Inorg. Chem. **1985**, *24*, 1489–1492

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Synthesis and X-ray Crystal Structure of (2,2,2-crypt-K$^+$)$_3$(KSn$_9^{3-}$): A Compound Containing the Novel Anion $^1_\infty$[KSn$_9^{3-}$]

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Received July 16, 1984

The title compound is formed as the major product of the reaction of the ternary alloy composition KHgSn with 2,2,2-crypt in ethylenediamine followed by precipitation with ethylamine. The composition and structure were established with the aid of 6936 reflections ($I > 3\sigma(I)$, $2\theta < 45°$) collected on an automated diffractometer at −100 °C with monochromatized Mo Kα radiation. The compound is triclinic, space group $P\bar{1}$, with a = 16.146 (6) Å, b = 20.488 (5) Å, c = 15.824 (5) Å, α = 98.56 (3)°, β = 118.21 (3)°, γ = 106.01 (3)°, V = 4186 (2) Å^3, and Z = 2. The structure was solved by direct methods and refined by full-matrix least squares to R = 0.075 and R_w = 0.090 for 92 non-hydrogen atoms. In addition to six 2,2,2-crypt-K$^+$ cations per cell, the structure contains infinite chains of K$_a$–(Sn$_9$)–K$_b$–(Sn$_9$)··· running diagonally through the cell, with K$_a$ and K$_b$ at centers of symmetry; the anion can be simply represented as $^1_\infty$[KSn$_9^{3-}$]. The nine-atom tin cluster is a monocapped square antiprism, with only small distortions from that previously found in (2,2,2-crypt-Na$^+$)$_4$Sn$_9^{4-}$. The bridging potassium atoms occur in distorted trigonal antiprisms of tin atoms and show no evidence for coordinated ethylenediamine. The structure represents a partial transition to intermetallic-like bonding.

Introduction

In recent papers we have described the preparation and X-ray structural characterization of several examples of heteropolyatomic anions containing the heavy post transition metals gold, mercury, thallium, lead, and bismuth, all as salts of 2,2,2-crypt-K$^+$.[3–7] In the case of mercury, extraction of the alloy composition KHgTe with 2,2,2-crypt in ethylenediamine at room temperature led to the formation of the HgTe$_2^{2-}$ anion, while no reaction was observed with KHgSb under the same conditions.[4] A similar reaction of KHgSn produced a good yield of a mercury-free phase containing, formally, the previously reported Sn$_9^{4-}$ anion[8] together with both sequestered and nonsequestered potassium ions. We report here the preparation and X-ray crystal structure of (2,2,2-crypt-K$^+$)$_3$(KSn$_9^{3-}$), a novel structure that contains K–(Sn$_9$)–K–(Sn$_9$)–K··· chains and therefore represents a partial transition to intermetallic bonding as found in, for example, some Zintl alloys.[9] The existence of this compound has been noted previously.[10]

Experimental Section

Synthesis. The alloy composition KHgSn was prepared by reaction of stoichiometric quantities of K (J. T. Baker Purified), Hg (triply distilled), and Sn (Baker Analyzed) in a sealed tantalum tube at 600 °C for 6 h followed by quenching to room temperature. The entire product was ground before use. Typical reactions of 0.096 g (0.266 mmol presuming it was homogeneous) of this alloy with 0.100 g (0.266 mmol) of 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Merck) in ca. 8 cm^3 of dry ethylenediamine (en) quickly produced a red-brown solution, the color of which intensified on standing for 1 week. Attempts to isolate crystals suitable for X-ray diffraction by slow removal of solvent after decantation of the solution from the residual alloy were unsuccessful. However, suitable crystals were obtained by the careful addition of an equal amount of dry ethylamine, in which the product(s) is insoluble, to the ethylenediamine solution such that two layers formed. Slow intermixing of the amines produced deep red-brown crystals on the walls of the vessel. (Care must be taken to obtain two layers since immediate mixing of the amines produced a pale brown precipitate.) After isolation, the crystals were transferred to a drybox where they were mounted in 0.3- or 0.5-mm i.d. capillaries. Crystals of two different morphologies were observed, and oscillation and Weissenberg photographs on the rhombohedrally shaped crystals (ca. 70% of the total) gave a unit cell of triclinic symmetry. The other, morphologically distinct crystals diffracted very poorly, and no estimate of their unit cell size could be obtained. The latter mercury-containing solute, also obtained from KHgTe (microprobe data),[4] is anionic and considerably more soluble; similar solutions but only poorly formed crystals were obtained with liquid NH$_3$ at room temperature as the solvent.

