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Homopolyatomic Anions of the Post Transition Elements. Synthesis and Structure of Potassium–crypt Salts of the Tetraantimonide(2–) and Heptaantimonide(3–) Anions, Sb_4^{2-} and Sb_7^{3-}

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Reaction of the alloy KGeSb with 2,2,2-crypt in ethylenediamine (en) produces a dark red solution from which crystals of both (2,2,2-crypt–K^+)$_2Sb_4^{2-}$ (I) and (2,2,2-crypt–K^+)$_3Sb_7^{3-}$·2en (II) can be isolated. The former has also been obtained from like reactions of KAuSb and KPbSb compositions. Four octants of X-ray diffraction data were collected for each complex on an automated diffractometer using monochromated Mo Kα radiation, at room temperature for I and at –80 °C for II. Compound I crystallizes in the space group $P\bar{1}$ with $a = 11.555$ (1) Å, $b = 11.795$ (1) Å, $c = 11.067$ (1) Å, $\alpha = 97.60$ (1)°, $\beta = 97.80$ (1)°, $\gamma = 61.24$ (1)°, $V = 1306.1$ (2) Å^3, and $Z = 1$ and is isostructural with the known (2,2,2-crypt–K^+)$_2Bi_4^{2-}$. Refinement of positional and anisotropic thermal parameters for all 29 non-hydrogen atoms by full-matrix least-squares techniques yields $R = 0.081$ and $R_w = 0.113$ for 3909 independent observed reflections. The Sb_4^{2-} anion is effectively square planar (D_{4h}), with bond lengths of 2.749 (1) and 2.751 (1) Å and bond angles of 90.05 (3)° and 89.95 (3)°. Compound II also occurs in space group $P\bar{1}$ with $a = 14.589$ (2) Å, $b = 21.753$ (3) Å, $c = 13.857$ (2) Å, $\alpha = 92.46$ (1)°, $\beta = 99.63$ (2)°, $\gamma = 89.12$ (2)°, $V = 4331$ (1) Å^3, and $Z = 2$. Positional and thermal parameters (anisotropic for all but carbon) for the 96 non-hydrogen atoms were refined to $R = 0.075$ and $R_w = 0.093$ for 7281 independent observed reflections. This structure contains the Sb_7^{3-} anion with approximately C_{3v} symmetry; the anion was previously known (but less well defined) in the (2,2,2-crypt–Na^+)$_3Sb_7^{3-}$ salt, but the two compounds are not isostructural.

Introduction

In the last 10 years, many polyatomic anions of the post transition elements, Bi_4^{2-},[2] Sb_7^{3-},[3] and As_{11}^{3-}[4] in group 5, for example, have been isolated as stable salts by the reaction of their alkali-metal alloys with 2,2,2-crypt, an excellent complexing agent for the metal cation Recent investigations have included reactions to produce heteropolyatomic clusters of group 4 and 5 elements in order to explore new electronic configurations and structures; $Sn_2Bi_2^{2-}$[5] and $Pb_2Sb_2^{2-}$[6] are two examples of such anions that have recently been structurally characterized.

As part of this study we explored the reactions of a KGeSb alloy. Instead of the expected heteropolyatomic Ge/Sb anions, two antimony clusters were produced as the K^+–crypt salts. One compound contained the new Sb_4^{2-} anion, and the second, the Sb_7^{3-} anion in a new structure.

Experimental Section

Materials and Synthesis. All manipulations were performed either in an inert-atmosphere drybox or on a vacuum line. Antimony (99.999% pure) was obtained from A. D. Mackay, Inc., potassium ("purified") from J. T. Baker Chemical Co., germanium (zone refined) from United Mineral and Chemical, and the 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) from Merck. Ethylenediamine (en) (Fisher Scientific Co.) was first dried by refluxing over CaH_2 and then stored over molecular sieves. The ternary alloy composition KGeSb was prepared by the fusion at 970 °C of stoichiometric amounts of the elements in a sealed tantalum tube enclosed in a fused silica jacket, followed by quenching which yielded a dark gray, microcrystalline product. Vessels for the crypt-alloy reactions have been previously described.[3,7]

