drogen production; (ii) the absorption of visible light by the Co(III) complexes filtering light in the region of maximum absorption of the sensitizer; (iii) shorter lived sacrificial cycles.

Overall, this work has indicated that the advantages of the cage complexes seem to lie in their larger turnover numbers. There are numerous prospects for increasing their inherent electron-transfer rate constants through the use of either unsaturated derivatives of cage complexes or cage complexes having different donor atoms or alternative polycyclic topologies. These aspects are at present being explored.

Acknowledgment. P.A.L. gratefully acknowledges the award of a CSIRO postdoctoral fellowship. We are also grateful for support from a CSIRO/ANU Collaborative Research Grant. We also thank D. Wells for HPLC experiments and Dr. N. Sutin for communication of results prior to publication.

Registry No. [Co(HYMEoxosar-H)]$^{2+}$, 85664-20-6; [Co(CMMEabsar)]$^{3+}$, 85680-90-6; [Co(EFMEoxosar-H)]$^{2+}$, 85664-18-2; [Co(sar)]$^{3+}$, 85664-13-7; [Co(AZAMEsar)]$^{3+}$, 85664-08-0; [Co(AMMEsar)]$^{3+}$, 85663-97-4; [Co(diAZAchar)]$^{3+}$, 96930-84-6; [Co(CLsar)]$^{3+}$, 85663-92-9; [Co(sep)]$^{3+}$, 72496-77-6; [Co(MENOsar)]$^{3+}$, 85663-83-8; [Co(CLHOsar)]$^{3+}$, 96930-85-7; [Co(diCLsar)]$^{3+}$, 85663-90-7; [Co(diAMsar)]$^{3+}$, 85663-96-3; [Co(diAMchar)]$^{3+}$, 96997-84-1; [Co(CLNOsar)]$^{3+}$, 85663-78-1; [Co(diNOsar)]$^{3+}$, 85663-77-0; [Co(AZAcapten)]$^{3+}$, 81570-78-7; [Co(AMcapten)]$^{3+}$, 92490-34-1; [Ru(bpy)$_3$]$^{2+}$, 15158-62-0; [Ru(4,4′-Me$_2$bpy)$_3$]$^{2+}$, 32881-03-1; H_2O, 7732-18-5; H_2, 1333-74-0; Pt, 7440-06-4; methylviologen(2+), 4685-14-7; benzylviologen(2+), 13096-46-3.

Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Crystal and Molecular Structures of the Copper(II) and Copper(III) Dithiooxalate Complexes (18-crown-6)$_2$K$_2$Cu(S$_2$C$_2$O$_2$)$_2$ and ([(C$_6$H$_5$)$_3$P]$_2$N)Cu(S$_2$C$_2$O$_2$)$_2$

M. G. KANATZIDIS, N. C. BAENZIGER, and D. COUCOUVANIS*[1]

Received May 9, 1984

The crystal and molecular structures of (18-crown-6)$_2$K$_2$Cu(Dto)$_2$·DMF (I) and [(Ph$_3$P)$_2$N][Cu(Dto)$_2$] (II) are reported. I crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell. The cell dimensions are a = 11.488 (2) Å, b = 8.543 (2) Å, c = 23.527 (7) Å, and β = 93.71 (2)°. II crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell. The cell dimensions are a = 13.528 (2) Å, b = 18.456 (2) Å, c = 15.354 (2) Å, and β = 95.82 (1)°. Intensity data for both I and II were collected with a four-circle computer-controlled diffractometer with the use of the θ–2θ step scan technique. The non-hydrogen atoms in I and II were refined with anisotropic temperature factors. Refinement by full-matrix least-squares techniques of 352 parameters on 2783 data for I and of 244 parameters on 2547 data for II gave final R values of 0.06 and 0.05 for I and II, respectively. The hydrogen atoms in I and II were included in the structure factor calculations but were not refined. In I the two independent Cu^{II}–S bond lengths in the planar [Cu(Dto)$_2$]$^{2-}$ anion are 2.254 (2) and 2.268 (2) Å, and the C–C bond length of the Dto ligand is 1.547 (7) Å. The (18-crown-6)K$^+$ cations are bound to the α-diketone portion of the coordinated Dto ligand and weakly interact with the oxygen atom of a DMF molecule of crystallization. The $\overline{\text{K–O}}$ distance within the crown ether is 2.91 (8) Å, and the K–O(Dto) distance is 2.78 (2) Å. In II the Cu^{III}–S bond lengths within the [Cu(Dto)$_2$]$^-$ anion are 2.164 (1) and 2.178 (1) Å. The C–C bond length of the Dto ligand in II, which readily undergoes photolytic cleavage, is 1.524 (7) Å.