Data Collection and Processing. A crystal of dimensions 0.35 × 0.32 × 0.20 mm was initially indexed on a four-circle automated diffractometer (Ames Laboratory) to provide verification of the unit cell information obtained photographically. The crystal was then transferred to a Syntex P2$_1$ diffractometer for data collection at low temperature. Data were recorded at −100 (±10) °C for the octants HKL, $\bar{H}\bar{K}L$, $\bar{H}K\bar{L}$, and $H\bar{K}\bar{L}$ with Mo Kα radiation monochromatized with graphite (λ = 0.71007 Å) for 12423 reflections out to $2\theta = 45°$. An ω-scan method was employed over the range of ±1° in ω from the peak, with stationary background counts at ±1.5° being recorded at each end of the scan, each for one-fourth of the scan time. Scan rates varied from 3.145 to 29.30° min^{-1}, depending on the intensity of a preliminary count. One standard reflection was measured every 50 reflections to check on crystal alignment and decay, with six check reflections ($13.6° < 2\theta < 17.1°$) used for reorientation when necessary. Data were corrected for Lorentz and polarization effects, and for both a 12% decay in the beam based on the intensity of the standard reflection (according to a third-order polynomial as a function of reflection number) and a 29% decay that occurred in two discontinuous steps during warmup while the liquid N$_2$ supply was replenished. An empirical absorption correction (μ = 29.02 cm^{-1}) using a ϕ-scan method[11] (ϕ = 0–350° with $\Delta\phi$ = 10°) was applied to the data; transmission coefficients ranged from 0.68 to 1.00. The final data set consisted of 6936 reflections after averaging 7854 data with $I > 3\sigma(I)$ and $F > 3\sigma(F)$ in $P\bar{1}$ ($R(I)$ = 0.036 with only two reflections eliminated by the criterion $|F_o - \bar{F}| > 6\sigma(F)$).

Precise unit cell dimensions were obtained on the same crystal at −100 °C by a least-squares fit to the average 2θ values of 28 reflections in the range $24.2° < 2\theta < 33.8°$ that had been tuned on both Friedel-related peaks to avoid centering and instrumental errors. The triclinic cell has dimensions of a = 16.146 (6) b = 20.488 (5) Å, c = 15.824 (5) Å, α = 98.56 (3)°, β = 118.21 (3)°, γ = 106.01 (3)°, and V = 4186 (2) Å^3.

Structure Solution and Refinement. A preliminary Howells–Phillips–Rogers statistical test was highly indicative of a centric cell, and solution of the structure was achieved in space group $P\bar{1}$ by direct methods using MULTAN 80[12] and data out to $2\theta = 43°$. The solution from the Fourier step with the highest figure of merit indicated a nine-atom polyhedron, similar to that of Sn$_9^{4-}$, with distances ranging from 2.9 to 3.5 Å. All atoms in the cluster were initially assumed to be tin, and R ($=\sum||F_o| - |F_c||/F_o|$) dropped 0.32 after several cycles of block-diagonal least-squares refinement of positional parameters (B's were set equal to 3.48 Å^2, from a Wilson plot). A Fourier map revealed all of the atoms in three crypt-K$^+$ cations as well as two more large peaks ($Z \sim 19$) at the centers

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(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

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Table I. Positional Parameters for (2,2,2-crypt-K^+)$_3$(KSn_9^{3-})

