

## Metal Complexes as Ligands. 9.<sup>1</sup> Crystal and Molecular Structure of Potassium Bis(tri-*p*-tolylphosphine)copper(I) Bis(dithiooxalato-*O,O'*)stannate(IV)-2-Acetone, $\text{KSn}[(\text{S}_2\text{C}_2\text{O}_2)_3\text{Cu}(\text{P}(\text{C}_7\text{H}_7)_3)_2] \cdot 2\text{C}_3\text{H}_6\text{O}$

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Potassium bis(tri-*p*-tolylphosphine)copper(I) bis(dithiooxalato-*O,O'*)stannate(IV)-2-acetone crystallizes in the triclinic space group  $P\bar{1}$  with two molecules per unit cell. The cell dimensions are  $a = 10.981(2) \text{ \AA}$ ,  $b = 11.136(2) \text{ \AA}$ ,  $c = 26.337(6) \text{ \AA}$ ,  $\alpha = 106.69(2)^\circ$ ,  $\beta = 99.97(2)^\circ$ , and  $\gamma = 78.39(2)^\circ$ . Intensity data were collected with monochromatic  $\text{Mo K}\alpha$  radiation to a maximum  $2\theta$  of  $40^\circ$  with a four-circle computer-controlled diffractometer using the  $\theta$ - $2\theta$  scan technique. The carbon and hydrogen atoms in the phenyl rings were constrained to refine as groups of fixed geometry, and all of the remaining nonhydrogen atoms, with the exception of the acetone carbon atoms, were refined with anisotropic thermal parameters. Refinement by blocked-diagonal-matrix least-squares followed by a final full-matrix refinement of 352 parameters on 4399 data gave final  $R_1$  and (weighted)  $R_2$  values of 0.036 and 0.051, respectively. The tin is found in distorted octahedral coordination by two oxygen and four sulfur atoms contributed by two S,S-chelated and one O,O-chelated dithiooxalate ligands. The O,O-chelated ligand is bridging, via the S,S-chelating site, to the bis(tri-*p*-tolylphosphine)copper(I) cation. The copper atom is four-coordinate and adopts a slightly distorted tetrahedral geometry. Average values of selected structural parameters are as follows: Sn-S, 2.470 (15)  $\text{\AA}$ ; Sn-O, 2.157 (4)  $\text{\AA}$ ; Cu-S, 2.320 (4)  $\text{\AA}$ ; Cu-P, 2.277 (5)  $\text{\AA}$ ; S-Cu-S, 91.5 (1) $^\circ$ ; P-Cu-P, 118.3 (1) $^\circ$ . Intraligand angles: S-Sn-S, 88.8 (6) $^\circ$ ; O-Sn-O, 74.47 (17) $^\circ$ . Interligand (cis) angles: S-Sn-S, 99 (4) $^\circ$ ; S-Sn-O, 84.8 (1) $^\circ$ .

### Introduction

The multifunctional nature of the dithiooxalate ligand is now well established.<sup>3</sup> The ability of this ligand to serve as either an  $\alpha$ -diketonate or a dithiolate chelate results in unique coordination properties.<sup>4</sup> Outstanding among these properties is a facility in bridging various metal ions in polynuclear complexes.<sup>4,5</sup> A general class of such polynuclear complexes is obtained, when the inert counterions that accompany the ionic dithiooxalate complexes are replaced by coordinately unsaturated cationic complexes.<sup>3</sup> In one such reaction, the S,S-chelated  $\text{K}_2\text{Sn}(\text{S}_2\text{C}_2\text{O}_2)_3$  complex<sup>1</sup> undergoes partial cation exchange with the bis(tri-*p*-tolylphosphine) copper(I) cation,  $\text{Cu}(\text{P}(\text{C}_7\text{H}_7)_3)_2^+$ , and a crystalline complex of the stoichiometry  $\text{KSn}[(\text{S}_2\text{C}_2\text{O}_2)_3\text{Cu}(\text{P}(\text{C}_7\text{H}_7)_3)_2]$  is isolated. In the infrared spectrum of this complex, both high ( $1627 \text{ cm}^{-1}$ ) and low ( $1371 \text{ cm}^{-1}$ ) carbonyl frequencies are observed. The low-energy carbonyl absorption suggests that one of the ligands has assumed S,S chelation to the copper and consequently is O,O chelated to the tin. Precedent for this type of isomerization exists with similar derivatives of the dithiooxalate complexes of iron(III), Cr(III), and Zn(II). Structural<sup>4,5</sup> and chemical<sup>3</sup> studies on these complexes indicate complete cation exchange and a concomitant ligand isomerization. A structure determination of the title complex was undertaken to (a) establish the partial ligand isomerization suggested by its properties and (b) compare the structural parameters of the dithiooxalate ligands in, apparently, different coordination modes on the same central metal ion.

### Experimental Section

The complex, in microcrystalline form, was isolated following a synthesis similar to the one previously described for the triphenylphosphine analogue.<sup>1</sup> Single crystals were obtained from an acetone solution by the slow diffusion of *n*-pentane at  $10^\circ\text{C}$  for ca. 10 h. The complex crystallized with two molecules of acetone.

**Data Collection.** The crystals were sealed in quartz capillaries to reduce crystal deterioration during data collection. Preliminary precession photos showed no symmetry, indicating the triclinic space groups  $P1$  or  $P\bar{1}$ . The latter was confirmed by successful refinement of the structure.