Introduction

Recently we reported[2] in detail on the rates of the facile oxidation of the [Cu(Dto)$_2$]$^{2-}$ anion (Dto = (C$_2$O$_2$S$_2$)$^{2-}$, dithiooxalate) with such oxidants as Cu(II) and Fe(III). The [Cu(Dto)$_2$]$^-$ oxidation product undergoes a light-activated, intramolecular Dto → Cu^{III} electron transfer with cleavage of the C–C bond in the Dto^{2-} ligand[2] and generation of gaseous SCO. The same intramolecular electron transfer also is promoted by triphenylphosphine in the presence or absence of light and results in the cleavage of the C–C bond. The crystal and molecular structures of the (18-crown-6)$_2$K$_2$Cu(Dto)$_2$·DMF (I) and [(Ph$_3$P)$_2$N]Cu(Dto)$_2$ (II) complexes reported in this paper were carried out primarily to determine the C–C bond lengths in the coordinated Dto ligands and the exact coordination geometries around the copper ions in I and II.

Experimental Section

Synthesis. The syntheses of I and II have been reported in detail previously.[2]

X-ray Diffraction Measurements. Collection and Reduction of Data. Specific details concerning crystal characteristics and X-ray diffraction methodology for (KC$_{12}$H$_{24}$O$_6$)$_2$Cu(Dto)$_2$·DMF and (PPN)Cu(Dto)$_2$ (PPN = bis(triphenylphosphine)nitrogen(1+)) are shown in Table I. A green crystal of I with well-developed faces was selected from a batch of crystals obtained by vapor diffusion of diethyl ether into a DMF solution of the former complex. Red prisms of (PNP)Cu(Dto)$_2$ were obtained by the slow diffusion of pentane into a solution of this complex in CH$_2$Cl$_2$.

Intensity data for the [Cu(Dto)$_2$]$^{2-}$ salt were obtained on a Nicolet P3/F four-circle diffractometer automated by a Data General Nova 3 computer with 32K (16 bit words) of memory, a Data General disk unit, and a nine-track tape. The diffractometer was equipped with a molybdenum target X-ray tube (λ(Mo Kα_1), 0.709 30 Å) and a graphite crystal monochromator (2$\theta_{\max}$ = 12.20°) mounted with equatorial geometry. The lattice constants were determined from the least-squares refinement of 2θ, ω, ϕ, and χ diffractometer angles of 25 carefully centered reflections with 2θ values between 25 and 40°. Intensity data were collected by a θ(crystal)–2θ(counter) scan in 96 steps using a bisecting geometry. The scan was from [2θ(MoKα_1) − 1.0]° to [2θ(MoKα_2) + 1.0]°. The scan speed was variable from 3.92 to 29.3°/min, depending on the intensity of the reflection. The stability of the crystal was monitored by measuring 3 strong reflections every 80 reflections. No significant changes were observed over the data collection period. Intensity data for the (PPN)Cu(Dto)$_2$ complex were obtained from a crystal lodged in a capillary, which was coated with black enamel paint. A Picker-Nuclear four-circle diffractometer was used. The description of the instrument and the protocol for data acquisition have been described previously.[3] The raw data for both structures were reduced to net intensities, Lorentz–polarization corrections were applied, and the equivalent reflections were averaged.[4] The scattering factors of the neutral nonhydrogen atoms

---

(1) Present address: Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.

(2) Imamura, T.; Ryan, M.; Gordon, G.; Coucouvanis, D. *J. Am. Chem. Soc.* **1984**, *106*, 984. Dto = C$_2$O$_2$S$_2$$^{2-}$ ligand.

(3) Coucouvanis, D.; Kanatzidis, M.; Simhon, E.; Baenziger, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 1874.

