $P2_1/c$ with unit cell dimensions of $a = 9.805$ (3) Å, $b = 26.202$ (7) Å, $c = 10.924$ (3) Å, $\beta = 111.79$ (2)°, and $Z = 4$. The structure refined routinely to a final R of 6.6%. The structural results indicate that the original phosphine has undergone oxidation and replacement of an imidazole by OH^-, the latter process apparently being promoted by the presence of $ZnCl_2$. This result indicates that tris(imidazol-2-yl)phosphine–Zn^{2+} complexes, which are catalytically active models for the active site of carbonic anhydrase, suffer an apparent Zn^{2+}-promoted decomposition, which accounts for the observed loss of activity when they are allowed to stand in solution.

Introduction

Some time ago we initiated a project to synthesize tris(imidazol-2-yl)phosphines (**1**) and investigate their M^{2+} chelates (**1**:M^{2+}) as models for the active site in carbonic anhydrase. During the course of these studies,[1-3] two general aspects of the chemistry became clear, first that the ligands themselves

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[1] (a) Brown, R. S.; Curtis N. J.; Huguet, J. *J. Am. Chem. Soc.* **1981**, *103*, 6953. (b) Brown, R. S.; Huguet, J. *Ibid.* **1980**, *102*, 7571.

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