Following the preliminary studies, a fresh crystal measuring approximately  $0.17 \times 0.24 \times 0.40 \text{ mm}$  was mounted on a Picker-Nuclear four-circle diffractometer, automated by a DEC PDP8-I computer with FACS-I DOS software, and used for all further work.

The unit cell parameters were determined by least-squares refinement on the  $2\theta$  values of 28 reflections between  $2\theta$  of 25 and  $30^\circ$

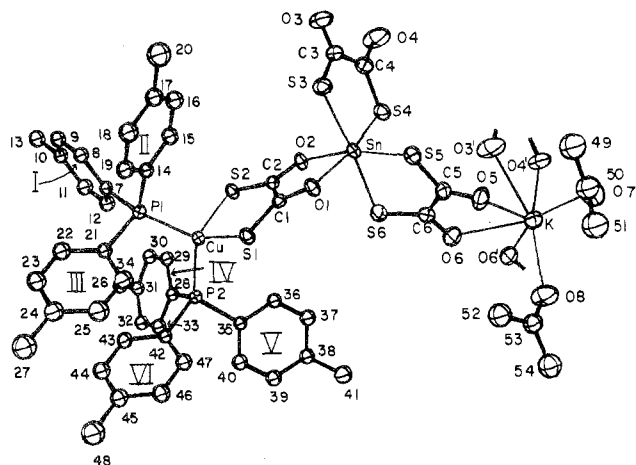
carefully centered on a diffractometer using graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda 0.7107 \text{ \AA}$ ,  $2\theta = 12.20^\circ$ ). The cell constants obtained were  $a = 10.981(2) \text{ \AA}$ ,  $b = 11.136(2) \text{ \AA}$ ,  $c = 26.337(6) \text{ \AA}$ ,  $\alpha = 106.69(2)^\circ$ ,  $\beta = 99.97(2)^\circ$ , and  $\gamma = 78.39(2)^\circ$ . The calculated density, assuming two molecules per unit cell ( $1.33 \text{ g/cm}^3$ ), agrees well with the pycnometrically determined density of  $1.37(2) \text{ g/cm}^3$ . Intensity data were collected over the hemisphere of reciprocal space  $+H, \pm K, \pm L$  to a maximum  $2\theta$  of  $40^\circ$  [ $(\sin \theta)/\lambda \leq 0.481$ ] using the  $\theta$ - $2\theta$  scan technique. In all, 6040 data were collected. Peaks were scanned at a speed of  $1^\circ/\text{min}$  in  $2\theta$  over a base width centered on  $\text{Mo K}\alpha_1$  ( $\lambda 0.70926 \text{ \AA}$ ) and expanded at the high- $2\theta$  side to allow for the  $\alpha_1, \alpha_2$  separation. A base width of  $1^\circ$  was used below  $20^\circ$ , and the base width was increased to  $1.2^\circ$  above  $20^\circ$ . Backgrounds were counted for 10 s at the beginning and end of each scan. Zirconium attenuator foils were inserted in the diffraction beam whenever the peak intensity exceeded 10000 counts/s and the peak and backgrounds were remeasured with the foils in place. Three reflections were monitored after every 50 data points to determine the crystal and instrument stability. The intensity of these reflections showed an approximately linear decrease of 3% over the data collection period. Intensities were corrected for this decomposition, and attenuator, Lorentz, and polarization factors were applied. Equivalent reflections were averaged to yield 5635 unique reflections, of which 4399 had  $F^2 > 3\sigma(F^2)$  and were used in the refinement. Standard deviations were taken as the larger of those calculated from counting statistics or from the scatter of individual measurements. An ignorance factor,  $\rho$ , of 0.04 was used in eq 1 to decrease the weight of intense

$$\sigma(F^2) = [\sigma_o^2(F^2) + (\rho F^2)^2]^{1/2} \quad (1)$$

reflections.

The function minimized by least-squares was  $\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2$ . The weight,  $w$ , was set equal to 0.0 when  $F^2 \leq 3\sigma(F^2)$  and was equal to  $1/\sigma^2(F)$  for all other reflections. Scattering factors for the zerovalent nonhydrogen atoms were obtained from listings of Doyle and Turner.<sup>6</sup> Hydrogen scattering factors were taken from the best fit spherical density case of Stewart, Davidson, and Simpson.<sup>7</sup> The real and imaginary dispersion corrections<sup>8</sup> for all nonhydrogen atoms were included in the calculations. The linear absorption coefficient,  $\mu$ , was  $11.5 \text{ cm}^{-1}$  and no absorption correction was applied to the data.<sup>9,10</sup>

**Structure Solution and Refinement.** The positions of the tin, copper, six sulfur, and two phosphorus atoms were determined from a three-dimensional Patterson synthesis. One cycle of full-matrix least-squares refinement led to an  $R_1$  of 0.48 ( $R_1 = \sum |F_o| - |F_c| / \sum F_o$ ). From a Fourier synthesis phased on these atoms the parameters of the remaining nonhydrogen atoms were determined. Four cycles of refinement with isotropic thermal parameters resulted in  $R_1 = 0.126$ . At this point a difference Fourier indicated the presence of the two



**Figure 1.** Molecular structure and labeling of the  $\text{KSn}[(\text{C}_2\text{O}_2\text{S}_2)_3\text{Cu}(\text{P}(\text{tol})_3)_2] \cdot 2\text{CH}_3\text{COCH}_3$ . The thermal ellipsoids represent the 50% probability surfaces.

acetones of crystallization and these were refined isotropically for three cycles to  $R_1 = 0.084$ .