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Sn1	0.3422 (1)	0.31993 (9)	0.1093 (1)	N21	0.738 (1)	0.1817 (10)	0.945 (1)
Sn2	0.4857 (1)	0.34870 (7)	0.3261 (1)	N22	0.696 (1)	0.4660 (8)	0.923 (1)
Sn3	0.2569 (1)	0.33897 (8)	0.2371 (1)	N31	0.248 (1)	0.4028 (8)	0.667 (1)
Sn4	0.1707 (1)	0.19050 (9)	0.0624 (1)	N32	−0.174 (1)	0.3344 (9)	0.551 (1)
Sn5	0.4077 (1)	0.20203 (8)	0.1580 (1)	O11	0.714 (1)	−0.1503 (7)	0.256 (1)
Sn6	0.3674 (1)	0.30015 (8)	0.4198 (1)	O12	0.662 (1)	−0.1290 (7)	0.402 (1)
Sn7	0.1639 (1)	0.19360 (9)	0.2468 (1)	O13	0.606 (1)	0.0117 (7)	0.183 (1)
Sn8	0.2614 (1)	0.10591 (8)	0.1921 (1)	O14	0.624 (1)	0.0611 (7)	0.370 (1)
Sn9	0.4609 (1)	0.20961 (7)	0.3668 (1)	O15	0.937 (1)	0.0738 (7)	0.383 (1)
K1	0.7490 (3)	−0.0091 (2)	0.3604 (3)	O16	0.933 (1)	0.0724 (7)	0.559 (1)
K2	0.7189 (3)	0.3245 (2)	0.9364 (3)	O21	0.911 (1)	0.3219 (8)	0.065 (1)
K3	0.0346 (3)	0.3669 (2)	0.6076 (3)	O22	0.895 (1)	0.4510 (7)	0.025 (1)
K4	0.0	0.0	0.0	O23	0.667 (1)	0.2200 (8)	0.761 (1)
K5	0.5	0.5	0.5	O24	0.616 (1)	0.3429 (7)	0.746 (1)
N11[a]	0.767 (1)	0.0301 (8)	−0.181 (1)	O25	0.612 (1)	0.2369 (7)	0.004 (1)
N12	0.736 (1)	0.0154 (9)	0.542 (1)	O26	0.628 (1)	0.3809 (7)	0.030 (1)
O31	0.071 (1)	0.2925 (7)	0.473 (1)	C111	0.597 (2)	0.057 (1)	0.445 (2)
O32	−0.126 (1)	0.2856 (7)	0.400 (1)	C112	0.694 (2)	0.070 (1)	0.546 (2)
O33	0.168 (1)	0.3459 (7)	0.790 (1)	C113	0.863 (2)	0.029 (1)	0.205 (2)
O34	−0.044 (1)	0.2832 (7)	0.703 (1)	C114	0.954 (2)	0.045 (1)	0.306 (2)
O35	0.160 (1)	0.5124 (7)	0.652 (1)	C115	0.028 (2)	0.099 (1)	0.481 (2)
O36	−0.026 (1)	0.4824 (7)	0.642 (1)	C116	0.010 (2)	0.130 (1)	0.561 (2)
C11	0.775 (2)	−0.100 (1)	0.156 (2)	C117	0.920 (2)	0.099 (1)	0.640 (2)
C12	0.692 (2)	−0.163 (1)	0.153 (2)	C118	0.838 (2)	0.041 (1)	0.636 (2)
C13	0.635 (2)	−0.205 (1)	0.255 (2)	C21	0.839 (2)	0.197 (1)	0.038 (2)
C14	0.666 (1)	−0.194 (1)	0.364 (2)	C22	0.925 (2)	0.254 (2)	0.045 (2)
C15	0.688 (2)	−0.117 (1)	0.506 (2)	C23	0.994 (2)	0.379 (1)	0.075 (2)
C16	0.668 (2)	−0.051 (1)	0.538 (2)	C24	0.986 (2)	0.450 (1)	0.107 (2)
C17	0.676 (2)	−0.030 (1)	0.090 (2)	C25	0.883 (2)	0.516 (1)	0.047 (2)
C18	0.645 (2)	−0.029 (1)	0.119 (2)	C26	0.800 (2)	0.521 (1)	0.958 (2)
C19	0.567 (2)	0.064 (1)	0.203 (2)	C27	0.724 (2)	0.142 (1)	0.851 (2)
C110	0.535 (2)	0.050 (1)	0.275 (2)	C28	0.636 (2)	0.147 (1)	0.757 (2)
C29	0.596 (2)	0.228 (1)	0.670 (2)	C35	0.227 (2)	−0.261 (1)	0.379 (2)
C210	0.628 (2)	0.302 (1)	0.672 (2)	C36	0.241 (2)	−0.315 (1)	0.434 (2)
C211	0.633 (2)	0.416 (1)	0.739 (2)	C37	0.310 (2)	0.408 (1)	0.772 (2)
C212	0.620 (2)	0.455 (1)	0.817 (2)	C38	0.263 (2)	0.343 (1)	0.800 (2)
C213	0.655 (2)	0.139 (1)	0.958 (2)	C39	0.126 (2)	0.287 (1)	0.813 (2)
C214	0.645 (2)	0.179 (1)	0.036 (2)	C310	0.025 (1)	0.290 (1)	0.804 (1)
C215	0.603 (2)	0.275 (1)	0.079 (2)	C311	−0.137 (1)	0.280 (1)	0.691 (1)
C216	0.558 (2)	0.327 (1)	0.041 (2)	C312	−0.210 (1)	0.271 (1)	0.578 (1)
C217	0.583 (2)	0.430 (1)	0.989 (2)	C313	0.288 (2)	0.473 (1)	0.658 (2)
C218	0.664 (2)	0.490 (1)	0.991 (2)	C314	0.271 (2)	0.531 (1)	0.704 (2)
C31	0.250 (2)	0.343 (1)	0.601 (2)	C315	0.143 (2)	0.566 (1)	0.702 (2)
C32	0.169 (2)	0.321 (1)	0.486 (2)	C316	0.027 (2)	0.550 (1)	0.640 (2)
C33	0.007 (2)	−0.263 (1)	0.366 (2)	C317	−0.133 (2)	0.466 (1)	0.590 (2)
C34	0.106 (2)	−0.230 (1)	0.353 (2)	C318	−0.185 (2)	0.396 (1)	0.598 (2)

