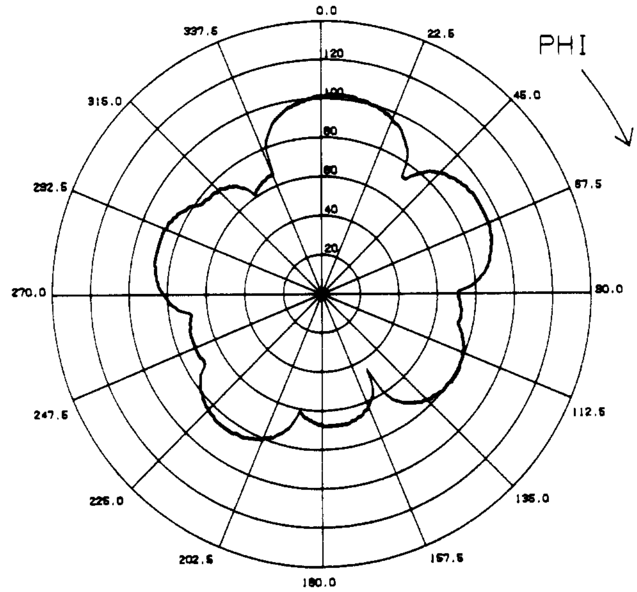

Figure 2. Ligand profile ($\theta/2$ vs. ϕ) about the Pd–P bond.

and maintains a reasonable contact between C(4) and C(2) (120.4 (5)°).

The steric bulk of tertiary phosphine ligands has been described by Tolman[23] in terms of cone angles. Various authors[24-26] have expanded this concept using crystallographic structural data to calculate half-cone angles ($\theta/2$) as a function of rotation (ϕ) about the metal to phosphorus bond, thereby generating a "ligand profile". The ligand profile defined by the tri-*tert*-butylphosphine of **1** is shown in Figure 2. The metalated carbon atom C(4) was omitted from the calculation so the resultant $\theta/2$ values would not be dominated by its contribution. This profile is surprisingly similar to that of the tri-*tert*-buytylphosphine ligand in $(CH_3CO_2)_2HgP(t\text{-}Bu)_3$.[21]

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Note Added in Proof. After this article was accepted for publication, we learned other researchers had solved the structure of this complex and that of the isomorphous Pt(II) analogue and had published a communication describing that crystallographic study.[27] The results of the two independent investigations are virtually identical in every detail.

Registry No. **1**, 69393-58-4.

Supplementary Material Available: Listings of anisotropic thermal parameters, H atom parameters, nonessential bond lengths and bond angles, and structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Heteropolyatomic Anions of the Post Transition Metals. Synthesis and Structure of the Ditindibismuthide(2–) Anion, $Sn_2Bi_2^{2-}$

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Reaction of the binary alloys KSn_2 and K_3Bi_2 or of the ternary alloy composition KSnBi with 2,2,2-crypt in ethylenediamine (en) produces a dark red-brown solution from which black crystals of $(2,2,2\text{-crypt-}K^+)_2Sn_2Bi_2^{2-}\cdot en$ may be precipitated. The anion was originally thought[2] to be Sn_4^{2-} before atomic absorption and microprobe analysis established its composition to be $Sn_2Bi_2^{2-}$. The compound crystallizes in the monoclinic space group $P2_1$ with a = 12.640 (3) Å, b = 20.943 (5) Å, c = 12.353 (3) Å, β = 118.97 (2)°, V = 2861 (1) Å^3, and Z = 2. X-ray diffraction data were collected over two octants on an automated diffractometer at room temperature using monochromatized Mo Kα radiation, and the structure was solved by conventional Patterson and Fourier methods. Positional and thermal parameters of the 62 non-hydrogen atoms, with anisotropic thermal parameters for bismuth, tin, and potassium, were refined by full-matrix, least-squares techniques to R = 0.088 and R_w = 0.107 for 2944 independent reflections ($I > 3\sigma_I$). The structure contains $Sn_2Bi_2^{2-}$ anions with the metal atoms disordered equally over the four sites; the geometry is effectively tetrahedral, the bond distances ranging from 2.934 (3) to 2.971 (6) Å. $Sn_2Bi_2^{2-}$ is the first heteroatomic member of the P_4 family of 20-electron tetrahedral clusters, in contrast to the butterfly shape of the isoelectronic $Tl_2Te_2^{2-}$.