Cost considerations dictated further refinement to proceed in block-diagonal form. One block contained the parameters for the tin, two acetones, and six tolyl groups, while the other block contained the parameters for the rest of the molecule and shared those of the tin and acetone. The blocks were refined alternately while the number of atoms refined with anisotropic thermal parameters was increased to include all nonhydrogen atoms except the carbon atoms of the acetones and the tolyl groups. Due to space limitations the tolyl groups were refined with fixed geometries<sup>11</sup> ( $C_{\text{phenyl}}-C_{\text{phenyl}} = 1.390 \text{ \AA}$ ,  $C_{\text{phenyl}}-\text{CH}_3 = 1.530 \text{ \AA}$ , and  $C_{\text{phenyl}}-\text{H} = 0.95 \text{ \AA}$ ). The isotropic thermal parameters of the tolyl carbons and the ring hydrogens were allowed to refine.

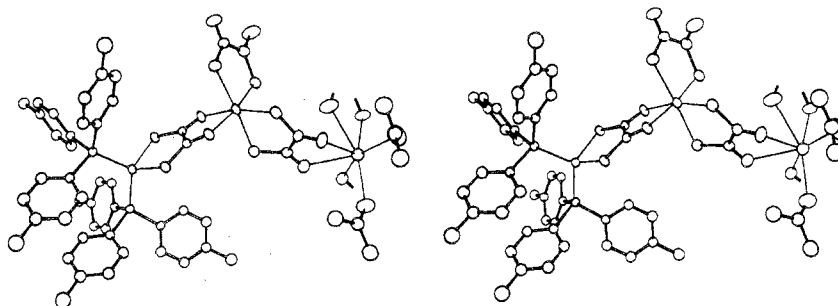
A difference Fourier calculated at an intermediate stage showed that the methyl hydrogens were poorly resolved. They were included in their calculated positions (with half-weight to each of the equally

preferred positions for the tolyl methyl groups) but not allowed to refine. The tolyl methyl hydrogens were given an isotropic thermal parameter,  $B$ , of  $10.00 \text{ \AA}^2$  and the acetone methyl hydrogens were given  $B = 15.0 \text{ \AA}^2$ .

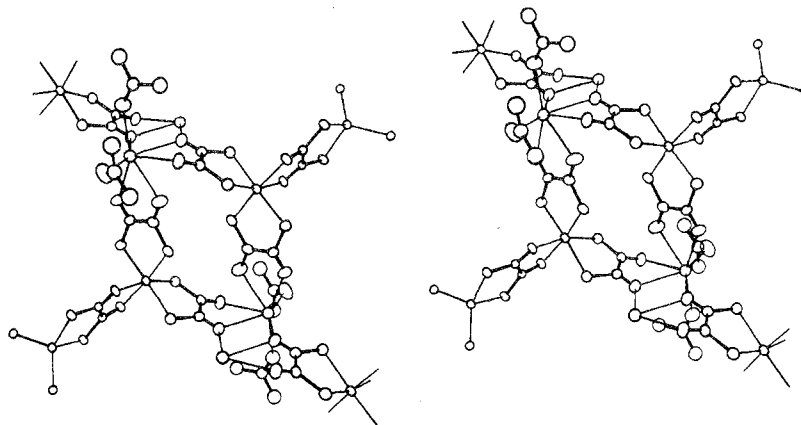
A final cycle of least-squares refinement was performed with all parameters in a single matrix and resulted in an  $R_1$  value of 0.036. The final weighted  $R_2$  value was 0.051,  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ , and the standard deviation of an observation of unit weight ("goodness of fit"),  $[\sum w(|F_o| - |F_c|)^2 / (n_o - n_p)]^{1/2}$ , was 1.67. In the last cycle no parameter was shifted by more than 0.5 times its estimated standard deviation as determined from the inverse least-squares matrix. A difference Fourier calculated following the last cycle showed no peaks greater than  $0.3 \text{ e/\AA}^3$ . The final parameters and their esd's are given in Table I. Tables of the observed structure factors, the carbon atom positions generated by the group parameters, and the calculated hydrogen positions are available as supplementary material.

## Results and Discussion

The solution of the structure confirms the anticipated, mixed sulfur-oxygen coordination of the tin. The individual bond distances and angles are given in Tables II and III and the numbering system is shown in Figure 1. The coordination of the tin is a distorted octahedron. The primary deviation from octahedral geometry is the distortion of the  $\text{O}_1\text{O}_2\text{S}_4\text{S}_5$  plane from a square to a trapezoid. The short,  $2.611(5) \text{ \AA}$ ,  $\text{OO}$  bite reduces the  $\text{O}_1-\text{Sn}-\text{O}_2$  angle from  $90$  to  $74.5(2)^\circ$  and allows the  $\text{S}_4-\text{Sn}-\text{S}_5$  angle to open to  $103.5(1)^\circ$ . A secondary distortion is also present in a tilt of the  $\text{Sn}-\text{S}_3$  axis toward the  $\text{S}_4-\text{O}_2$  side. The remaining  $\text{S}_{\text{ax}}-\text{Sn}-\text{S}_{\text{eq}}$  and  $\text{O}_{\text{ax}}-\text{Sn}-\text{S}_{\text{eq}}$  angles are nearly  $90^\circ$  (Table III). The  $\text{Sn}-\text{S}$  bond distances are slightly longer than the sum of the covalent radii of  $2.44 \text{ \AA}$ <sup>12</sup> and compare to distances of  $2.557(7)$  and  $2.534(7) \text{ \AA}$  for the tin dithiocarbamate complex,  $\text{Sn}(\text{dtc})_4$ .<sup>13</sup> The distances are similar to the  $2.47(1) \text{ \AA}$  reported for the monodentate dimethyldithiocarbamate complex  $(\text{CH}_3)_2\text{Sn}(\text{dtc})$ .<sup>14</sup> The differences of the  $\text{Sn}-\text{S}$  distances are statistically significant and are probably the result of packing forces in the crystal. The  $\text{Sn}-\text{O}$  distances of  $2.156(4)$  and  $2.159(4) \text{ \AA}$  are similar to