[a] The first digit identified the cation.

of symmetry 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ for potassium that evidently bridged between the tin clusters. The residual dropped to 0.108 after several more cycles of block-diagonal refinement of positional and isotropic thermal parameters. Anisotropic temperature factors (of the form $\exp[-^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$) were then introduced for the tin and potassium atoms, and full-matrix least-squares refinement gave $R = 0.075$ and R_w ($=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.090, where $w = \sigma(F)^{-2}$. In the final cycle of refinement the largest Δ/σ was 0.01 for all atoms and 0.03 for the scale factor. Introduction of anisotropic temperature factors for N and O was not statistically significant according to Hamilton's criteria.[13] A final Fourier difference map was flat to ±0.6 e Å^{-3} except in the vicinity of the cluster where there were a small number of peaks and troughs; the larger maxima at 0.9–1.4 e Å^{-3} were all only 1.0–1.5 Å from the tin atoms, while the largest peak anywhere near K4 and K5 was only 0.6 e Å^{-3}, both being scaled to observed K at 19.

None of the thermal parameters give any evidence of a misassignment and the presence of mercury. Also, attempts to place half a Hg^{2+} atom (formally necessary for charge conservation) each at the K4 and K5 positions caused R and R_w to increase to 0.084 and 0.103, respectively, and gave B_{ii} parameters that ranged from 14 to 20, which is not surprising since $Z(Hg) \simeq 4Z(K)$. Moreover, variation of both the occupancies and temperature parameters of the isolated potassium atoms left R and R_w unaltered, and the values obtained for the former were not statistically different from unity (K4 at 1.028 (27), K5 at 0.981 (26)).