KGeSb reacts with a stoichiometric amount of crypt in en to give a dark red solution. Crystals were grown at room temperature after 5–7 days by slow removal of the solvent (1–2 weeks). If the solution is decanted from the alloy residue before crystal growth, large crystals of the Sb_4^{2-} phase (I) deposit irreversibly, though the majority of the product is an unknown phase that is blade or needle shaped but poorly crystalline. If crystal growth occurs with the solution in contact with unreacted alloy, the Sb_4^{2-} phase crystallizes first, as before, but two other phases (II and III) that are indistinguishable by eye also form. Phase II, which contains the Sb_7^{3-} anion, crystallizes with a unit cell at room temperature of $a = 14.72$ Å, $b = 21.87$ Å, $c = 13.98$ Å, $\alpha = 92.7°$, $\beta = 99.9°$, $\gamma = 89.3°$, and $V = 4428$ Å^3 (parameters after tuning on three standard reflections on the diffractometer). Phase III may also contain Sb_7^{3-}, perhaps with a different packing arrangement, since the unit cell parameters are similar for the main part: $a = 14.85$ Å, $b = 22.02$ Å, $c = 13.97$ Å, $\alpha = 93.7°$, $\beta = 106.1°$, $\gamma = 91.7°$, $V = 4373$ Å^3. Also, microprobe analyses cannot distinuish between II and III and indicate the absence of Ge in both. The phase (2,2,2-crypt–K^+)$_2Sb_4^{2-}$ has also been observed as the major product of the reaction of the alloy KAuSb with crypt.[8] The alloy KPbSb will similarly react to produce both phase I and III (each identified by the unit cell parameters obtained after tuning on three standard reflections on the diffractometer), but only when crystals are grown with the solution in contact with the alloy residue. The product of this reaction was also analyzed by microprobe, and again no significant amount of the other alloy component (Pb) was found in either phase I or phase III crystals. Therefore it is clear all three phases must contain only homopolyatomic antimony anions.

The crystals were rinsed with dry heptane to remove any unreacted crypt, and then suitable crystals were mounted into 0.3- or 0.5-mm capillaries in a drybox. (2,2,2-crypt–K^+)$_2Sb_4^{2-}$ occurs as hard, black, wedge-shaped crystals that have very reflective, bluish colored faces and are insoluble in en. (2,2,2-crypt–K^+)$_3Sb_7^{3-}$·2en crystallizes as dark red rods which can be redissolved in en.

Data Collection and Reduction. (2,2,2-crypt–K^+)$_2Sb_4^{2-}$ (I). A strongly diffracting crystal of dimensions 0.62 × 0.30 × 0.17 mm was examined by using Mo Kα radiation monochromatized with graphite ($\lambda = 0.71034$ Å) on an automated four-circle diffractometer designed and built in the Ames Laboratory.[9] A total of 5371 reflections were collected at ~25 °C for the four octants HKL, $\bar{H}L$, $\bar{H}\bar{K}L$, and $H\bar{K}L$ with $2\theta < 50°$. Three standard reflections that were measured every 75 reflections showed only a 7% decay in intensity during data collection (in sharp contrast to the isostructural Bi_4^{2-} salt, which decayed so rapidly two crystals were necessary to obtain a complete data set[2]). An empirical absorption correction using a ϕ-scan method ($\mu = 22.8$ cm^{-1}, $\phi = 0$–$350°$, $\Delta\phi = 10°$) was applied with the program ABSN;[10]

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

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transmission coefficients ranged from 0.75 to 0.99. After the data were corrected for decay, absorption, Lorentz, and polarization effects and averaged in the space group $P\bar{1}$ (R_{av} = 0.035), the final data set consisted of 3909 independent observed reflections ($I > 3\sigma(I)$ and $F > 3\sigma(F)$).

Precise lattice dimensions of a = 11.555 (1) Å, b = 11.795 (1) Å, c = 11.067 (1) Å, α = 97.60 (1)°, β = 97.80 (1)°, γ = 61.24 (1)°, and V = 1306.1 (2) Å^3 (Z = 1, d_{calcd} = 1.68 g/cm^3, M_r = 1318) were obtained by a least-squares fit to the 2θ values of 24 reflections in the range 36° < 2θ < 42° which had been tuned on both Friedel-related peaks to eliminate any instrument or centering errors. This cell compares well with that for (2,2,2-crypt-K$^+$)$_2$Bi$_4^{2-}$ salt: a = 11.604 (4) Å, b = 11.796 (4) Å, c = 11.096 (3) Å, α = 98.12 (3)°, β = 98.02 (3)°, γ = 61.37 (3)°, and V = 1315.2 (7) Å^3;[2] the two are clearly isostructural.

(2,2,2-crypt-K$^+$)$_3$Sb$_7^{3-}$·2en (II). Data were collected by using a crystal of dimensions 0.42 × 0.13 × 0.04 mm at low temperature (-80 °C) on the Ames Laboratory diffractometer. The crystal was not a strong diffractor, but the diffraction peaks were very sharp. A total of 12 049 reflections with 2θ < 44° in the four octants HKL, $\bar{H}\bar{K}L$, $\bar{H}K\bar{L}$, and $H\bar{K}\bar{L}$ were measured. The data were corrected for decay (according to a 22% decrease in the integrated intensities of three standard reflections), Lorentz, polarization, and absorption effects (by the ϕ-scan method, μ = 23.8 cm^{-1}; transmission coefficients ranged from 0.73 to 0.99). The final data set contained 7281 independent observed reflections after averaging in the space group $P\bar{1}$ (R_{av} = 0.033).