0020-1669/85/1324-2680$01.50/0 © 1985 American Chemical Society

Table I. Summary of Crystallographic Data for the $Cu(Dto)_2^{2-/-}$ Complexes

compd	$(KC_{12}H_{24}O_6)_2Cu(S_2C_2O_2)_2\cdot HCON(CH_3)_2$	$[(C_6H_5)_6P_2N][Cu(S_2C_2O_2)_2]$
mol wt	982.6	819.5
a, Å	11.488 (2)	13.528 (2)
b, Å	8.543 (2)	18.456 (2)
c, Å	23.526 (7)	15.354 (2)
β, deg	93.71 (2)	95.82 (1)
V, Å^3	2303.7	3813.7
Z	2	4
space group	$P2_1/c$	$C2/c$
d_{calcd}, g/cm^3	1.42	1.43
d_{obsd},[a] g/cm^3	1.41	1.41
cryst dimens, cm	(001) 0.0047, (203) 0.0059, $(\bar{1}\bar{1}\bar{1})$ 0.017	0.02 × 0.02 × 0.02[b]
abs coeff (μ), cm^{-1}	9.0	9.3
radiation used	Mo ($\lambda K\alpha_1 = 0.709\,26$)	Mo ($\lambda K\alpha_1 = 0.709\,26$)
$2\theta_{max}$	50°; $h,k,\pm l$	50°; $h,k,\pm l$
no. of unique data	4372	3369
no. of data used in refinement, $[F_o^2 > 3\sigma(F_o^2)$	2783	2547
no. of atoms in asym unit	67	27
no. of variables	352	244
error in observn of unit wt	2.57	1.94
R[c]	0.060	0.050
R_w[d]	0.076	0.066

[a] Determined by flotation in a CCl_4/pentane mixture. [b] Approximation values. [c] See ref 7. [d] See ref 7.

Table II. Positional Parameters for the Non-Hydrogen Atoms in $(18\text{-crown-}6)_2K_2Cu(Dto)_2$

atom	x	y	z
Cu(1)	0	2/2	2/2
K	0.3397 (1)	0.5766 (1)	0.84729 (5)
S(1)	−0.0210 (2)	0.6082 (3)	0.41263 (7)
S(2)	0.1893 (1)	0.9233 (2)	1.00995 (6)
C(1)	0.2126 (5)	0.8295 (7)	0.9478 (2)
C(2)	0.1111 (5)	0.8109 (7)	0.9019 (2)
O(1)	0.3077 (3)	0.7760 (6)	0.9370 (2)
O(2)	0.1323 (4)	0.7420 (6)	0.8585 (2)
O(3)	0.2418 (5)	0.6224 (9)	0.7298 (3)
O(4)	0.1909 (6)	0.343 (1)	0.7878 (3)
O(5)	0.3664 (7)	0.2298 (8)	0.8645 (3)
O(6)	0.5158 (5)	0.449 (1)	0.9204 (2)
O(7)	0.5768 (5)	0.7173 (8)	0.8595 (3)
O(8)	0.4066 (6)	0.8331 (7)	0.7797 (3)
N	−0.012 (1)	0.499 (2)	0.0380 (6)
O(S)	0.1970 (9)	0.448 (1)	−0.0522 (5)
C(1S)	0.054 (2)	0.452 (3)	−0.006 (1)
C(2S)	0.032 (1)	0.545 (2)	0.0904 (9)
C(3S)	0.119 (1)	0.484 (2)	−0.0191 (8)
C(3)	0.1252 (8)	0.552 (1)	0.7287 (4)
C(4)	0.143 (1)	0.377 (2)	0.7317 (6)
C(5)	0.2133 (9)	0.184 (1)	0.7931 (5)
C(6)	0.263 (1)	0.158 (1)	0.8480 (8)
C(7)	0.403 (1)	0.209 (1)	0.9242 (4)
C(8)	0.515 (2)	0.291 (2)	0.9328 (6)
C(9)	0.6264 (8)	0.520 (2)	0.9306 (4)
C(10)	0.609 (1)	0.694 (2)	0.9201 (5)
C(11)	0.360 (1)	0.848 (1)	0.7211 (5)
C(12)	0.515 (1)	0.905 (2))	0.7814 (7)
C(13)	0.565 (1)	0.879 (1)	0.8491 (6)
C(14)	0.246 (2)	0.784 (2)	0.7162 (9)
O(3′)	0.201 (2)	0.547 (2)	0.7385 (6)
O(4′)	0.226 (1)	0.309 (2)	0.8200 (7)
O(5′)	0.429 (1)	0.280 (2)	0.8918 (7)
O(6′)	0.566 (2)	0.549 (2)	0.9145 (6)
O(7′)	0.553 (1)	0.780 (2)	0.8288 (6)
O(8′)	0.351 (1)	0.812 (2)	0.7555 (7)
C(3′)	0.163 (3)	0.302 (4)	0.766 (2)
C(4′)	0.118 (3)	0.426 (5)	0.750 (1)
C(5′)	0.257 (6)	0.136 (7)	0.872 (3)
C(6′)	0.338 (3)	0.200 (4)	0.897 (2)
C(7′)	0.536 (4)	0.284 (6)	0.945 (2)
C(8′)	0.592 (3)	0.395 (4)	0.933 (1)
C(9′)	0.651 (2)	0.673 (3)	0.904 (1)
C(10′)	0.609 (2)	0.789 (4)	0.887 (1)
C(11′)	0.229 (4)	0.797 (6)	0.714 (2)
C(12′)	0.452 (2)	0.885 (2)	0.745 (1)
C(13′)	0.526 (3)	0.905 (4)	0.802 (1)
C(14′)	0.173 (2)	0.695 (3)	0.719 (1)