Table II. Bond Distances (Å) in the Anion Unit [KSn_9^{3-}]

atom 1	atom[a] 2	dist	atom 1	atom 2	dist
1	2	2.935 (2)	5	9	2.962 (2)
1	3	2.972 (2)	6	7	2.969 (3)
1	4	2.946 (3)	6	9	2.949 (2)
1	5	2.956 (2)	7	8	2.973 (2)
2	3	3.203 (2)	8	9	2.931 (3)
2	5	3.171 (2)	2	4	4.539 (3)
2	6	2.984 (2)	3	5	4.579 (3)
2	9	2.977 (2)	6	8	4.229 (3)
3	4	3.217 (3)	7	9	4.129 (3)
3	6	2.961 (2)	4	K4	3.762 (2)
3	7	3.006 (2)	8	K4	3.552 (2)
4	5	3.303 (2)	7	K4	4.220 (2)
4	7	2.963 (2)	2	K5	3.700 (2)
4	8	2.997 (2)	3	K5	4.114 (3)
5	8	2.950 (2)	6	K5	3.743 (2)

[a] Tin unless noted otherwise.

Sources of all programs, procedures, and netural-atom scattering data (including corrections for the real and imaginary parts of anomalous dispersion) were as previously reported.[3,5]

Results and Discussion

The final atomic positional parameters for the 92 non-hydrogen atoms in (2,2,2-crypt-K^+)$_3$(KSn_9^{3-}) are given in Table I. Im-

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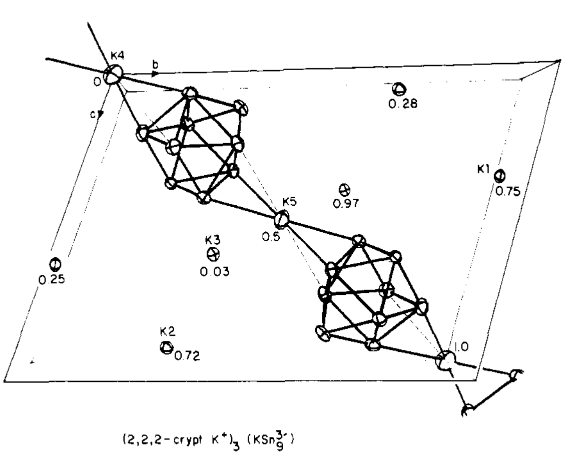

Figure 1. Unit cell of $(2,2,2\text{-crypt-K}^+)_3(\text{KSn}_9{}^{3-})$ ($P\bar{1}$) showing the potassium centers of the cations and a portion of the infinite anion chain (50% thermal ellipsoids). Numbers indicate the *x* fractional coordinates of potassium.

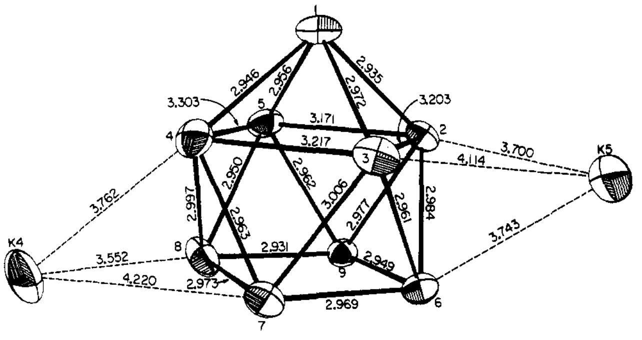

Figure 2. Independent unit in $^1_\infty[\text{KSn}_9{}^{3-}]$ with distances in Å ($\sigma = (2\text{–}3) \times 10^{-3}$). K4 and K5 lie on inversion centers.

portant distances in the anion unit $\text{KSn}_9{}^{3-}$ are given in Table II, while other distances relevant to the structure are discussed below. The supplementary material contains thermal parameters, interedge angles within the tin cluster, bond distances and angles for the 2,2,2-crypt-K$^+$ cations, and the observed and calculated structure factor amplitudes.