Precise unit cell dimensions are a = 14.589 (2) Å, b = 21.753 (3) Å, c = 13.857 (2) Å, α = 92.46 (1)°, β = 99.63 (2)°, γ = 89.12 (2)°, and V = 4331 (1) Å^3 obtained, as before, from 24 reflections with 25° < 2θ < 34°; Z = 2, d_{calcd} = 1.70 g/cm^3, M_r = 2219.

Structure Solution. (2,2,2-crypt-K$^+$)$_2$Sb$_4^{2-}$ (I). Since the unit cell parameters indicated the compound was isostructural with the Bi$_4^{2-}$ salt,[2] the least-squares refinement began with the Bi atom coordinates for the two Sb positions, which immediately gave an agreement factor $R = 0.305 = \sum||F_o| - |F_c||/\sum|F_o|$. Further full-matrix least-squares refinement and Fourier electron density syntheses located all the crypt atoms (in essentially the same positions as in the Bi$_4^{2-}$ structure) to give R = 0.080 when all 29 atoms were allowed to have anisotropic thermal parameters (of the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$). At this point, both electron density and difference maps indicated a disorder in the crypt carbons α and β to the nitrogen nearest the Sb$_4^{2-}$ anion, similar to that found in the Bi$_4^{2-}$ structure. In particular, C1, C2, C11, C12, and C22 were resolvable into pairs (a and b) with separations of 0.7–1.0 Å. (The "thermal" ellipsoid for C21 is also considerably elongated but not enough to make resolution feasible.) With isotropic thermal parameters and a multiplicity of 0.50 for these carbon atoms (from which they do not appear to vary significantly), the residuals were essentially unchanged at R = 0.081 and $R_w = 0.113 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = \sigma_F^{-2}$. This disordered model is clearly the preferred one in terms of chemical sensibility as otherwise the N–C and C–C bond distances are much too short.

(2,2,2-crypt-K$^+$)$_3$Sb$_7^{3-}$·2en (II). Analysis of a conventional Patterson map clearly showed a seven-atom cluster with bond distances and configuration indicative of Sb$_7^{3-}$ (as in the known crypt-Na$^+$ salt[3]). Least-squares refinement of the seven Sb and three K positions obtained from the Patterson map immediately yielded R = 0.223. The crypt atoms and two en solvent molecules were located on an electron density map, and subsequent refinement of all 96 atoms with isotropic thermal parameters gave R = 0.104 and R_w = 0.131. Final block-diagonal least-squares refinement allowing the Sb, K, O, and N atoms (in crypt, not the solvent molecules) to be anisotropic converged at R = 0.075 and R_w = 0.093.

For each structure, the final difference map was essentially flat to ± 2 e/Å^3 near the antimony atoms and less than ±1 e/Å^3 in the rest of the map. The 72 hydrogen atoms for structure I and 124 for II have not been located or estimated in the structure factor calculations; these represent 11.0% and 11.3% of the total electron density, respectively. Structure factor calculations and least-squares refinements were carried out by using the block matrix/full matrix program ALLS,[11] and Fourier series calculations were done with the program FOUR.[12] The neutral atom scattering factors[13] included corrections for the real and imaginary parts of anomalous dispersion for antimony and potassium.

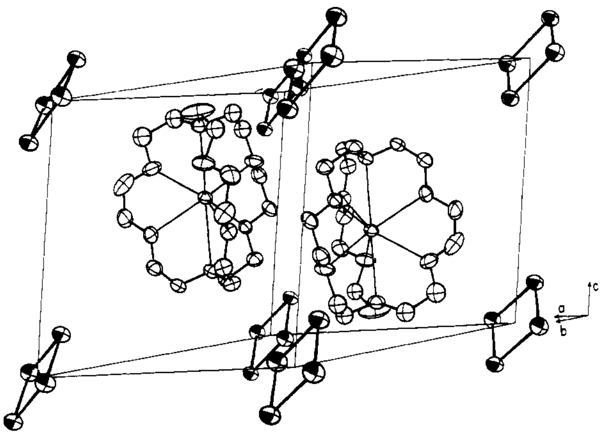

Figure 1. Approximate [$\bar{1}$10] view of the unit cell of (2,2,2-crypt-K$^+$)$_2$Sb$_4^{2-}$ with thermal ellipsoids at the 30% probability level. For clarity, only one consistent set (b) of the disordered carbon atoms is shown.

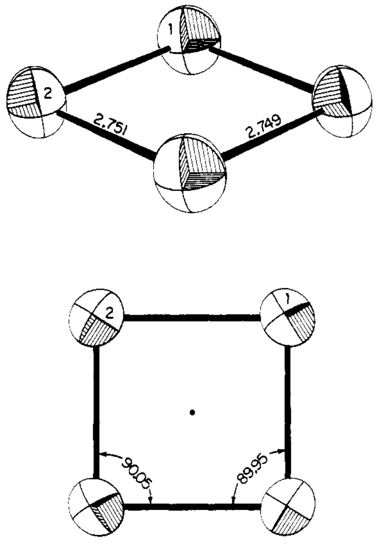

Figure 2. Two views of the Sb$_4^{2-}$ anion. Thermal ellipsoids are drawn at the 50% probability level.