Introduction

Recent application of 2,2,2-crypt as an alkali metal complexing agent has made possible the isolation of stable salts of many polyatomic "Zintl" anions[3,4] from alloys of the post transition elements. The complexing serves both to increase the solubility of the salt and to prevent the reversion to the otherwise more stable intermetallic phases. Homopolyatomic anions such as Sn_9^{4-},[5] Ge_9^{4-} and Ge_9^{2-},[6] Pb_5^{2-} and Sn_5^{2-},[7] Bi_4^{2-},[8] Sb_4^{2-},[9] and Sb_7^{3-} [10] and, more recently, the heteropolyatomic

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anions $TlSn_8^{3-}$ and $TlSn_9^{3-}$[11] and $Tl_2Te_2^{2-}$[12] have been synthesized and structurally characterized in our laboratories. Rudolph and co-workers have also identified anions such as $Sn_{9-x}Pb_x^{4-}$[13] and $Sn_{9-x}Ge_x^{4-}$[14] (x = 0–9) in ethylenediamine solutions by ^{119}Sn and ^{207}Pb NMR and have found evidence for a Sn–Sb anion with nine Sn atoms but of otherwise unknown composition.[14]

Recently we have been investigating the mixed-metal systems of post-transition groups 4 and 5 since these elements are the richest in their ability to form a wide variety of clusters. We report here the synthesis and crystal structure of a salt containing the $Sn_2Bi_2^{2-}$ anion.

Experimental Section

Materials and Synthesis. All manipulations were performed either in an inert-atmosphere drybox or on a vacuum line. Tin and potassium ("purified") were obtained from J. T. Baker Chemical Co., and the 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was obtained from Merck. Ethylenediamine (Fisher Scientific Co.) was first dried by refluxing over CaH_2 and then stored over molecular sieves. Alloys of composition K_3Bi_2,[8] KSn_2, and KSnBi were prepared by fusion of stoichiometric amounts of the appropriate elements in a sealed tantalum tube enclosed in a quartz jacket. K_3Bi_2 was heated to 700 °C and then slowly cooled; the last two were fused at 975 °C followed by quenching of the container in water to give a microcrystalline product.

The reaction of KSn_2 and K_3Bi_2 with crypt in either a 7:1 (I) or a 1:1 (II) Sn:Bi ratio produces the $Sn_2Bi_2^{2-}$ salt as one of several phases, while the reaction of the composition KSnBi (III) gives almost exclusively large crystals of the $Sn_2Bi_2^{2-}$ phase in about 75% yield. In each case, en was added to 0.1 g of crypt and the appropriate amounts of the alloys for a 1:1 K:crypt mole ratio. Reaction vessels used in these reactions have been described previously.[10] Crystals were best formed by either allowing the solution to stand over the alloy for about 1 week or heating to ~35 °C for several days, after which the solution was decanted off the alloy residue and crystals were grown by slow removal of the solvent (over ~1 week). Reactions I and III form dark reddish brown solutions while II is greenish red. When the binary alloys first dissolve, both red and green colors are observed, suggesting that homopolyatomic anions (presumably Sn_9^{4-} and Bi_4^{2-}, respectively) form initially, which must then react with each other or with the alloys to produce mixed-metal species. In contrast, the ternary alloy gives an initial gold-colored solution, so one or more heterospecies is probably present from the beginning.

The other products formed in reaction I are of unknown composition. One is triclinic but poorly diffracting (unit cell deduced on diffractometer: a = 15.44 Å, b = 20.21 Å, c = 14.80 Å, α = 94.2°, β = 109.2°, γ = 89.9°, V = 4349 Å^3). The other is monoclinic, but the unit cell is so large a crystal structure study is impractical (a = 30.51 Å, b = 36.01 Å, c = 17.82 Å, β = 93.1°, V = 19550 Å^3). Volume considerations[11] would suggest these both contain a nine-atom mixed-metal species such as $BiSn_8^{3-}$. Reaction II also produces some of the triclinic phase plus crystals of the known compound (2,2,2-crypt-K^+)$_2Bi_4^{2-}$.[8]

(2,2,2-crypt-K^+)$_2Sn_2Bi_2$·en crystallizes as black plates, often with a pseudohexagonal habit. Suitable crystals were mounted in a drybox using 0.3- and 0.5-mm capillaries. The crystal used for data collection (from reaction I) had dimensions 0.62 × 0.52 × 0.13 mm.

Data Collection and Reduction. Preliminary oscillation and Weissenberg photographs indicated monoclinic symmetry with the extinction $0k0$, $k = 2n + 1$. Two octants of data (HKL and $\bar{H}\bar{K}L$) were measured at ~25 °C by using Mo Kα radiation monochromatized with graphite (λ = 0.71034 Å) on an automated four-circle diffractometer designed and built in the Ames Laboratory.[15] A total of 5639 reflections with $2\theta \leq 50°$ were collected. Three standard reflections, which were monitored every 75 reflections, showed a 16% decay in the sum of their integrated intensities during data collection. As the crystal is both large and relatively thin, an absorption correction was very necessary even though the calculated linear absorption coefficient is not that large (μ = 68.9 cm^{-1}). For this correction a ϕ-scan method (ϕ = 0–350°, $\Delta\phi$ = 10°) developed by Karcher and Jacobson was employed.[16] Transmission coefficients ranged from 0.98 to 0.17. The data were corrected for absorption, decay (by a third-order polynomial), and Lorentz and polarization effects to yield 2963 observed reflections ($I > 3\sigma_I$ and $F > 3\sigma_F$) and 2944 independent reflections after averaging in $P2_1$.