The structure contains infinite chains of K4–(Sn$_9$)–K5–(Sn$_9$) running diagonally through the cell, with uncomplexed atoms K4 and K5 on the centers of symmetry at 0, 0, 0, and $^1/_2$, $^1/_2$, $^1/_2$, respectively, and bridging opposite edges of the tin clusters. It is therefore useful to represent the anion as $^1_\infty[\text{KSn}_9{}^{3-}]$. This chain and the potassium centers of the six 2,2,2-crypt-K$^+$ cations that fill out the unit cell are shown in Figure 1. The independent anion unit and distances therein are illustrated in Figure 2. The $(01\bar{1})$ planes of the structure contain all of the chains, which are observed to zigzag somewhat when viewed in this direction, a circumstance that can also be judged from Figure 2 when it is noted that both K4 and K5 lie toward the viewer with respect to the bridged edges Sn4–Sn8 and Sn2–Sn6. The chains are well sheathed by the cryptated cations, with the smallest Sn–Sn separation between chains being 9.80 Å compared with 6.68 and 6.82 Å between clusters along the chains. There is no significant shift of any potassium atom toward one end of its 2,2,2-crypt ligand as has been observed in related salts.[4,14] All distances between tin in the anion and light atoms in the cations are 3.92 Å or greater (neglecting undetermined hydrogen atom positions), which is normal[5] and indicative of little interaction between these moieties. The shortest distance from a light atom in a 2,2,2-crypt ligand to an unsequestered potassium atom is 4.27 (2) Å for K5–C211.

The $^1_\infty[\text{KSn}_9{}^{3-}]$ chain exhibits a number of remarkable features. The potassium atoms K4 and K5 bridge opposite edges of the waist of the nine-atom tin cluster (Figure 2) to give each potassium four tin neighbors at 3.552 (2) to 3.762 (2) Å (average 3.69 Å), with two more tin atoms at a greater distance of either 4.114 (3) or 4.220 (2) Å completing a distorted trigonal antiprism about potassium. Importantly, there is no evidence (±0.5 e Å^{-3}) of coordinated ethylenediamine groups about either of these potassium atoms. The above K–Sn distances may be compared with those found in the intermetallic phase KSn in which there are discrete tin tetrahedra (Sn–Sn = 2.98 Å) and each potassium has six or eight tin neighbors in the range 3.70–3.85 Å (maximum deviation ~0.03–0.05 Å).[15] Thus, the potassium–tin interactions in the present work appear normal except perhaps for the somewhat short pair at 3.55 Å about K4.

The nine-atom tin cluster, formally $\text{Sn}_9{}^{4-}$ in the limit of complete electron transfer to the cluster, has the expected monocapped square-antiprismatic geometry previously reported for $\text{Sn}_9{}^{4-}$ in $(2,2,2\text{-crypt-Na}^+)_4\text{Sn}_9{}^{4-}$.[8] Surprisingly, the distances within the cluster seem at first consideration to be scarcely altered by the presence of K4 and K5. Thus, the group of shortest Sn–Sn distances, i.e., those to the capping atom, between the square planes, and in the open face, all of which are essentially equal, average 2.964 (2) Å in the present example compared with 2.966 (5) Å in $(\text{crypt-Na}^+)_4\text{Sn}_9{}^{4-}$, with individual differences between the averages of the different types of bonds of 0.9σ, 0.7σ, and 1.4σ, respectively. The smaller set of somewhat greater Sn–Sn distances within the capped face averages 3.224 (2) Å in $\text{KSn}_9{}^{3-}$ and 3.243 (4) Å in $\text{Sn}_9{}^{4-}$, a difference of 0.019 Å (4.2σ). It should be noted that these comparisons are clouded by the fact that the two sets of structural data were recorded at −100 and 5 °C, respectively, so that some expansion of the cluster in $\text{KSn}_9{}^{3-}$ would probably be seen in an isothermal comparison.