Results and Discussion

The final positional data for all atoms in (2,2,2-crypt-K$^+$)$_2$Sb$_4^{2-}$ and (2,2,2-crypt-K$^+$)$_3$Sb$_7^{3-}$·2en are listed in Tables I and II, respectively. Distances and angles for the Sb$_7^{2-}$ anion are given in Table III, while characteristic distances for the Sb$_7^{3-}$ anion together with comparable values from the crypt-Na$^+$ salt are give in Table IV. Bond angles for Sb$_7^{3-}$, thermal parameters for all atoms, distances and angles for the cations and en molecules, and the observed and calculated structure factors for the two compounds appear in the supplementary material.

The Sb$_4^{2-}$ salt is indeed isostructural with the Bi$_4^{2-}$ compound. A drawing of the unit cell presented in Figure 1 demonstrates the pseudohexagonal close packing of the anions, a feature that is common for 2– anions.[2,5,14] It is amazing how similar the disorder of the α- and β-carbon atoms is in the two compounds, in spite of the smaller Sb$_4^{2-}$ anion, supporting the assumption that the disorder is real and correctly treated. This disorder represents a choice of whether the

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Table I. Final Positional Parameters for $(2,2,2\text{-crypt-K}^+)_2\text{Sb}_4{}^{2-}$

atom	x	y	z	atom	x	y	z
Sb1	0.18408 (6)	0.86645 (7)	0.00182 (6)	C25	0.6544 (9)	0.0627 (9)	0.4697 (10)
Sb2	0.02067 (6)	0.06419 (6)	0.85552 (6)	C7	0.1467 (9)	0.3058 (10)	0.6514 (8)
K	0.3232 (2)	0.3242 (1)	0.4082 (1)	C17	0.3088 (9)	0.5695 (8)	0.6609 (8)
O3[a]	0.0967 (8)	0.3211 (10)	0.2767 (6)	C27	0.5702 (8)	0.1587 (8)	0.6606 (8)
O13	0.3303 (8)	0.5186 (6)	0.2866 (5)	C8	0.2802 (9)	0.2755 (9)	0.7219 (7)
O23	0.5212 (8)	0.1058 (6)	0.2865 (5)	C18	0.2741 (9)	0.4856 (8)	0.7250 (7)
O6	0.1732 (5)	0.2568 (6)	0.5262 (5)	C28	0.4835 (8)	0.2890 (8)	0.7293 (7)
O16	0.5644 (5)	0.1774 (5)	0.5371 (5)	C1a[b]	0.200 (2)	0.278 (2)	0.086 (2)
O26	0.2691 (5)	0.5615 (5)	0.5343 (5)	C1b	0.156 (3)	0.343 (3)	0.097 (2)
N0	0.3026 (9)	0.3043 (8)	0.1372 (6)	C11a	0.282 (2)	0.425 (2)	0.093 (2)
N9	0.3426 (6)	0.3463 (6)	0.6817 (5)	C11b	0.357 (3)	0.386 (2)	0.101 (2)
C21	0.4102 (18)	0.1831 (16)	0.0937 (11)	C2a	0.075 (2)	0.350 (2)	0.145 (2)
C4	0.0814 (11)	0.2242 (13)	0.3294 (13)	C2b	0.113 (2)	0.257 (3)	0.155 (2)
C14	0.2399 (9)	0.6413 (9)	0.3395 (9)	C12a	0.358 (2)	0.490 (2)	0.154 (2)
C24	0.6455 (13)	0.0857 (11)	0.3401 (11)	C12b	0.262 (2)	0.533 (2)	0.158 (2)
C5	0.0567 (10)	0.2590 (13)	0.4544 (11)	C22a	0.482 (2)	0.094 (2)	0.148 (2)
C15	0.2846 (10)	0.6500 (7)	0.4728 (8)	C22b	0.542 (2)	0.123 (2)	0.167 (2)

[a] The last digit indicates the position along the crypt chain; the first digit (0 (missing), 1 or 2) identifies the chain. [b] a and b denote the disordered pairs of carbon atoms (0.50 occupancy).