were obtained from the tables of Doyle and Turner.[5] The spherical hydrogen scattering factors of Stewart, Davidson, and Simpson[6] were used. No absorption corrections were applied to the data (Table I).

Determination of the Structures. A. $(KC_{12}H_{24}O_6)_2Cu(S_2C_2O_2)_2\cdot HCON(CH_3)_2$. Space group considerations require that the Cu atom be situated on a crystallographic center of symmetry. An electron density map calculated with only the copper atoms in the cell revealed the positions of the potassium and sulfur atoms. The remaining atoms in the $Cu(Dto)_2^{2-}$ anion and the oxygen and carbon atoms of the crown ether molecules were located in subsequent Fourier synthesis maps. Refinement with isotropic temperature factors for the atoms in the anions and cations in the unit cell converged to R_1 and R_w values[7] of 0.114 and 0.118, respectively. At this stage the carbon and oxygen atoms of the crown ether molecules displayed abnormally high temperature factors. A positional disorder of the crown ether molecule was suspected and was revealed in a Fourier difference map. This map, which was calculated by assigning half-occupancy to the crown ether carbon and oxygen atoms, showed new electron density maxima, which corresponded to another crown ether molecule at the same site rotated relative to the input crown ether molecule by 18°. The rotation is around an axis that passes through the common potassium atom and is perpendicular to the O_6 "crown". Refinement with different fractional occupancies for the two crown ether molecules at the site resulted in a minimum R_1 value of 8.69% with occupation factors of 0.65 and 0.35, respectively, for the two crown ether molecules. A difference Fourier at this stage revealed the atoms of the DMF molecule close to the potassium atom at half-occupancy. Refinement with anisotropic temperature factors for all nonhydrogen atoms in the unit cell (except for the atoms in the minor component of the crown ether molecule) converged to a conventional R_1 value of 6.2%. At this point the hydrogen atoms were included in their calculated positions (C–H = 0.95 Å) but were not refined. Refinement of the non-hydrogen atoms, with the hydrogen atoms included in the structure factor calculation, converged to final values of 0.060 and 0.076, respectively, for R_1 and R_w. In the last cycle of refinement all parameter shifts were less than 10% of their esd's.

B. $[[(C_6H_5)_3P]_2N][Cu(S_2C_2O_2)_2]$. With four ion pairs in the unit cell, space group ($C2/c$) considerations require that both the anion and cation be located on special positions. The positions of the copper and of the cation nitrogen atoms at 0, 0, 0 and $^1/_2$, $\bar{y}$, $^3/_4$, respectively, as well as the positions of two sulfur atoms and the phosphorus atoms were revealed by direct methods calculations using the program MULTAN.[8] These positions were verified in a three-dimensional Patterson synthesis map.

---

(4) The intensity (I) and its standard deviation ($\sigma(I)$) were calculated as follows: $I = SC - \tau(B_1 + B_2)$; $\sigma(I) = [SC + \tau^2 (B_1 + B_2)]^{1/2}$, where SC is the count during the scan, τ is the scan time to background time time ratio and B_1 and B_2 are the right and left backgrounds, respectively. The structure factor amplitude $|F_o|$ and standard deviation $\sigma(F)$ are given by $|F_o| = (I/Lp)^{1/2}$ and $\sigma(F) = \sigma(I)/2Lp|F_o|$ where (for the monochromator)

$$Lp = \frac{0.5}{\sin 2\theta}\left(\frac{1 + (\cos^2 2\theta_m)(\cos^2 2\theta)}{1 + \cos^2 2\theta_m} + \frac{1 + \cos 2\theta_m \cos^2 2\theta}{1 + \cos 2\theta_m}\right)$$

and $2\theta_m = 12.20°$ for Mo Kα radiation.

(5) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1968**, *A24*, 390.

(6) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(7) The agreement factors are $R_1 = \sum(|F_o| - k|F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |kF_c|)^2/\sum w|F_3|^2]^{1/2}$. The least-squares program minimizes the function $\sum w(\Delta F)^2$.