The present $\text{Sn}_9{}^{4-}$ cluster does appear slightly stretched by the two potassium atoms, making the Sn6–Sn8 diagonal of the base 0.10 Å longer than the other and angles therein up to 2° from 90°. Dihedral angles for the two pairs of opposed triangles around the base that would (for $\delta = 180°$) define the basal planes of a tricapped trigonal prism[8] now differ by 4° but still average the value for $\text{Sn}_9{}^{4-}$ while the base is planar within 1°. A careful comparison of distances also reveals what appears to be a perceptible distortion of the cluster in the new anion by the two potassium atoms. Thus, within the group of shorter Sn–Sn distances (average 2.964 Å), those where *both* atoms have potassium neighbors are longer by an average of 0.016 Å (5.7σ). According to extended-Hückel[16] and relativistic extended-Hückel[17] calculations on $\text{Sn}_9{}^{4-}$, the most negative sites are the atoms in the open face followed by the capping atom. These are not the same atoms that are found to interact with potassium; of course, these calculations included no consideration of polarization by counterions. Furthermore, the exigencies of packing of the 2,2,2-crypt-K$^+$ cations may dictate something of the orientation of the tin cluster, as has been noted before with thallium-tin polyhedra.[5]

Although electron transfer to potassium is seemingly not large enough to alter the tin cluster very much, this and the packing of the cryptated cations are sufficient to eliminate the relatively weak tendency for potassium to coordinate ethylenediamine. The only alternative seems like an unlikely one—that the missing en are so disordered that nothing is resolvable even at the level of $Z > 1$—and even then there does not appear to be sufficient room. It will also be recalled that this phase came from a reaction in which sufficient crypt was present in solution nominally to complex all of the potassium in the alloy; however, it seems very likely that the mixed-phase alloy samples selected for use were rich in the lighter tin (KSn$_2$?), and therefore the reaction was crypt deficient.

With these somewhat unusual features inherent in the structure, it is reassuring to find other examples in the literature that involve association of a cluster with an alkali-metal cation. The most closely related is found in the (partial) crystal structure solution of $[(\text{Na}^+)_4{\cdot}7\text{en}]\text{Sn}_9{}^{4-}$.[18] Here, the en molecules coordinated to

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the sodium ions could not be well resolved ($\bar{B} \sim 14$ Å^2, R = 11.7%) and thermal ellipsoids for two tin atoms were quite elongated. Nonetheless, a most interesting fact was clear, that the sequestering of Na^+ by en was incomplete and several short Na–Sn distances remained. The resulting cluster arrangement can be described approximately in terms of a nominal tricapped trigonal prism of tin in which two sodium ions with only three bonded nitrogen (from en) also bridge two of the three long edges of the trigonal prism ($\bar{d}$(Na–Sn) = 3.53 Å) and thereby elongate these edges by over 0.5 Å relative to the third. (This distortion is not along the pathway associated with $D_{3h} \rightleftarrows C_{4v}$ interconversion of nine-atom polyhedra.[8]) However, these Na–Sn distances appear relatively (~0.2 Å) long compared with those found here (with higher symmetry and much less distortion) when it is noted that the difference in crystal radius of the two cations is 0.36 Å.

Also, in $Rb_3As_7{\cdot}3en$,[19] the rubidium atoms all bridge between the two-coordinate atoms in the As_7^{3-} anion, with the ethylenediamine molecules coordinated to the alkali metal only on the outside of the "Rb_3As_7" complex. A similar mode of coordination also occurs in $Na_4P_{14}{\cdot}6en$. Also of note is the ternary compound Rb_7NaGe_8 (and the isotypic K_7NaGe_8) in which tetrahedra of Ge_4^{4-} are linked in pairs by sodium to give a "linear" [$(Ge_4)Na(Ge_4)$] unit, the sodium having six equivalent germanium neighbors in a trigonal-antiprismatic arrangement through coordination to two faces of the opposed tetrahedra.[20] The Ge–Ge distances in these faces are notably greater than the other distances in the tetrahedron (2.62 vs. 2.53 Å), while the Na–Ge and Rb–Ge bond distances are in the usual ranges found in their respective binary alloys that also contain tetrahedra.