Precise unit cell dimensions were obtained by a least-squares fit to the average 2θ values of 18 reflections with $27° \leq 2\theta \leq 35°$ which were tuned on both Friedel-related peaks to eliminate any instrument or centering errors. The final cell parameters are a = 12.640 (3) Å, b = 20.943 (5) Å, c = 12.353 (3) Å, β = 118.97 (2)°, and V = 2861 (1) Å^3 with Z = 2, d_{calcd} = 1.80 g cm^{-3}, and fw = 1546.6. This unit cell and volume (which is highly dependent on the number of crypts in this type of structure) suggested the presence in the cell of four 2,2,2-crypt-K^+ cations, two 2− anions, and probably two solvent molecules.

Structure Solution. Analysis of a conventional Patterson map clearly indicated the presence of two four-atom clusters of tetrahedral geometry in the cell related only by a 2_1 screw axis, which restricts the choice of space group to acentric $P2_1$. Even though a mixed Sn/Bi anion was anticipated, the fact that both electron densities and bond distances in the cluster were essentially equal suggested (incorrectly) a model where all four atoms were tin. A Sn_4^{2-} anion would not have been unprecedented; there is evidence of its existence in solution by NMR[14] and a prediction of a fluxional, nearly tetrahedral, geometry,[17] and the analogous anion Ge_4^{2-} is believed present in another crypt salt.[2] Therefore the structure was initially solved as (2,2,2-crypt-K^+)$_2Sn_4^{2-}$·en.

Successive least-squares refinement and electron density maps located the 54 atoms of the two independent crypts. Refining all atoms with isotropic temperature factors led to $R = 0.142 = \sum||F_o| - |F_c||/\sum|F_o|$. Introduction of anisotropic temperature factors (of the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$) for the tin and potassium atoms reduced R to 0.103. At this point both electron density and difference maps showed the presence of an ethylenediamine solvent molecule, though it was not well-defined. Refinements using several different sets of initial solvent atom positions converged to the same positions, and the en molecule was chosen to have a cis-type geometry as this gave the most rational bond distances. Full-matrix least-squares refinement of all 62 atoms converged at R = 0.094 and $R_w = 0.115 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = \sigma_F^{-2}$. A final difference map for the model was essentially flat to ±1.1 e/Å^3 (<0.2 of a carbon atom).

It was at this point that the reaction of the ternary alloy KSnBi produced relatively large quantities of the phase in an essentially pure form, so that it was possible to have a bulk analysis by atomic absorption performed. This proved bismuth was present in the crystals, and the approximately 1:1 Sn:Bi mole ratio found could only be rationalized by a diamagnetic $Sn_2Bi_2^{2-}$ anion rather than Sn_4^{2-}. Anal. Calcd: Bi, 27.0; Sn, 15.3; K, 5.06. Found: Bi, 25.2; Sn, 15.0; K, 5.47. An analysis of individual crystals including the data crystal by electron microprobe also gave mole ratios near 1:1 for Sn:Bi; however, the weight percentages were very inconsistent and the values for potassium were always quite high.

Therefore the anion was concluded to be $Sn_2Bi_2^{2-}$, but with completely disordered heavy atoms since the structural results indicated the four positions were equivalent. Using this model, full-matrix least-squares refinement of all atoms converged at R = 0.088 and R_w = 0.107, which are significantly lower. The data set was reweighted in 40 groups sorted on F_o, as a dependence of $\sum w(|F_o| - |F_c|)^2$ on the magnitude of F_o was observed. This did not change the residuals, but it did slightly improve the standard deviations of the atom parameters. The final difference map was flat to ±1.5 e/Å^3.