Table II. Final Positional Parameters for $(2,2,2\text{-crypt-K}^+)_3\text{Sb}_7{}^{3-}\cdot 2\text{en}$

atom	x	y	z	atom	x	y	z
Sb1	0.31262 (9)	0.15894 (6)	0.79123 (9)	O123	0.3424 (8)	0.9028 (6)	0.2396 (8)
Sb2	0.36995 (9)	0.24997 (7)	0.66639 (10)	N200	0.3506 (10)	0.3742 (6)	0.2053 (10)
Sb3	0.20155 (9)	0.18220 (6)	0.60189 (9)	N209	0.2120 (15)	0.5829 (8)	0.4348 (12)
Sb4	0.23242 (10)	0.22837 (6)	0.92250 (9)	O203	0.2280 (9)	0.3566 (6)	0.3519 (8)
Sb5	0.31312 (10)	0.35957 (7)	0.74188 (10)	O206	0.1979 (10)	0.4558 (6)	0.4782 (9)
Sb6	0.05935 (9)	0.25747 (6)	0.63954 (10)	O212	0.2218 (8)	0.4684 (6)	0.1116 (8)
Sb7	0.15470 (9)	0.32173 (6)	0.80308 (10)	O215	0.1289 (10)	0.5496 (7)	0.2278 (11)
K1	0.8189 (3)	0.0255 (2)	0.8112 (3)	O220	0.4749 (9)	0.4679 (6)	0.3160 (10)
K2	0.2790 (3)	0.4783 (2)	0.3173 (3)	O223	0.4036 (12)	0.5779 (6)	0.3874 (11)
K3	0.7745 (3)	0.3084 (2)	0.0782 (3)	N300	0.0484 (9)	0.6845 (7)	0.7874 (10)
N100[a]	0.0264 (10)	0.9632 (7)	0.3033 (11)	N309	0.3976 (10)	0.6990 (7)	0.0565 (10)
N109	0.3386 (11)	0.9871 (7)	0.0726 (11)	O303	0.1581 (8)	0.5741 (5)	0.8464 (8)
O103	0.1003 (8)	0.0851 (6)	0.2630 (8)	O306	0.3475 (8)	0.5874 (6)	0.9286 (8)
O106	0.2660 (9)	0.0891 (5)	0.1811 (9)	O312	0.2092 (8)	0.7480 (6)	0.7374 (9)
O112	0.0231 (10)	0.9144 (6)	0.0985 (9)	O315	0.3570 (9)	0.7797 (6)	0.8900 (9)
O115	0.1575 (12)	0.9402 (6)	0.9807 (10)	O320	0.0637 (8)	0.7410 (5)	0.9851 (8)
O120	0.2097 (8)	0.9100 (5)	0.3680 (8)	O323	0.2219 (7)	0.7182 (5)	0.1254 (8)
C101	0.980 (1)	0.0247 (10)	0.309 (2)	C219	0.504 (2)	0.4275 (11)	0.242 (2)
C102	0.050 (1)	0.0762 (10)	0.340 (2)	C221	0.521 (2)	0.5256 (10)	0.316 (2)
C104	0.168 (1)	0.1338 (9)	0.288 (1)	C222	0.500 (2)	0.5660 (11)	0.399 (2)
C105	0.214 (1)	0.1427 (9)	0.200 (1)	C224	0.380 (2)	0.6176 (15)	0.466 (2)
C107	0.316 (1)	0.0988 (10)	0.103 (1)	C225	0.278 (2)	0.6344 (14)	0.437 (2)
C108	0.385 (2)	0.0472 (11)	0.102 (2)	C301	0.010 (1)	0.6233 (8)	0.791 (1)
C110	0.957 (1)	0.9182 (10)	0.248 (1)	C302	0.080 (1)	0.5704 (10)	0.769 (1)
C111	0.938 (2)	0.9266 (12)	0.137 (2)	C304	0.228 (1)	0.5312 (9)	0.822 (1)
C113	0.005 (2)	0.9068 (12)	0.993 (2)	C305	0.304 (1)	0.5292 (9)	0.911 (1)
C114	0.087 (2)	0.8938 (12)	0.957 (2)	C307	0.421 (1)	0.5861 (9)	0.012 (1)
C116	0.242 (2)	0.9319 (11)	0.935 (2)	C308	0.464 (1)	0.6505 (9)	0.030 (1)
C117	0.306 (2)	0.9840 (11)	0.968 (2)	C310	0.060 (1)	0.6990 (10)	0.685 (1)
C118	0.061 (1)	0.9424 (10)	0.403 (1)	C311	0.116 (1)	0.7584 (10)	0.683 (1)
C119	0.128 (1)	0.8897 (9)	0.402 (1)	C313	0.265 (1)	0.8007 (10)	0.735 (1)
C121	0.278 (1)	0.8637 (9)	0.375 (1)	C314	0.363 (1)	0.7905 (10)	0.791 (2)
C122	0.363 (1)	0.8877 (10)	0.340 (1)	C316	0.447 (1)	0.7774 (9)	0.948 (1)
C124	0.426 (1)	0.9261 (10)	0.209 (2)	C317	0.441 (1)	0.7598 (9)	0.052 (1)
C125	0.404 (2)	0.9344 (10)	0.099 (2)	C318	0.983 (1)	0.7317 (8)	0.821 (1)
C201	0.302 (1)	0.3175 (9)	0.221 (1)	C319	0.975 (1)	0.7270 (9)	0.929 (1)
C202	0.292 (1)	0.3099 (9)	0.329 (1)	C321	0.058 (1)	0.7401 (9)	0.088 (1)
C204	0.214 (2)	0.3478 (11)	0.452 (2)	C322	0.150 (1)	0.7592 (8)	0.149 (1)
C205	0.151 (2)	0.3992 (11)	0.481 (2)	C324	0.308 (1)	0.7319 (9)	0.186 (1)
C207	0.155 (2)	0.5026 (12)	0.532 (2)	C325	0.381 (1)	0.6909 (9)	0.157 (1)
C208	0.219 (2)	0.5607 (12)	0.536 (2)	Nen1	0.300 (2)	0.0356 (12)	0.482 (2)
C210	0.331 (1)	0.3871 (9)	0.099 (1)	Cen1	0.366 (2)	0.0184 (14)	0.571 (2)
C211	0.234 (1)	0.4080 (10)	0.065 (2)	Cen2	0.303 (2)	0.9778 (13)	0.633 (2)
C213	0.129 (1)	0.4925 (10)	0.076 (2)	Nen2	0.366 (2)	0.9657 (11)	0.725 (2)
C214	0.120 (2)	0.5555 (11)	0.128 (2)	Nen3	0.434 (2)	0.0859 (11)	0.353 (2)
C216	0.113 (2)	0.6086 (13)	0.275 (2)	Nen4	0.529 (2)	0.2354 (11)	0.453 (2)
C217	0.119 (2)	0.5994 (13)	0.388 (2)	Cen3	0.441 (3)	0.168 (2)	0.371 (3)
C218	0.449 (1)	0.3669 (10)	0.240 (2)	Cen4	0.517 (3)	0.157 (2)	0.423 (3)