(8) Main, P.; Woolfson, M. M.; Germain, G. "MULTAN, A Computer Program for the Automatic Solution of Crystal Structures"; University of York: York, England, 1971.

Table III. Selected Interatomic Distances (Å) and Angles (deg) in (18-crown-6)$_2$K$_2$Cu(Dto)$_2$·DMF (I) and [(PPh$_3$)$_2$N][Cu(Dto)$_2$] (II)

dist	I	II	dist	I	II	dist	I	II
Cu–S(1)	2.268 (2)	2.164 (1)	K–O(4)	2.921 (9)		K–O(8′)	2.96 (2)	
Cu–S(2)	2.253 (2)	2.178 (1)	K–O(5)	3.003 (7)		mean	2.92 (12)	
S(1)–C(1)	1.704 (5)	1.737 (5)	K–O(6)	2.789 (6)		K–O$_{\text{DMF}}$	3.16 (1)	
S(2)–C(2)	1.702 (5)	1.723 (5)	K–O(7)	2.973 (6)		$\overline{\text{C}(i)\text{–O}(j)}^{c}$	1.42 (3)	
C(1)–C(2)	1.545 (7)	1.524 (7)	K–O(8)	2.844 (6)		$\overline{\text{C}(i')\text{–O}(j')}^{d}$	1.48 (19)	
C(1)–O(1)	1.226 (6)	1.217 (6)	mean[a]	2.91 (8)		$\overline{\text{C–C}}$	1.50 (1)	
C(2)–O(2)	1.217 (6)	1.186 (6)	K–O(3′)[b]	2.93 (2)		$\overline{\text{C}'\text{–C}'}^{f}$	1.25 (17)	
S(1)–S(2) (bite)	3.165 (2)	3.137 (2)	K–O(4′)	2.69 (2)		P–N		1.583 (2)
K–O(1)	2.757 (4)		K–O(5′)	2.90 (2)		$\overline{\text{P–C}}^{g}$		1.803 (8)
K–O(2)	2.796 (4)		K–O(6′)	2.96 (2)		$\overline{\text{C–C}}^{h}$		1.380 (18)
K–O(3)	2.942 (6)		K–O(7′)	3.05 (1)				

angles	I	II	angles	I	II
S(1)–Cu–S(2) (interligand)	91.1 (10)	92.52 (5)	O(1)–K–O(6)	84.0 (2)	
S(1)–Cu–S(2) (intraligand)	88.85 (7)	87.48 (5)	O(1)–K–O(7)	81.0 (2)	
Cu–S(1)–C(1)	104.5 (2)	105.7 (1)	O(1)–K–O(8)	90.4 (2)	
Cu–S(2)–C(2)	105.0 (2)	105.5 (2)	O(2)–K–O(3)	75.4 (2)	
S(1)–C(1)–C(2)	119.7 (3)	117.5 (2)	O(2)–K–O(4)	85.1 (2)	
S(2)–C(2)–C(1)	119.6 (3)	117.6 (2)	O(2)–K–O(5)	124.4 (2)	
O(1)–C(1)–C(2)	117.3 (5)	120.5 (4)	O(2)–K–O(6)	136.6 (2)	
O(2)–C(2)–C(1)	117.0 (5)	120.8 (4)	O(2)–K–O(7)	124.5 (2)	
S(1)–C(1)–O(1)	123.1 (3)	121.9 (3)	O(2)–K–O(8)	85.8 (2)	
S(2)–C(2)–O(2)	123.4 (3)	121.5 (3)	$\overline{\text{O}(i)\text{–K–O}(j)}^{i}$	57.6 (8)	
K–O(2)–C(2)	122.8 (3)		$\overline{\text{O}(i')\text{–K–O}(j')}^{j}$	58 (2)	
K–O(1)–C(1)	123.7 (3)		P–N–P		135.63 (12)
O(1)–K–O(2)	57.2 (1)		$\overline{\text{N–P–C}(i)}^{k}$		111.3 (3.5)
O(1)–K–O(3)	125.2 (2)		$\overline{\text{C–P–C}}^{l}$		107.4 (1.3)
O(1)–K–O(4)	133.2 (2)		$\overline{\text{C–C–C}}^{m}$		120.0 (1.0)
O(1)–K–O(5)	121.5 (2)				