**Figure 2.** Stereographic pair of the molecular structure of  $\text{KSn}[(\text{C}_2\text{S}_2\text{O}_2)_3\text{Cu}(\text{P}(\text{tol})_3)_2] \cdot 2\text{CH}_3\text{COCH}_3$ . The view and ellipsoids are as in Figure 1.



**Figure 3.** Packing diagram of  $\text{KSn}[(\text{C}_2\text{S}_2\text{O}_2)_3\text{Cu}(\text{P}(\text{tol})_3)_2] \cdot 2\text{CH}_3\text{COCH}_3$  showing the linkage between the complexes through the coordination of the potassium. The tolyl groups have been omitted for clarity. The view direction is as in Figure 2.

Table I. Final Positional and Thermal Parameters for  $\text{KSn}[(\text{C}_2\text{S}_2\text{O}_2)_3\text{Cu}(\text{P}(\text{tol})_3)_2] \cdot 2\text{CH}_3\text{COCH}_3$ , <sup>a,b</sup>

(A) Parameters of the Individually Refined Atoms									
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
Sm	0.143 78 (4)	-0.013 77 (4)	0.140 20 (2)	3. 83 (3)	4.15 (2)	3.48 (3)	-0.37 (2)	-0.07 (2)	1.77 (2)
O(7)	0.314 6 (7)	-0.587 8 (6)	-0.013 0 (2)	15.4 (6)	7.4 (3)	5.8 (3)	0.4 (3)	1.3 (4)	-0.3 (3)
O(8)	0.625 8 (7)	-0.747 4 (8)	0.034 3 (3)	9.5 (4)	18.3 (6)	5.6 (3)	-5.8 (4)	-1.1 (3)	1.5 (4)
Cu	0.373 32 (7)	-0.308 21 (6)	0.295 57 (3)	3.15 (4)	3.74 (4)	3.13 (4)	-0.57 (3)	0.09 (3)	1.41 (3)
K	0.413 3 (2)	0.174 7 (2)	-0.016 74 (7)	5.84 (9)	6.37 (9)	6.04 (10)	-1.58 (7)	0.22 (8)	1.83 (7)
P(1)	0.265 4 (1)	-0.307 8 (1)	0.362 30 (6)	3.18 (8)	3.47 (7)	3.34 (8)	-0.58 (6)	0.45 (6)	1.17 (6)
P(2)	0.571 5 (1)	-0.417 6 (1)	0.293 31 (6)	2.86 (8)	3.62 (7)	3.30 (8)	-0.70 (6)	0.26 (6)	1.20 (6)
S(1)	0.354 4 (2)	-0.096 5 (1)	0.295 57 (6)	4.63 (9)	3.59 (7)	3.26 (8)	-1.24 (6)	-0.66 (7)	1.05 (6)
S(2)	0.253 6 (2)	-0.354 0 (1)	0.212 95 (6)	4.53 (9)	3.39 (7)	3.48 (8)	-1.14 (6)	-0.75 (7)	1.18 (6)
S(3)	-0.064 2 (2)	0.032 0 (2)	0.171 51 (8)	4.57 (10)	6.89 (11)	4.65 (10)	-0.70 (8)	0.79 (8)	1.12 (8)
S(4)	0.046 7 (2)	-0.096 0 (2)	0.048 63 (7)	5.25 (11)	7.29 (11)	3.41 (9)	-0.56 (8)	-0.16 (8)	1.81 (8)
S(5)	0.156 2 (2)	0.207 5 (2)	0.144 48 (8)	5.12 (10)	4.52 (9)	6.69 (12)	-0.11 (7)	0.51 (9)	2.51 (8)
S(6)	0.354 3 (2)	-0.077 2 (2)	0.108 76 (8)	4.97 (10)	5.78 (10)	6.12 (11)	0.20 (8)	1.10 (9)	2.52 (8)
O(1)	0.229 9 (4)	0.007 4 (4)	0.221 8 (2)	5.1 (2)	2.9 (2)	3.8 (2)	-0.5 (2)	-0.5 (2)	1.0 (2)
O(2)	0.176 0 (4)	-0.201 3 (3)	0.152 6 (2)	5.1 (2)	3.8 (2)	2.8 (2)	-0.8 (2)	-0.4 (2)	1.3 (2)
O(3)	-0.261 1 (6)	-0.048 9 (6)	0.113 4 (2)	5.2 (3)	12.0 (4)	7.3 (4)	-2.5 (3)	0.7 (3)	1.4 (3)
O(4)	-0.185 9 (7)	-0.103 0 (8)	0.019 6 (3)	8.3 (4)	21.1 (8)	6.0 (4)	-7.1 (5)	-1.1 (4)	1.1 (4)
O(5)	0.301 8 (5)	0.270 6 (5)	0.092 5 (2)	8.5 (4)	6.6 (3)	9.8 (4)	-1.9 (3)	2.0 (3)	4.1 (3)
O(6)	0.441 9 (5)	0.050 2 (5)	0.060 4 (2)	6.4 (3)	8.2 (3)	7.2 (3)	-0.6 (3)	2.0 (3)	2.8 (3)