[a] The first digit identifies the crypt cation, the next two the position therein.

conformations of the N–Cα–Cβ fragments at the two ends of each crypt chain are placed in an essentially eclipsed (a) or crossed (b) manner when viewed down the N–K–N axis, the latter being the normal configuration for 2,2,2-crypt–K^+ salts.

Table III. Distances and Angles for Sb_4^{2-} in $(crypt\text{-}K^+)_2Sb_4^{2-}$

atom 1	atom 2	*d*, Å	atoms	angle, deg
Sb1	Sb2	2.749 (1)	1-2-1′	89.95 (3)
Sb1	Sb2′	2.751 (1)	2-1-2′	90.05 (3)
Sb1	Sb1′	3.888 (1)		
Sb2	Sb2′	3.891 (1)		

Table IV. Comparative Distances for Sb_7^{3-} Anions

Sb-Sb	$(crypt\text{-}K)_3Sb_7\cdot 2en$[a]	$(crypt\text{-}Na)_3Sb_7$[b]
1-2	2.906 (2)	2.856 (4)
1-3	2.904 (2)	2.880 (4)
2-3	2.876 (2)	2.838 (3)
1-4	2.717 (2)	2.693 (4)
2-5	2.735 (2)	2.706 (4)
3-6	2.728 (2)	2.711 (4)
4-7	2.782 (2)	2.824 (4)
5-7	2.741 (2)	2.755 (4)
6-7	2.785 (2)	2.776 (4)
1-7	4.207 (2)	4.210 (4)
2-7	4.180 (2)	4.159 (4)
3-7	4.159 (2)	4.209 (4)
4-5	4.183 (2)	4.313 (4)
4-6	4.359 (2)	4.253 (4)
5-6	4.345 (2)	4.397 (4)

[a] This work. [b] Reference 3.

The disordered end of the crypt does have the closer interactions with the anion, which undoubltedly influences this behavior.

The Sb_4^{2-} is truly square planar (D_{4h}), Figure 2 and Table III, although the point symmetry is only required to be C_i. As with Bi_4^{2-} and Te_4^{2+}, the MO diagram implies a bond order of 1.25, with four bonding levels (a_{1g}, b_{2g}, e_u, a_{2u}) and one nonbonding (actually slightly antibonding) level (e_g) accommodating the 14 skeletal electrons.[2] The average Sb–Sb bond distance of 2.750 Å is significantly shorter than that in Sb_7^{3-}, 2.797 Å.

It is odd that the Sb_4^{2-} anion was never found in earlier studies of Na/Sb binary alloy reactions with crypt, in spite of the fact that alloy compositions ranging from NaSb to $NaSb_3$ were investigated; rather $(2,2,2\text{-crypt–}Na^+)_3Sb_7^{3-}$ was the only product. However, the ternary alloys KGeSb, KAuSb, and KPbSb demonstrate facile formation of Sb_4^{2-}. Although binary K/Sb alloys have not been investigated, presumably Sb_4^{2-} could be readily produced from these as well unless the ternary alloys serve in some unusual way as reducing agents. There is a cell volume decrease expected on switching from crypt–K^+ to crypt–Na^+ cations (approximately 30 $Å^3$ per crypt[15]) that may destabilize the smaller anion. More likely, the growth conditions used for the earlier Na/Sb reactions, namely solvent evaporation after a few days, may have been inadequate for formation of Sb_4^{2-} crystals that spontaneously precipitate over longer periods.