Since the structure is in the acentric space group $P2_1$, a refinement of the enantiomorphic image was also performed, but this converged at much higher residuals; R = 0.099 and R_w = 0.121. Any attempt to partially or completely order the Sn's and Bi's also caused a sharp increase in the residuals. Actually, there is no reason the Sn and Bi percentages must be exactly 50% at each atom position; in fact, the

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Table I. Positional and Thermal Parameters for $(2,2,2\text{-crypt-K}^+)_2Sn_2Bi_2^{2-}\cdot en$[a]

atom	x	y	z	B_{11}[c]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
SnBi1[b]	0.0413 (2)	0.0	0.8771 (2)	8.1 (1)	15.2 (3)	7.0 (1)	0.3 (2)	1.30 (9)	−3.8 (2)
SnBi2	0.1202 (2)	0.0015 (3)	0.1453 (2)	10.3 (1)	9.8 (2)	8.1 (1)	−0.7 (2)	6.0 (1)	−0.5 (1)
SnBi3	0.3001 (2)	0.0035 (3)	0.0574 (2)	6.24 (8)	8.8 (1)	7.67 (9)	1.3 (1)	3.28 (7)	1.1 (1)
SnBi4	0.1469 (2)	0.1175 (3)	0.0226 (2)	8.5 (1)	7.9 (1)	7.3 (1)	1.6 (1)	3.31 (9)	0.7 (1)
K1	0.8351 (6)	0.2057 (5)	0.3704 (6)	5.6 (3)	7.5 (5)	4.9 (3)	0.4 (4)	2.6 (3)	0.5 (4)
K2	0.5030 (6)	0.1823 (5)	0.6949 (6)	5.0 (3)	6.9 (5)	4.7 (3)	−0.3 (3)	2.2 (3)	−0.5 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
N10[d]	0.808 (3)	0.064 (2)	0.375 (3)	7.8 (7)	C42	0.323 (4)	0.070 (3)	0.742 (4)	8.7 (11)
C11	0.888 (4)	0.033 (3)	0.332 (5)	10.3 (13)	O43	0.305 (2)	0.129 (1)	0.703 (2)	7.1 (6)
C12	0.017 (4)	0.066 (3)	0.384 (4)	8.3 (10)	C44	0.241 (4)	0.172 (3)	0.754 (4)	8.8 (11)
O13	0.999 (2)	0.129 (1)	0.347 (2)	7.5 (6)	C45	0.226 (3)	0.237 (2)	0.711 (4)	7.2 (9)
C14	0.110 (3)	0.148 (2)	0.366 (4)	7.4 (9)	O46	0.345 (3)	0.261 (2)	0.744 (3)	9.0 (7)
C15	0.098 (3)	0.218 (2)	0.315 (3)	6.4 (8)	C47	0.330 (5)	0.325 (3)	0.703 (5)	10.6 (14)
O16	0.047 (2)	0.259 (1)	0.374 (2)	6.6 (5)	C48	0.452 (6)	0.355 (3)	0.725 (6)	13.3 (17)
C17	0.036 (4)	0.323 (2)	0.336 (4)	7.9 (10)	N49	0.511 (3)	0.320 (2)	0.668 (3)	8.7 (9)
C18	0.980 (4)	0.364 (3)	0.397 (4)	9.8 (12)	C51	0.569 (4)	0.021 (3)	0.844 (4)	9.5 (11)
N19	0.857 (2)	0.348 (2)	0.365 (3)	6.7 (7)	C52	0.697 (3)	0.055 (2)	0.892 (4)	8.0 (10)
C21	0.685 (4)	0.044 (3)	0.295 (5)	10.2 (13)	O53	0.690 (2)	0.121 (1)	0.911 (2)	6.6 (5)
C22	0.627 (5)	0.086 (3)	0.168 (5)	10.7 (14)	C54	0.807 (3)	0.151 (2)	0.967 (3)	6.1 (8)
O23	0.622 (2)	0.148 (2)	0.197 (2)	7.5 (6)	C55	0.792 (4)	0.217 (3)	0.979 (4)	8.4 (10)
C24	0.540 (4)	0.183 (2)	0.089 (4)	7.9 (9)	O56	0.723 (2)	0.245 (1)	0.852 (2)	7.3 (6)
C25	0.536 (3)	0.248 (2)	0.113 (3)	6.9 (8)	C57	0.718 (4)	0.314 (2)	0.850 (4)	7.6 (10)
O26	0.655 (2)	0.279 (1)	0.170 (2)	7.2 (6)	C58	0.645 (4)	0.338 (3)	0.733 (5)	10.2 (12)
C27	0.647 (3)	0.342 (2)	0.188 (3)	6.9 (8)	C61	0.532 (5)	0.006 (4)	0.634 (5)	11.4 (13)
C28	0.776 (4)	0.369 (3)	0.238 (4)	9.0 (11)	C62	0.452 (4)	0.037 (2)	0.495 (4)	8.4 (10)
C31	0.839 (4)	0.042 (3)	0.496 (5)	10.3 (14)	O63	0.490 (2)	0.103 (1)	0.502 (2)	6.5 (5)
C32	0.804 (4)	0.089 (3)	0.595 (4)	8.8 (11)	C64	0.425 (3)	0.136 (2)	0.374 (3)	6.1 (8)
O33	0.848 (3)	0.146 (2)	0.577 (3)	9.3 (8)	C65	0.466 (4)	0.196 (2)	0.386 (4)	8.1 (10)
C34	0.831 (4)	0.187 (2)	0.661 (4)	8.2 (10)	O66	0.449 (2)	0.236 (1)	0.463 (2)	7.2 (6)
C35	0.893 (3)	0.243 (2)	0.684 (4)	7.4 (9)	C67	0.485 (5)	0.296 (3)	0.455 (5)	10.6 (15)
O36	0.839 (2)	0.279 (2)	0.566 (2)	7.3 (6)	C68	0.451 (5)	0.338 (3)	0.532 (5)	11.4 (14)
C37	0.890 (4)	0.339 (2)	0.582 (4)	7.9 (10)	N1(en)	0.209 (15)	0.363 (10)	0.103 (15)	39 (8)
C38	0.826 (4)	0.377 (3)	0.457 (4)	9.0 (11)	C1(en)	0.217 (14)	0.306 (9)	0.116 (15)	25 (6)
N40	0.494 (3)	0.042 (2)	0.714 (3)	8.1 (8)	C2(en)	0.169 (12)	0.333 (9)	0.950 (13)	26 (5)
C41	0.365 (4)	0.025 (3)	0.681 (4)	10.2 (13)	N2(en)	0.187 (10)	0.392 (7)	0.918 (11)	29 (4)