[a] Esimated standard deviations calculated from scatter of values around mean $s \simeq \sigma = [\sum_i(x_i^2 - n_{\bar{x}}^2)/(n-1)]^{1/2}$. [b] Primed atoms reside within the minor component at the crown ether site (the minor component is rotated by 18.1 (3)° relative to the major component). [c] For the major component at the crown ether site, i and j cycle from 3 to 8. Range: 1.369 (16)–1.466 (13) Å. [d] Minor crown ether component. Range: 1.25 (4)–1.94 (6) Å. [e] Range: 1.33 (2)–1.67 (2) Å. [f] Range: 1.10 (6)–1.54 (3) Å. [g] Range: 1.794 (3)–1.808 (3) Å. [h] Range: 1.343 (9)–1.409 (6) Å. [i] Internal angles within the K–crown ether complex. Range: 56.1 (2)–58.4 (2)°. [j] Range: 55.9 (5)–59.5 (5)°. [k] Range: 107.4 (2)–113.8 (1)°. [l] Tetrahedral angles. Range: 106.3 (2)–108.9 (2)°. [m] Range: 118.0 (4)–121.8 (5)°.

The remaining non-hydrogen atoms were located on subsequent Fourier syntheses following least-squares refinements of the input atomic coordinates. The refinement of all atoms in the unit cell with isotropic temperature factors in the space group $C2/c$ gave an R_1 value of 0.13. Refinement of the atoms in the anion with anisotropic temperature factors converged to a conventional R value of 0.09. Finally, assignment of anisotropic temperature factors to all of the non-hydrogen atoms in the unit cell and least-squares refinement gave a final R_1 value of 0.064. The introduction of the hydrogen atoms in the cation, fixed at their calculated positions (0.95 Å from the C atoms), and further refinement of the non-hydrogen atom positional and thermal parameters converged to final values for R_w and R_1 of 0.066 and 0.050, respectively. During the last cycle of refinement all parameter shifts were less than 10% of their esd's.

Crystallographic Results for ($KC_{12}H_{24}O_6)_2Cu(S_2C_2O_2)_2\cdot HCON(CH_3)_2$ (I) and ($C_{36}H_{30}P_2N)Cu(S_2C_2O_2)_2$ (II). The final atomic positional and thermal parameters with standard deviations are compiled in Tables II and IV respectively. Intromolecular distances and angles are given in Table III, and the atom-labeling scheme for the [Cu(Dto)$_2$]$^-$ anion is the same as that shown in Figure 1 for the [Cu(Dto)$_2$]$^{2-}$ anion. Deposited with the microfilm version of the journal are (a) tables of the observed values of F, their esd's, and the $|F_o| - |F_c|$ values and (b) the final atomic positional and thermal parameters for the hydrogen atoms.

Results and Discussion

The K(18-crown-6)$^+$ and the [Cu(Dto)$_2$]$^{2-}$ ions in the crystalline lattice of I interact strongly, and the crown ether chelated K$^+$ ions are chelated further by the α-diketone "ends" of the [Cu(Dto)$_2$]$^{2-}$ complex. Similar interactions of Lewis acids with dithiooxalate complexes are well-known and have been studied extensively in the [(SnX$_4$)$_n$M(Dto)$_2$]$^{2-}$ and K$_2$Ni(Dto)$_2$ complexes,[9] the [(PPh$_3$)$_2$M]$_n$[M′(Dto)$_n$] complexes[10] (M = Cu$^{\text{I}}$, Ag$^{\text{I}}$; M′ = Ni, n = 2. M′ = Cr(III), Co(III), Al(III), Fe(III), n = 3) the M$_2$(H$_2$O)$_{2n}$Ni$_3$(Dto)$_6$·xH$_2$O complexes[11] (M = rare earth), and the M$_2$Ni(Dto)$_2$ complexes (M = Na$^+$, Li$^+$;[12a] M$_2$ = Ba^{+2} [12b]).

Table IV. Positional and Parameters for the Non-Hydrogen Atoms in [Ph$_3$PNPPh$_3$]Cu(Dto)$_2$