The unit cell for $(2,2,2\text{-crypt-}K^+)_3Sb_7^{3-}\cdot 2en$ bears no obvious resemblance to that of the previously known $(2,2,2\text{-crypt–}Na^+)_3Sb_7^{3-}$ salt[3] ($P2_1/n$ with $a = 23.292$ (7) Å, $b = 13.791$ (6) Å, $c = 25.355$ (6) Å, $\beta = 108.56$ (2)°, $V = 7721$ $Å^3$, and 643 $Å^3$/crypt). Instead, the present phase's large volume (722 $Å^3$/crypt) and close similarity in dimensions to other cells containing six crypt-K^+ ions such as $(2,2,2\text{-crypt-}K^+)_3(TlSn_8^{3-}\text{-}TlSn_9^{3-})_{1/2}\cdot en$[16] led to an expectation of a nine-atom cluster. The packing of the ions in the unit cell is indeed similar, with the center of the anion and the three independent potassium atoms in essentially the same positions as in the Tl/Sn salt although the N–K–N axes of the cations are oriented in different directions. The second solvent molecule compensates for the smaller Sb_7^{3-} anion. The 2,2,2-crypt-K^+ cations in this structure have normal conformations, with the potassium centrally located along the N–N axis.

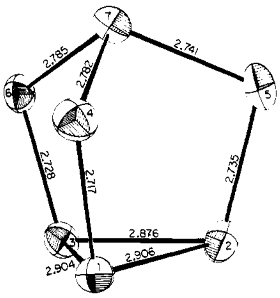

Figure 3. The Sb_7^{3-} anion with the approximate C_{3v} axis vertical. Thermal ellipsoids are drawn at the 50% probability level.

This structure is very well behaved, with small thermal parameters originating from both the low temperature of the data collection and the good quality of the crystal; even the en solvent molecules show none of the usual disorder. Consequently, the standard deviations for the bond distances are generally about half those observed for the crypt–Na^+ salt (see Table IV). The Sb_7^{3-} anion depicted in Figure 3 has an approximate C_{3v} configuration, analogous to the isoelectronic P_7^{3-} anion[17] or P_4S^3 molecule.[18] It is interesting that the anion chooses to be distorted somewhat from C_{3v} symmetry in that the Sb2–Sb3 bond distance is significantly shorter than Sb1–Sb2 and Sb2–Sb3 in the triangular base and Sb5–Sb7 is shorter than Sb4–Sb7 and Sb6–Sb7 to the trigonal apex. There is one fairly short contact to a crypt carbon, Sb5–C221 at 3.71 (2) Å, which may be pertinent to the latter difference. The shortest distance to an en atom is Sb3–NEN1 at 3.90 (3) Å, which is much too long to allow contemplation of any hydrogen bonding interaction. However, there does appear to be hydrogen bonding between the two en molecules, with a NEN1–NEN3 distance of 3.10 (3) Å. The average distance observed for common N–H···N hydrogen bonds is 3.1 Å.[19] These two nitrogen atoms are also surprisingly close to two crypt oxygens, with distances NEN3–O106 and NEN1–O120 of 3.12 (2) Å and 3.27 (3) Å, respectively.

The distortions in the Sb_7^{3-} anion found in the crypt–Na^+ salt are qualitatively somewhat similar but there are also major differences, e.g., in Sb4–Sb7 (Table IV). In general, comparable distances in the two clusters differ by 2–10σ, changes in the crystal packing of the surrounding crypt cations undoubltedly being the prime factor here. However, it is surprising that the result of the crypt-K^+ structure solution at −80 °C actually has the longer average Sb–Sb bond distances, 2.797 Å, compared with the room temperature results for crypt–Na^+ salt of 2.782 Å.

It is clear that the presence of alloy residue during crystal growth greatly enhances the production of the homopolyatomic anions, especially for the more soluble elements. In the KPbSb reaction that produces Sb_4^{2-} and phase III (see Experimental Section), only small amounts of Pb are found in the products, while the heteroatomic $Pb_2Sb_2^{2-}$ anion is easily obtained from solutions decanted from the same alloy after 3 days.[6] Rudolph and co-workers[20] also observed during NMR investigations of similar ternary alloy systems dissolved in en that equilibration between anions in solution is very slow and occurs principally at the surface of the solid alloys. A much more germanium-rich alloy is probably required in order to produce

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Ge/Sb heteropolyatomic anions, since Ge homoatomic anions like Ge_9^{4-} and Ge_9^{2-}[21] and perhaps any mixed anions as well are much less soluble than the polyantimony anions. The situation with KAuSb is probably similar.