[a] Space group $P2_1$, a = 12.640 (3) Å, b = 20.943 (5) Å, c = 12.353 (3) Å, β = 118.97 (2)°. [b] 50:50 distribution of Sn and Bi. [c] Thermal parameters of the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [d] The first digit identifies the chain (1, 2, and 3, crypt 1; 4, 5, and 6, crypt 2), and the second, the position along the chain.

Table II. Some Distances and Angles in $(2,2,2\text{-crypt-K}^+)_2Sn_2Bi_2^{2-}\cdot en$

Distances

atom 1	atom 2	d, Å	atom 1	atom 2	d, Å
SnBi1	SnBi2	2.961 (3)	SnBi2	SnBi3	2.956 (3)
SnBi1	SnBi3	2.934 (3)	SnBi2	SnBi4	2.966 (6)
SnBi1	SnBi4	2.956 (5)	SnBi3	SnBi4	2.971 (6)
K1	N10	2.99 (4)	K2	N40	2.96 (4)
K1	N19	3.00 (4)	K2	N49	2.91 (4)
K1	O13	2.75 (3)	K2	O43	2.79 (2)
K1	O23	2.78 (3)	K2	O53	2.88 (2)
K1	O33	2.77 (3)	K2	O63	2.84 (3)
K1	O16	2.88 (2)	K2	O46	2.88 (3)
K1	O26	2.86 (3)	K2	O56	2.83 (3)
K1	O36	2.85 (3)	K2	O66	2.84 (3)

Angles in $Sn_2Bi_2^{2-}$ Cluster

atoms	angle, deg	atoms	angle, deg
2-1-3	60.20 (7)	1-3-2	60.35 (7)
2-1-4	60.17 (12)	1-3-4	60.08 (8)
3-1-4	60.58 (12)	2-3-4	60.06 (13)
1-2-3	59.45 (7)	1-4-2	59.99 (12)
1-2-4	59.84 (9)	1-4-3	59.34 (12)
3-2-4	60.22 (13)	2-4-3	59.72 (13)

slight inequality of the bond distances suggests this may not be the case, though it could also arise from the effect of the local environment. However, a refinement in which multiplicities were allowed to vary demonstrated that any deviation from 50:50 Sn:Bi is insignificant. The occupancies found ranged from 0.968 (9) to 1.009 (9) of the ideal 50:50 atoms.

The 80 hydrogen atoms in the asymmetric unit have not been located or estimated in the structure factor calculations; these represent 10.7% of the total electron density. Sources of the programs and the scattering factor data were as previously reported,[10,11] the neutral-atom scattering factors also including corrections for the real and imaginary parts of anomalous dispersion for bismuth, tin, and potassium. The disordered cluster atoms were treated as if they were an atomic number of 66.5, with scattering factor tables which represent the average of those for Sn and Bi.

Results and Discussion

The final positional and thermal parameters for $(2,2,2\text{-crypt-K}^+)_2Sn_2Bi_2^{2-}\cdot en$ are listed in Table I. All bond distances and angles for the $Sn_2Bi_2^{2-}$ anion along with potassium-ligand distances in the crypt cations are given in Table II. The remaining distances and angles for the cations and the ethylenediamine molecule as well as the observed and calculated structure factors appear in the supplementary material.