Acknowledgment. We thank Professor R. A. Jacobson and the members of his research group for the use of the diffractometer and for helpful suggestions during the refinement of this structure.

Supplementary Material Available: Listings of thermal parameters, interbond angles for the nonastannide unit, bond distances and angles in the 2,2,2-crypt-K^+ cations, and structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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Complex Chemistry of Reactive Organic Compounds. 48.[1] σ-Alkyl, π-Allyl, and π-Olefin Coordination of Diphenylketene: Neutron Diffraction Studies of the Carbonyliron Complexes $Fe(CO)_3[\eta^3{:}\eta^1\text{-}(C_6H_5)_2CCO]$ and $Fe_2(CO)_6[CH(C_6H_5)(C_6H_4)]$

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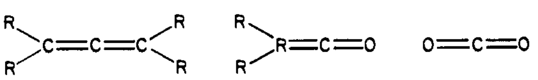
Received July 17, 1984

Photolysis of pentacarbonyliron in the presence of diphenylketene yields the novel $\eta^1{:}\eta^3$-diphenylketene complex of composition $Fe(CO)_3[(C_6H_5)_2C_2O]$ (**1**). This compound, according to a single-crystal neutron diffraction study, exhibits the heterocumulene precursor in a π-allyl/σ-acyl coordination: One phenyl ring engages in π bonding of this ligand to the transition-metal center. Crystallographic data: triclinic, space group $P\bar{1}$; a = 8.852 (2), b = 11.571 (4), c = 14.558 (6) Å; α = 106.94 (2), β = 89.76 (2), γ = 91.94 (2)°; V = 1425.6 (2) Å^3; Z = 4; $R(F^2)$ = 0.078 for all 5206 reflections measured at T = 15 K. Upon treatment of compound **1** with excess enneacarbonyldiiron, the dinuclear complex $Fe_2(CO)_6[CH(C_6H_5)(C_6H_4)]$ (**3**) is formed in 77% yield. This molecule was shown by neutron diffraction techniques to contain a bridging hydrocarbon ligand related to the original ketene ligand in **1** by decarbonylation and 1,3-hydrogen shift. Crystal data: monoclinic, space group $P2_1/n$; a = 8.298 (3), b = 12.463 (6), c = 17.380 (3) Å; β = 97.95 (1)°; V = 1780 (1) Å^3; Z = 4; $R(F^2)$ = 0.111 for 2622 neutron reflections with $F_o^2 > 1.5\sigma(F_o^2)$ measured at T = 230 K.

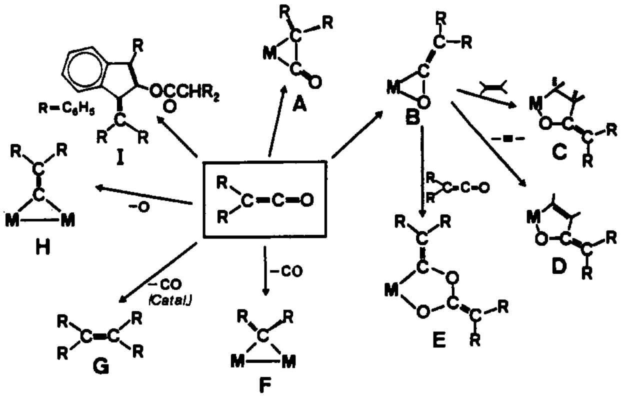
Introduction

The coordination chemistry of ketenes evidences an amazing array of metal fixation, fragmentation, and coupling reactions. The cumulene structure of ketenes effectively interlinks allenes and carbon dioxide and results in behavior similar to reactions of these latter well-studied species with transition-metal complexes.[3]



$$R_2C{=}C{=}CR_2 \qquad R_2R{=}C{=}O \qquad O{=}C{=}O$$

Scheme I



If the integrity of the ketene cumulene framework is retained upon complexation, two major coordination modes, A and B, occur: Electron-rich metal centers such as manganese(I) and platinum(0)

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