atom	x	y	z
Cu(1)	0	0	0.500
N	0.500	0.2613 (2)	0.750
S(1)	−0.0560 (1)	−0.00263 (6)	0.62755 (8)
S(2)	−0.0272 (1)	0.11597 (6)	0.48562 (9)
C(1)	0.5840 (3)	0.4133 (2)	0.3485 (3)
O(1)	0.6210 (3)	0.3968 (2)	0.2820 (2)
C(2)	0.5606 (4)	0.3553 (2)	0.4144 (4)
O(2)	0.5683 (4)	0.2929 (2)	0.3980 (3)
P	0.60876 (6)	0.22887 (4)	0.75361 (5)
C(3)	0.6260 (2)	0.1648 (2)	0.6674 (2)
C(4)	0.6525 (3)	0.1894 (2)	0.5892 (3)
C(5)	0.6579 (5)	0.1421 (3)	0.5188 (3)
C(6)	0.6345 (5)	0.0694 (3)	0.5294 (4)
C(7)	0.6076 (5)	0.0454 (2)	0.6064 (4)
C(8)	0.6026 (4)	0.0923 (2)	0.6781 (3)
C(9)	0.6484 (2)	0.1874 (2)	0.8576 (2)
C(10)	0.6064 (3)	0.2123 (2)	0.9306 (2)
C(11)	0.6378 (4)	0.1850 (3)	1.0132 (3)
C(12)	0.7099 (4)	0.1315 (3)	1.0217 (3)
C(13)	0.7500 (4)	0.1070 (3)	0.9496 (3)
C(14)	0.7208 (3))	0.1340 (2)	0.8667 (3)
C(15)	0.6918 (2)	0.3028 (2)	0.7389 (2)
C(16)	0.7931 (3)	0.2882 (2)	0.7345 (3)
C(17)	0.8554 (3)	0.3458 (3)	0.7207 (3)
C(18)	0.8212 (4)	0.4144 (3)	0.7135 (3)
C(19)	0.7224 (4)	0.4292 (2)	0.7184 (3)
C(20)	0.6570 (3)	0.3725 (2)	0.7313 (3)

---

(9) Coucouvanis, D.; Baenziger, N. C.; Johnson, S. M. *J. Am. Chem. Soc.* **1973**, *95*, 3875.

(10) Coucouvanis, D.; Piltingsrud, D. *J. Am. Chem. Soc.* **1973**, *95*, 5556.

(11) Trombe, J. C.; Gleizes, A.; Galy, J. *Inorg. Chim. Acta* **1984**, *87*, 129.

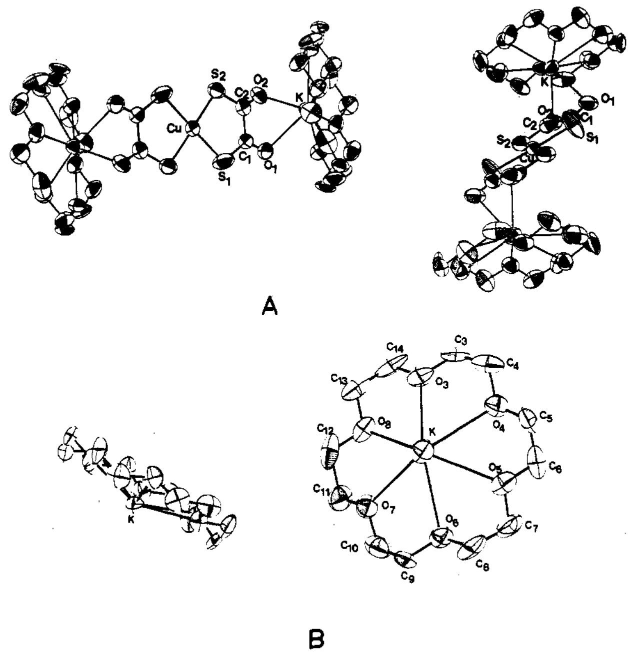

Figure 1. Structure and labeling of the (18-crown-6)$_2$K$_2$Cu(Dto)$_2$ complex (A) and of the major component of the (18-crown-6) K$^+$ cation (B). Thermal ellipsoids as drawn by ORTEP (Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965) represent the 50% probability surfaces. The labeling of the Cu(Dto)$_2{}^{2-}$ anion is identical with that in the [Cu(Dto)$_2$]$^-$ anion in the structure of the [(Ph$_3$P)$_2$N][Cu(Dto)$_2$] complex.

The K–O(Dto) bonds in I at 2.757 (4) and 2.796 (4) Å are similar to the K–O bond in the K$_2$Ni(Dto)$_2$ complex[9] (2.73 (2) Å) and shorter than the K–O bonds within the crown ether K$^+$ complex, which are found in the range 2.844 (6)–3.003 (7) Å. The range for the K–O distances in I contains slightly longer distances than the range in the K(18-crown-6)NCS salt[13] (2.77–2.83 Å), and is similar to those in the K(18-crown-6)$^+$ salt of the ethylacetoacetate anion[14] (2.83–3.02 Å). In the latter, chelation of the anion to the potassium atom in the K(18-crown-6)$^+$ complex results in the elevation of the K$^+$ ion 0.9 Å above the plane defined by the six crown ether oxygen donor atoms. A similar elevation by 0.8 Å out of the O$_6$ plane is apparent for the nine-coordinate K$^+$ ion in I with two, "out-of-plane", K–O(Dto) "bonds" and a weak interaction with the oxygen atom of the DMF solvent molecule at 3.16 (1) Å.