The unit cell contains two $Sn_2Bi_2^{2-}$ anions, four 2,2,2-crypt-K$^+$ cations, and two en molecules, as shown in Figure 1, with the disposition of these species exhibiting a marked pseudohexagonal character. Of course, the a and c axes are nearly equal and β is very close to 120°, but also the anion and two crypt cations each have approximate threefold axes which are nearly parallel to the b axis. In addition, if one considers only the lower or upper half of the cell along the b axis, the two crypt axes are located at translations in x and z of about $^1/_3$, $^2/_3$ and $^2/_3$, $^1/_3$ from the anion axis. Since the $Sn_2Bi_2^{2-}$ anion is positioned off the b axis, the 2_1 screw symmetry creates a zigzag channel containing the anions, with an en molecule filling the empty space directly above each anion. There is, however, no significant interaction between the clusters and the solvent molecules, the shortest distance being SnBi4–C1(en) at 4.1 (2) Å—in fact, there are similar distances

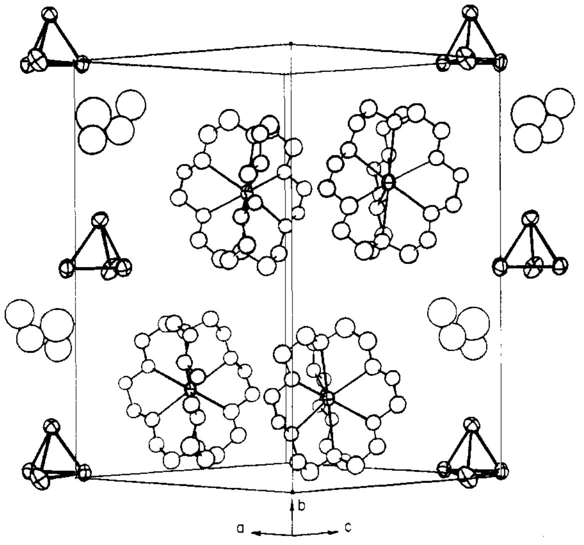

Figure 1. Approximate [$\bar{1}0\bar{1}$] view of the unit cell of (2,2,2-crypt-K$^+$)$_2$Sn$_2$Bi$_2$$^{2-}$·en. For clarity the anions and en molecules along the (0, *y*, 0) and (1, *y*, 1) axes are not included. Thermal ellipsoids are shown at the 30% probability level.

to crypt carbon atoms, for example, SnBi2–C12 at 3.99 (4) Å. The 2,2,2-crypt-K$^+$ cations in this structure have conformations comparable to those in other crypt sturctures, with the potassium more or less centrally located along the N–N axis.

In passing, it is interesting to note that essentially all crypt structures with polyatomic anions of 2– charge exhibit a certain degree of hexagonal character in their packing. In general, these structures[7–9,11,18–21] have unit cells with two axes near 12 Å, one axis a multiple of approximately 10.5 Å, and an opposing angle near 60 or 120°. The potassium examples are less likely to pack in a high-symmetry group and are usually triclinic and contain solvent molecules. crypt-Na$^+$ structures are however trigonal in general, though of course the anion must possess a threefold axis for a trigonal cell to occur. These similarities are quite useful in the prediction of possible anions for a new cell.

The most interesting feature of the structure is the anion shown in Figure 2. Of course, since the Sn$_2$Bi$_2$$^{2-}$ is disordered, the observed cluster geometry represents merely a mean configuration; each bond distance should be an average of one Sn–Sn, one Bi–Bi, and four Sn–Bi distances. The cluster found is substantially tetrahedral with bond distances ranging from 2.934 (3) to 2.971 (6) Å, with an average of 2.957 Å, and bond angles that vary from 59.3 (4) to 60.6 (1)°. The SnBi1–SnBi3 distance of 2.934 (3) Å is significantly shorter than the other five, possibly implying greater than average Sn–Sn character. In spite of the positional disorder, the thermal parameters for the atoms are quite normal for this type of structure except for SnBi1, which is elongated in a direction approximately tangent to the sphere of the cluster. This presumably arises from poor overlap of the positionally disordered atoms on this site.

The average bond length of 2.957 Å for the cluster is perhaps somewhat smaller than one would expect for what essentially represents a Sn–Bi bond. The only known bismuth polyanion Bi$_4$$^{2-}$ has an average bond length of 2.938 Å, but the Bi–Bi bonds have a bond order of 1.25 so this is not directly comparable. The cationic species Bi$_9$$^{5+}$[21] has an average distance of 3.14 Å, but all atoms exhibit a higher connectivity.