C(1)	0.269 0 (5)	-0.094 2 (6)	0.237 7 (2)	3.1 (3)	3.6 (3)	3.1 (3)	-0.6 (2)	0.5 (2)	0.9 (3)
C(2)	0.228 6 (5)	-0.214 6 (5)	0.197 7 (2)	3.0 (3)	3.9 (3)	2.7 (3)	-0.6 (2)	0.4 (3)	1.1 (3)
C(3)	-0.155 2 (7)	-0.036 9 (6)	0.112 2 (3)	3.8 (4)	5.7 (4)	6.1 (5)	-0.6 (3)	0.5 (3)	2.3 (3)
C(4)	-0.106 2 (8)	-0.080 5 (8)	0.057 4 (3)	5.5 (5)	7.9 (5)	4.7 (4)	-2.2 (4)	-1.2 (4)	1.9 (4)
C(5)	0.277 3 (6)	0.184 1 (7)	0.105 5 (3)	5.0 (4)	5.8 (4)	4.3 (4)	-1.3 (3)	0.1 (3)	2.1 (3)
C(6)	0.363 4 (7)	0.053 2 (7)	0.088 2 (3)	4.1 (4)	5.8 (4)	5.2 (4)	-0.8 (3)	0.1 (3)	1.9 (3)
C(49)	0.160 1 (11)	-0.482 8 (10)	0.042 9 (4)	10.4 (3) (B)					
C(50)	0.288 5 (9)	-0.510 6 (9)	0.027 7 (4)	7.3 (2) (B)					
C(51)	0.381 1 (11)	-0.440 5 (10)	0.064 7 (4)	10.4 (3) (B)					
C(52)	0.637 7 (9)	-0.700 0 (8)	0.128 0 (4)	8.7 (2) (B)					
C(53)	0.688 2 (8)	-0.717 9 (7)	0.077 1 (3)	6.0 (2) (B)					
C(54)	0.815 5 (10)	-0.694 1 (9)	0.080 5 (4)	9.1 (3) (B)					
(B) Group Refinement Parameters <sup>c</sup>									
Phenyl group	<i>x</i> <sub>g</sub>	<i>y</i> <sub>g</sub>	<i>z</i> <sub>g</sub>	$\phi$	$\theta$	$\rho$			
1	0.1476 (2)	-0.5648 (2)	0.3461 (1)	147.5 (1)	-8.1 (1)	150.6 (1)			
2	0.0185 (2)	-0.0936 (2)	0.3997 (1)	49.2 (1)	5.9 (1)	-78.9 (1)			
3	0.4258 (3)	-0.2617 (3)	0.4789 (1)	-97.6 (2)	65.3 (1)	149.1 (3)			
4	0.5935 (2)	-0.7240 (2)	0.2570 (1)	173.4 (1)	-14.9 (1)	-155.7 (1)			
5	0.7327 (2)	-0.3587 (2)	0.4099 (1)	-95.0 (2)	64.9 (1)	154.7 (3)			
6	0.7445 (3)	-0.3762 (2)	0.2142 (1)	-68.9 (1)	-40.7 (1)	-42.6 (2)			
Group 1 atom	<i>B</i>	Group 2 atom	<i>B</i>	Group 3 atom	<i>B</i>				
C(7)	3.1 (1)	C(14)	3.1 (1)	C(21)	3.2 (1)				
C(8)	3.9 (1)	C(15)	4.3 (1)	C(22)	4.9 (1)				
C(9)	4.3 (1)	C(16)	5.2 (2)	C(23)	5.7 (2)				
C(10)	4.1 (1)	C(17)	4.8 (1)	C(24)	5.5 (2)				
C(11)	5.1 (2)	C(18)	5.2 (2)	C(25)	6.2 (2)				
C(12)	4.8 (1)	C(19)	4.7 (1)	C(26)	5.2 (2)				
C(13)	5.7 (2)	C(20)	8.2 (2)	C(27)	8.9 (2)				
H(1)	10.7 (24)	H(8)	6.7 (16)	H(15)	5.5 (14)				
H(2)	10.1 (22)	H(9)	9.0 (20)	H(16)	9.5 (21)				
H(3)	15.8 (32)	H(10)	13.5 (29)	H(17)	13.6 (29)				
H(4)	10.0 (22)	H(11)	4.5 (12)	H(18)	6.8 (16)				
Group 4 atom	<i>B</i>	Group 5 atom	<i>B</i>	Group 6 atom	<i>B</i>				
C(28)	3.3 (1)	C(35)	3.3 (1)	C(42)	3.3 (1)				
C(29)	3.9 (1)	C(36)	4.2 (1)	C(43)	4.1 (1)				
C(30)	4.5 (1)	C(37)	5.1 (2)	C(44)	4.9 (2)				
C(31)	4.0 (1)	C(38)	5.4 (2)	C(45)	4.4 (1)				
C(32)	4.4 (1)	C(39)	5.1 (2)	C(46)	5.0 (2)				
C(33)	4.3 (1)	C(40)	5.5 (1)	C(47)	4.8 (1)				
C(34)	5.4 (2)	C(41)	8.9 (2)	C(48)	6.4 (2)				
H(22)	7.5 (17)	H(29)	6.2 (16)	H(36)	6.2 (16)				
H(23)	10.7 (23)	H(30)	18.4 (39)	H(37)	6.2 (15)				
H(24)	9.4 (22)	H(31)	11.9 (25)	H(38)	14.0 (31)				
H(25)	11.4 (25)	H(32)	8.1 (19)	H(39)	7.1 (17)				