In closing, it is interesting to speculate whether the unknown Bi_7^{3-} ion can be produced. Zintl et al.[22] reported a Bi_7^{3-} species from exhaustive extraction of bismuth-rich sodium alloys, but their analytical data are much more appropriate to the composition Bi_4^{2-}.[2] It should be noted that they also saw no evidence for Sb_4^{2-}, only Sb_3^{3-} and Sb_7^{3-}.[22,23] Reactions of various K/Bi alloys with crypt in en have produced only the Bi_4^{2-} salt, though various colored solutions have been noted in the course of the reaction.[2] Perhaps the use of Na/Bi alloys or an appropriate ternary composition would facilitate the isolation of a Bi_7^{3-} anion analogous to Sb_7^{3-}.

Registry No. I, 88524-92-9; II, 88510-57-0; KGeSb, 88510-55-8.

Supplementary Material Available: Listings of the positional and thermal parameters for all atoms, distances and angles in the crypt cations, and the observed and calculated structure factors for the Sb_4^{2-} and Sb_7^{3-} salts (37 pages). Ordering information is given on any current masthead page.

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Rate-Determining t_{2g}–t_{2g} Electron Transfer: Reaction of (3-Formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III) with Titanium(III) and Formation of (Pentane-2,4-dionato)titanium(III)

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The rate constants for the reaction of enol and keto forms of pentane-2,4-dione with Ti^{3+} (at 25 °C in 1 M LiCl) are 2.4 × 10^3 M^{-1} s^{-1} and 0.7 M^{-1} s^{-1}, respectively. (3-Formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III) oxidizes Ti(III) in a reaction that involves two relaxations with rate constants $k_f' \cong k[\mathrm{Ti(III)}]h[\mathrm{H}^+]^{-1} + k'$ and $k_s' \cong 20$ M^{-1} s^{-1}, where $h = [\mathrm{H}^+]/([\mathrm{H}^+] + 0.004\ \mathrm{M})$, $k = 2 \times 10^2$ M^{-1} s^{-1}, and $k' = 750$ M^{-1} s^{-1}. These results are interpreted as indicating rate-determining electron transfer within a deprotonated binuclear intermediate.

Previous work in this laboratory has demonstrated several mechanisms for reactions that involve titanium(III) species as reductants and ruthenium(III) complexes as oxidants. If the Ru(III) oxidant contains only ligands (such as NH_3 and en) that are not good bridging groups, then outer-sphere electron transfer (ET) occurs,[1] with $TiOH^{2+}$ acting as reductant. If pentane-2,4-dione, or another electron-delocalizing ligand, is present in the coordination sphere of the oxidant, then outer-sphere ET also involves Ti^{3+} as reductant.[2] If the oxidant contains carboxylate, or another effective lead-in group, then an inner-sphere mechanism dominates.[3] In all Ru(III)–Ti(III) inner-sphere reactions studied, formation of the binuclear intermediate is rate determining, through-bridge ET is rapid, and Ti^{3+} (rather than $TiOH^{2+}$) is the reductant. We now report a kinetic study of the formation of (pentane-2,4-dionato)titanium(III) and also of the reaction of Ti(III) with (3-formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III). We conclude that ET through the bridging ligand is rate determining for this redox reaction.[4]

Experimental Section

Methods and reagents were generally as described in previous papers.[1-4] During the course of this study, our stopped-flow spectrophotometers were interfaced to a microcomputer. Earlier data were stored temporarily in a Biomation transient recorder and permanently as charts of absorbance or transmission vs. time. These data were interpreted by using standard graphical techniques. Later data were recorded on diskettes and interpreted by using BASIC codes. For both sets, rate parameters were accepted if differences between simulation and experiment were comparable to experimental uncertainty.

(3-Formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III) (hereafter Ru(fpd)) was prepared by using procedures similar to those developed by Collman[5] and used by Balahura and Lewis[6] in analogous preparations. Phosphorus oxytrichloride (4.6 mL) was slowly added to 10 mL of freshly distilled dry dimethylformamide (DMF) in a 250-mL round-bottomed flask immersed in an ice bath. Tris(pentane-2,4-dionato)ruthenium(III),[2] hereafter $Ru(pd)_3$ (10 g), in dry freshly distilled DMF was added dropwise with stirring. The reaction mixture was warmed to room temperature and stirred for 4 h. An ice/water slurry of $NaHCO_3$ (10.6 g) was slowly added, and the reaction mixture was stirred until effervescence ceased (14 h). Aliquots were evaporated to dryness. Residues were dissolved in anhydrous methanol and passed through silica gel (60–200 mesh) columns, using methanol as eluant. The product moved as a single band; a black powder was obtained by evaporating the solvent from it. The IR spectrum (KBr disks) of the product was similar to that[2] of $Ru(pd)_3$, except for the presence of an additional absorption peak at 1670 cm^{-1}, which peak is assigned to the C=O stretch of a carbonyl group in conjugation with the pseudoaromatic ring. A peak at 1200 cm^{-1}, assignable to the C–H stretch involving the central carbon of the pd ligand, is present both in the spectrum of the product and also in that of the starting material. The intensity of this peak is less in

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