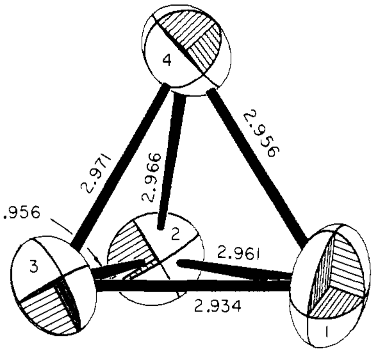

Figure 2. Structure of the Sn$_2$Bi$_2$$^{2-}$ anion, with *b* approximately vertical. Thermal ellipsoids are drawn at the 50% probability level.

However, a resonable estimate for a Bi–Bi single bond can be obtained by estimating the average bond length for a hypothetical "Bi$_7$$^{3-}$" anion on the basis of the known values for Bi$_4$$^{2-}$ together with Sb$_4$$^{2-}$ and Sb$_7$$^{3-}$ (2.750 and 2.857 Å, respectively); this yields a value of 3.05 Å. For a Sn–Sn bond, several polytin reference anions are known, including Sn$_9$$^{4-}$ with an average bond length of 2.99 Å and "Sn$_4$$^{4-}$" (isolated tetrahedra in the intermetallic phase KSn) with a distance of 2.98 Å.[22] A more reasonable distance is the average of 2.94 Å for Sn$_5$$^{2-}$ (D_{3h}) as this anion is more similar to Sn$_2$Bi$_2$$^{2-}$. This value together with 3.05 Å for Bi–Bi would imply a Sn–Bi bond distance of 3.00 Å, somewhat longer than the observed 2.957 Å. Perhaps a better estimate for the Sn–Sn distance is the average of only the equatorial–axial distances in Sn$_5$$^{2-}$, 2.87 Å, as the axial atoms are also triply bonded. This would then give a Sn–Bi estimated bond distance of 2.96 Å, which agrees well with observation.

The Sn$_2$Bi$_2$$^{2-}$ anion, though ideally a C_{2v} cluster, is the first heteroatomic member of the 20-electron tetrahedral family which includes P$_4$, As$_4$, Sb$_4$, Ge$_4$$^{4-}$, Sn$_4$$^{4-}$, and Pb$_4$$^{4-}$.[23] (The last three occur as isolated tetrahedra in intermetallic Zintl phases, but the formal 4– charge is derived only for complete electron transfer from the alkali metal to the cluster, which is not very plausible.) MO treatments and rationalizations of the bonding for such 20-electron tetrahedra are well-known.[23–25] In contrast, the isoelectronic Tl$_2$Te$_2$$^{2-}$ has a butterfly or folded diamond configuration with Tl atoms at the fold and is derived most easily from a D_{2h} square-planar geometry. This is energetically more favorable than a tetrahedral configuration, which would formally partition the charge to give positive and large negative charges on Te and Tl, respectively.[11] The Sn$_2$Bi$_2$$^{2-}$ anion by comparison can be credibly represented by a localized valence-bond cluster with negative formal charges on the tin atoms. A similar folded diamond shape for Sn$_2$Bi$_2$$^{2-}$ would be less favorable energetically as it would reduce the number of bonds and not allow the considerable delocalization of charge that the tetrahedral geometry does.

Continuing investigations in group 4 and 5 mixed-metal systems have produced evidence of the analogous Pb$_2$Sb$_2$$^{2-}$ anion. The 2,2,2-crypt-K$^+$ salt occurs in two modifications, one being isostructural with (2,2,2-crypt-K$^+$)$_2$Sn$_2$Bi$_2$·en (unit cell: $a = 12.590$ (2) Å, $b = 20.737$ (2) Å, $c = 12.200$ (2) Å, $\beta = 118.97$ (1)°, $V = 2786.5$ (5) Å^3).

Finally, it is sobering to realize that X-ray crystallography alone is not always sufficient for an analysis of a new phase, even when there are no apparent problems in the structural

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refinement or results. In the present instance, either Sn_4^{2-} or $Sn_2Bi_2^{2-}$ (disordered) produced a very satisfactory solution, with convergence at $R = 0.094$ and $R_w = 0.115$ for the former and $R = 0.088$ and $R_w = 0.107$ for the latter. Though the latter is of course significantly lower, a large part of this improvement arose from a better fit of the anomalous dispersion correction. Compared with those of other polyatomic anion and crypt structures, the agreement factors were better than average for either model. The final difference map, normally used as a concluding test for discrepancies in the final solution, was if anything cleaner for Sn_4^{2-} than for $Sn_2Bi_2^{2-}$.

The only crystallographic indication that the former model was incorrect is the fact that the thermal parameters for the crypt atoms (average $B = 10.8$ Å^2) were much larger than those found for the heavier anion atoms (8.2 Å^2). On the other hand, the values were relatively close, 8.3 and 8.7 Å^2, respectively, for the disordered $Sn_2Bi_2^{2-}$ model. Since the heavy atoms for the most part determine the structure, the mistake of assigning too small of a scattering factor for the anion atoms in the Sn_4^{2-} model was in effect simply compensated for by a decrease in the overall scale factor and an increase in light-atom thermal parameters. Thus the error in the heavy atoms showed up only in the light atoms. Of course, the problem is moot in this case as a conventional analysis was performed, but sometimes this is not possible when reactions produce very small quantities and multiphase products.