<sup>a</sup> The standard deviation of the least significant digit(s) appears in parentheses in this table. <sup>b</sup> The form of the temperature factor is  $T = \exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$  for anisotropic and  $T = \exp(-B \sin^2 \theta / \lambda^2)$  for isotropic thermal parameters (*B* in units of Å<sup>2</sup>). <sup>c</sup> Group parameters as defined in ref 5 and 11.

the distances reported for the 1:1 stannic chloride adduct of the S,S-chelated nickel dithiooxalate complex, of 2.17 (2) and 2.15 (1) Å.<sup>4</sup>

While the coordination environment of each of the three dithiooxalate ligands is different, the bond lengths and angles of the two Sn-SS chelated ligands are nearly the same and

**Table II.** Selected Bond Distances (Å) in  $\text{KSn}[(\text{C}_2\text{S}_2\text{O}_2)_3\text{Cu}(\text{P}(\text{C}_7\text{H}_7)_3)_2] \cdot 2\text{CH}_3\text{COCH}_3$ 

Sn-S(4)	2.455 (2)	C(1)-O(1)	1.286 (6)
Sn-S(5)	2.465 (2)	C(2)-O(2)	1.263 (7)
Sn-S(3)	2.469 (2)	C(3)-O(3)	1.204 (8)
Sn-S(6)	2.490 (2)	C(4)-O(4)	1.210 (9)
Sn-O(2)	2.156 (4)	C(5)-O(5)	1.201 (7)
Sn-O(1)	2.159 (4)	C(6)-O(6)	1.213 (8)
Cu-S(2)	2.316 (2)	C(1)-S(1)	1.650 (6)
Cu-S(1)	2.325 (2)	C(2)-S(2)	1.672 (6)
Cu-P(2)	2.272 (2)	C(3)-S(3)	1.762 (8)
Cu-P(1)	2.282 (2)	C(4)-S(4)	1.702 (8)
K-O(7)	2.629 (6)	C(5)-S(5)	1.752 (7)
K-O(8)	2.659 (7)	C(6)-S(6)	1.715 (7)
K-O(6)	2.715 (6)	C(1)-C(2)	1.540 (8)
K-O(6')	2.739 (6)	C(3)-C(4)	1.539 (11)
K-O(4')	2.753 (7)	C(5)-C(6)	1.562 (10)
K-O(3')	2.942 (6)	O(1)-O(2)	2.611 (5)
K-O(5)	3.137 (6)	O(3)-O(4)	2.608 (9)
		O(5)-O(6)	2.616 (8)
P(1)-C(21)	1.832 <sup>a</sup>	S(1)-S(2)	3.324 (2)
P(1)-C(7)	1.837	S(3)-S(4)	3.465 (3)
P(1)-C(14)	1.842	S(5)-S(6)	3.448 (3)
P(2)-C(35)	1.836		
P(2)-C(42)	1.843		
P(2)-C(28)	1.848		

<sup>a</sup> These carbon atoms were refined as groups.**Table III.** Selected Angles (deg) in  $\text{KSn}[(\text{C}_2\text{S}_2\text{O}_2)_3\text{Cu}(\text{P}(\text{C}_7\text{H}_7)_3)_2] \cdot 2\text{CH}_3\text{COCH}_3$ 

S(3)-Sn-S(4)	89.44 (8)	S(1)-Cu-S(2)	91.5 (1)
S(5)-Sn-S(6)	88.19 (8)	P(1)-Cu-P(2)	118.3 (1)
O(1)-Sn-O(2)	74.47 (17)	O(3)-K-O(4)	54.4 (2)
S(3)-Sn-S(5)	96.2 (1)	O(5)-K-O(6)	78.1 (2)
S(4)-Sn-S(5)	103.5 (1)	O(6)-K-O(6')	116.6 (2)
O(1)-Sn-S(4)	167.7 (1)	Cu-P(1)-C(7)	113.7 (2)
O(2)-Sn-S(6)	84.8 (1)	Cu-P(1)-C(14)	114.5 (2)
O(2)-Sn-S(5)	164.5 (2)	Cu-P(1)-C(21)	116.4 (2)
S(1)-C(1)-O(1)	123.5 (3)	Cu-P(2)-C(28)	111.6 (2)
S(2)-C(2)-O(2)	122.3 (3)	Cu-P(2)-C(35)	118.6 (2)
S(3)-C(3)-O(3)	120.0 (4)		
S(4)-C(4)-O(4)	121.0 (4)		
S(5)-C(5)-O(5)	121.1 (4)		
S(6)-C(6)-O(6)	121.2 (4)		

are similar to those reported for the  $\text{K}_2\text{Ni}(\text{S}_2\text{C}_2\text{O}_2)_2$  complex (Table IV).<sup>4</sup> The primary difference between the two ligands is that dithiooxalate 2 chelates the potassium, while dithiooxalate 3 chelates the potassium and additionally acts as a monodentate ligand for an additional potassium, K'. Both

ligands are nearly planar with the primary distortion being twists of the two SCO groups around the carbon-carbon single bond of 12.5 and 4.5°, respectively, for dithiooxalates 2 and 3. The coordination of the dithiooxalates to the tin and potassium is markedly nonplanar with the metal ions located above the respective planes. The tin is located 0.165 (1) and 0.595 (1) Å from the respective least-squares planes through dithiooxalates 2 and 3 and the potassium atoms are located 0.424 (2) and 1.364 (2) Å from these planes.