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Registry No. $(2,2,2\text{-crypt-K}^+)_2Sn_2Bi_2^{2-}\cdot en$, 82167-47-3; KSnBi, 82150-33-2; K_3Bi_2, 12598-61-7; KSn_2, 82150-34-3.

Supplementary Material Available: Listings of light-atom bond distances and angles for the cations (Table III) and structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

Contribution from Ames Laboratory—DOE[1] and Department of Chemistry,
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Two Zirconium Iodide Clusters. Hexazirconium Dodecaiodide (Zr_6I_{12}) and Cesium Hexazirconium Tetradecaiodide ($CsZr_6I_{14}$)

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Gem- or rod-shaped crystals of the title compounds are obtained from the reaction of ZrI_4, excess Zr strips and, for the latter, CsI at 850–925 °C for 15–40 days in welded tantalum containers. The structures of both were determined from diffraction data collected on a four-circle diffractometer with Mo Kα radiation at room temperature. Zr_6I_{12} (γ-ZrI_2) ($R\bar{3}$, $a = 14.502$ (2) Å, $c = 9.996$ (2) Å, $Z = 3$) contains a slightly compressed metal antiprism (d(Zr–Zr) = 3.204 (2) and 3.194 (1) Å) in which the six iodine atoms bridging waist edges of the metal antiprism also occupy exo positions in six other clusters, giving the representation $Zr_6I^i{}_6I^{i\text{-}a}{}_{6/2}I^{a\text{-}i}{}_{6/2}$ (i = inner, a = outer). Extended Hückel calculations support the notion that trigonal distortion of the metal cluster is responsible for its diamagnetism. The structure of $CsZr_6I_{14}$ (*Cmca*, $a = 15.833$ (2) Å, $b = 14.300$ (3) Å, $c = 12.951$ (2) Å, $Z = 4$) is derived from that known for Nb_6Cl_{14} and Ta_6I_{14} by addition of cesium to a large interstice. The unsymmetric bridging in $Cs(Zr_6I^i{}_{10}I^{i\text{-}a}{}_2I^a{}_{4/2})$ produces a tetragonally distorted metal octahedron with average distances of 3.29 Å (×8) and 3.35 Å (×4). The two structures also consist of approximately ccp M_6X_{12} units, with cesium in all octahedral holes in the latter. These and some related phases may also be described systematically in terms of close-packed halogen layers containing ordered vacancies, interstitials, and clusters of metal atoms in octahedral holes.

Introduction

Although $(Nb, Ta)_6X_{12}^{n+}$ and $(Mo, W)_6X_8^{m+}$ clusters with X = Cl, Br, I have been well-known for some time[2] the existence of clusters involving transition metals further to the left in the periodic table has been realized only relatively recently, namely, with Zr_6I_{12}, $(Zr_6Cl_{12})Cl_3$, $Sc(Sc_6Cl_{12})$,[3,4] and $La(La_6I_{12})$.[5] Among these elements those phases involving the dipositive oxidation state of zirconium have been the most studied, and 6–12-type clusters are now known for all three halides. Layered polymorphic forms of the zirconium dihalides are also found, $ZrCl_2$ and evidently $ZrBr_2$ occurring in MoS_2-type structures,[6,7] and ZrI_2 in extensively intergrown monoclinic (α)[8] and orthorhombic (β)[9] structures related to β-$MoTe_2$ and WTe_2, respectively. In the last two compounds the metal atoms are displaced from centers of antiprismatic sites in a CdI_2-like arrangement to form infinite zigzag chains (d(Zr–Zr) = 3.18 Å) between bucked iodine layers. The Zr_6I_{12} cluster polytype described herein is formed at higher temperatures than the other diiodides and is therefore designated γ-ZrI_2. It is the parent structure of the 6–12 clusters, the isostructural Zr_6Cl_{12} and Zr_6Br_{12} having been identified as microcrystalline products by Guinier power diffraction techniques[10] subsequent to preliminary notice[3] of the structure of Zr_6I_{12}.

The reduced zirconium iodides have a particular and continuing importance because of their prime relevance to the stress–corrosion–cracking of zirconium fuel cladding in water-cooled reactors that is evidently caused by fission product iodine.[11] A possible involvement of the abundant fission product cesium has also led to study of reduced phases in the CsI–ZrI_4–Zr system. The relatively oxidized $Cs_3Zr_2I_9$ has been

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