The bond lengths of the Sn-OO-C<sub>2</sub>-SS-Cu bonded dithiooxalate ligand are significantly different from those of the Sn-SS-C<sub>2</sub>-OO-K bonded ligands. Specifically the longer C-O and shorter C-S bonds in the former ligand indicate delocalization of charge from the sulfur to the oxygen and are similar to those observed<sup>4,5</sup> in other polynuclear dithiooxalate complexes (Table IV). The tin and copper are 0.111 (1) and 0.067 (1) Å above the weighted least-squares plane through the bridging ligand. The angle between the two SCO planes is 7.7° in this ligand.

The coordination of the copper forms a distorted tetrahedron. The dihedral angle between the CuS<sub>1</sub>S<sub>2</sub> and CuP<sub>1</sub>P<sub>2</sub> planes is 86° and is not a serious distortion from C<sub>2v</sub> symmetry. Several structural determinations of (Ph<sub>3</sub>P)<sub>2</sub>CuX complexes have been reported.<sup>15</sup> A feature common to the structures is a value for the P-Cu-P angle in the range of 120-130°. The surprising feature of this angle is that with the bidentate NO<sub>3</sub><sup>-</sup> anion the angle is 131.2° which is a large deviation from the ideal tetrahedral angle of 109.47° and has received much discussion.<sup>16,17</sup> The angle in this work is 118.3 (1)° and is smaller than any of the reported angles of triphenylphosphine complexes but is not greatly different from the 120.0° reported for the (PPh<sub>3</sub>)<sub>2</sub>CuB<sub>3</sub>H<sub>3</sub> complex.<sup>18</sup>

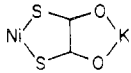
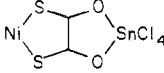
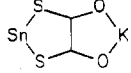
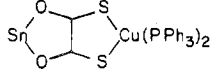
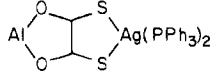
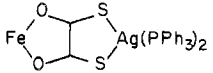
The potassium coordination geometry is an irregular polyhedron formed by seven oxygens, five from the dithiooxalate ligands and two from the acetone molecules. The K-O bond distances range from 2.629 (6) to 3.137 (6) Å with the shortest distances involving the two acetone oxygen atoms (Table II).

The potassium ions bind the Sn(C<sub>2</sub>S<sub>2</sub>O<sub>2</sub>)<sub>3</sub>Cu((P(*o*-tol)<sub>3</sub>)<sub>2</sub>)<sub>2</sub> groups into dimeric pairs which are further linked in chains along the x axis by the K'-O(6) linkages (Figure 3). The only nonhydrogen intermolecular contact less than 3.500 Å was the C(34)-O(3) contact of 3.401 (8) Å.

### Summary

The structure confirmed the postulated mixed SS and OO chelation of the tin. The complexes are linked in dimers by

**Table IV.** Average Bond Distances (Å) in Bridging Dithiooxalate Ligands

Complex	C-S	C-O	C-C	O-O	S-S	Sn-O(S)	Ref
	1.750 (9)	1.206 (10)	1.544 (10)	2.694 (8)	3.160 (3)		4
	1.670 (8)	1.263 (10)	1.513 (10)	2.647 (6)	3.156 (3)	2.213 (5)	
	1.744 (7)	1.207 (8)	1.540 (8)	2.611 (5)	3.465 (2)	2.472 (2)	This work
	1.661 (6)	1.274 (7)	1.550 (10)	2.612 (8)	3.324 (2)	2.157 (4)	This work
	1.65 (1)	1.28 (1)	1.55 (1)	2.49 (1)	3.447 (5)		5
	1.68 (3)	1.28 (2)	1.53 (2)	2.51 (2)	3.43 (1)		5

bridging dithiooxalate ligands and the dimers are linked in infinite chains of dimers through the potassium. The bond distances and angles of the Sn-SS and Sn-OO chelated ligands are profoundly different but are comparable to those reported for other dithiooxalate complexes. The bond distances in the Sn-OO-C<sub>2</sub>-SS-Cu bonded ligand indicates delocalization of charge from the sulfur to the oxygen.

A band at 1627 cm<sup>-1</sup> in the infrared spectrum of the complex is assigned to the C=O bond in the Sn-S<sub>2</sub>-C<sub>2</sub>-O<sub>2</sub>-K bonded ligand. The band at 1371 cm<sup>-1</sup> is assigned to the longer C-O bond in the Sn-O<sub>2</sub>-C<sub>2</sub>-S<sub>2</sub>Cu bonded ligand.

The infrared absorptions near ca. 1400 cm<sup>-1</sup>, in the spectra of similar polynuclear complexes,<sup>1</sup> are considered indicative of Sn-O<sub>2</sub>-C<sub>2</sub>-S<sub>2</sub>-Cu bonded ligands.

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**Registry No.** KSn[(S<sub>2</sub>C<sub>2</sub>O<sub>2</sub>)<sub>3</sub>Cu(P(tol)<sub>3</sub>)<sub>2</sub>]·2CH<sub>3</sub>COCH<sub>3</sub>, 62476-47-5.

**Supplementary Material Available:** A compilation of observed structure factor amplitudes, their estimated standard deviations, and the difference |F<sub>o</sub>| - |F<sub>c</sub>| and tables of the derived carbon atom positions of the phenyl rings and the calculated hydrogen atom positions (9

pages). Ordering information is given on any current masthead page.

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## Crystal Structure of Barium Neptunyl(V) Triacetate Dihydrate<sup>1</sup>

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Barium neptunyl(V) triacetate dihydrate was prepared from Np(V) in a concentrated acetate solution, and its crystal structure determined by x-ray diffraction methods. The body-centered tetragonal unit cell, with dimensions  $a = 19.167$  (5) and  $c = 9.476$  (3) Å, contains eight formula units of BaNpO<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·2H<sub>2</sub>O. The space group is  $I4_2d$ . Positions and anisotropic thermal parameters of the 11 independent atoms were refined by the least-squares method using 964 diffractometer-measured intensities, at the conclusion of which the agreement index,  $R_F$ , was 0.046. Linear NpO<sub>2</sub><sup>+</sup> entities are present in the crystal and have six oxygen atoms from three acetate ions in a planar hexagon around their equators. These hexagonal bipyramids are cross-linked by sharing their acetate oxygen atoms with Ba<sup>2+</sup> ions, each of which has six different oxygen atoms from acetate ions plus two water molecules in its coordination polyhedron. The neptunyl O atoms are bonded solely to the Np atom at bond lengths of 1.85 (2) Å, and the bonds between acetate O atoms and the Np atom range in length from 2.52 (2) to 2.56 (2) Å. These lengths are correlated with bond strengths and valence, and the geometries of actinyl(V) ions are put on a quantitative experimental basis.

### Introduction

The existence of ions of dioxygenated pentavalent and hexavalent actinides is well established, and their presence in the solid state is known for Np(V), Pu(V), Am(V), U(VI), Np(VI), Pu(VI), and Am(VI). Although the geometry of the UO<sub>2</sub><sup>2+</sup> ion has been studied in scores of crystalline compounds, little attention has been given to the structure of various species containing transuranic elements, because their radioactivity causes some handling difficulty. Recently the structures of two compounds containing the NpO<sub>2</sub><sup>2+</sup> ion were determined by single-crystal x-ray diffraction;<sup>3</sup> they are Na<sub>4</sub>NpO<sub>2</sub>(O<sub>2</sub>)<sub>3</sub>·9H<sub>2</sub>O and K<sub>4</sub>NpO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>. Also, before the present study, one structure containing the NpO<sub>2</sub><sup>+</sup> ion had been determined by similar methods;<sup>4</sup> it is that of Cs<sub>3</sub>NpO<sub>2</sub>Cl<sub>4</sub>. A number of powder x-ray diffraction studies of pentavalent actinide-dioxo compounds have been done (see Table I), but precise bond lengths are not available from these.

Infrared studies have been used by Vodovatov, Mashirov, Suglovov, and co-workers<sup>4,9-11</sup> as a means of comparing bond strengths among the transuranic actinyl species. They have evaluated the effect on the primary O=M=O bond strengths<sup>12</sup> (M = Np, Pu, Am) of several factors which include

Table I. Compounds Containing the MO<sub>2</sub><sup>+</sup> Ion, M = Np, Pu, Am

Structure type	Compd	Ref
KPuO <sub>2</sub> CO <sub>3</sub> (hexagonal)	KNpO <sub>2</sub> CO <sub>3</sub>	5
	KPuO <sub>2</sub> CO <sub>3</sub>	6
	KAmO <sub>2</sub> CO <sub>3</sub>	5
	NH <sub>4</sub> PuO <sub>2</sub> CO <sub>3</sub>	6
	RbAmO <sub>2</sub> CO <sub>3</sub>	6
CaUO <sub>2</sub> O <sub>2</sub> (rhombohedral)	CsAmO <sub>2</sub> CO <sub>3</sub>	7
	KAmO <sub>2</sub> F <sub>2</sub>	8
	RbNpO <sub>2</sub> F <sub>2</sub>	7
	RbPuO <sub>2</sub> F <sub>2</sub>	7
	RbAmO <sub>2</sub> F <sub>2</sub>	7
	NH <sub>4</sub> PuO <sub>2</sub> F <sub>2</sub>	7
Cs <sub>3</sub> NpO <sub>2</sub> Cl <sub>4</sub> (monoclinic)	Cs <sub>3</sub> NpO <sub>2</sub> Cl <sub>4</sub>	4
	Cs <sub>3</sub> PuO <sub>2</sub> Cl <sub>4</sub>	4
	Cs <sub>3</sub> AmO <sub>2</sub> Cl <sub>4</sub>	4

the valence of M, the atomic number, and the nature of the secondary ligands which bond to the linear ion around its equator. In making these comparisons they included the idea of Zachariasen<sup>13-15</sup> that the strengths of the primary and secondary bonds in these species are interdependent because of the need that the sum of bond strengths around a particular