The K(18-crown-6)$^+$ ion in I is positionally disordered in the lattice and occupies the same site in two orientations, in a 0.65:0.35 ratio. The two orientations are related by an 18° rotation about an axis that passes through the K$^+$ atom and is normal to the least-squares plane defined by the six crown oxygen atoms. Both crown ether components have similar structures and similar C–C and C–O bonds (Table III). The major component, only, is shown in Figure 1b.

The [(Ph$_3$P)N(PPh$_3$)]$^+$ (PPN) cations and the [Cu(Dto)$_2$]$^-$ anions in II are well separated in the lattice, and particularly short interionic contacts are not apparent. The structure of the PPN cation is unexceptional[15] with the P–N–P angle at 135.63 (12)° and the P–N distance at 1.583 (2) Å.

The [Cu^{II}(Dto)$_2$]$^{2-}$ and [Cu^{III}(Dto)$_2$]$^-$ Anions. The anions in I and II are planar with the copper ions in I and II located on centers of symmetry. The square-planar coordination of the Cu(II) in I should be contrasted with the copper coordination in the oxalate analogue, [Cu(ox)$_2$]$^{2-}$. In the latter the Cu(II) is six-coordinate with the fifth and sixth axial coordination sites being occupied by the "terminal" oxygens from oxalate ligands of neighboring [Cu(ox)$_2$]$^{2-}$ anions.[16] These interionic interactions result in the formation of chains of magnetically interacting [Cu(ox)$_2$]$^{2-}$ anions. The difference in coordination between I and [Cu(ox)$_2$]$^{2-}$, in addition to ligand atom size considerations, could well be attributed to extensive M(d$_\pi$)–S(Dto)(3π_v) bonding[17] in I, which renders the d$_{z^2}$ orbitals on the copper unavailable for secondary interactions.

A comparison of the structural parameters in the planar CuS$_4$ units in I and (II) (Table III) shows a major difference in the Cu–S bond lengths. The Cu–S bond in II at 2.171 (Å) is considerably shorter than the Cu–S bond in I (2.260 Å) and compares well with the Cu–S bonds in the planar [Cu(S$_2$C$_2$(CN)$_2$)$_2$]$^-$ complex[17] (2.170 (4) Å) and the [Cu(DED)$_2$]$^-$ complex[18] (DED = 1,1-dicarbethoxyethylenedithiolate) at 2.195 (5) Å. The latter two complexes are diamagnetic and formally contain Cu(III). The Ni–S bond lengths in the isoelectronic, d^8, Ni(II) analogue complexes, [Ni(Dto)$_2$]$^{2-}$ [9] and [Ni(S$_2$C$_2$(CN)$_2$)$_2$]$^{2-}$ [19] are similar to those in II at 2.178 (3) and 2.166 (6) Å, respectively.

The intraligand bonds in I and II are unexceptional and are similar to those reported for the coordinated Dto ligands in other complexes[20,9] (Table III). The C–C bond lengths of the Dto ligands in I and II at 1.545 (7) and 1.524 7 Å, respectively, are not unusual and are within 3σ from the "single" (C(sp^3)–C(sp^3)) bond length of 1.537 Å.[21] These data do not indicate an unusually long (weak) C–C bond in II and do not offer a structural reason for the reactivity of the [Cu(Dto)$_2$]$^-$ anion. The latter is known[2] to undergo readily a photoinduced, internal two-electron-transfer process that results in oxidative cleavage of the coordinated S$_2$C$_2$O$_2{}^{2-}$ ligand to two SCO molecules.

The structural results for I and II suggest that the highest half-filled MO in I or the lowest unoccupied MO in II arise primarily from contributions of Cu and S atomic functions and are antibonding in character. This ground-state electronic structure has been suggested[17] previously for the analogous [Ni(S$_2$C$_2$R$_2$)$_2$]$^{-/2-}$ (R = CN, CF$_3$).

Acknowledgment. This work has been generously supported by a grant from the National Institutes of Health (No. GM-18144-03).

Registry No. I, 97135-56-3; II, 97135-57-4.

Supplementary Material Available: Tables of observed structure factors for (KC$_{12}$H$_{24}$O$_6$)$_2$Cu(S$_2$C$_2$O$_2$)$_2$·HCON(CH$_3$)$_2$ and [(C$_6$H$_5$)$_6$P$_2$N]-[Cu(S$_2$C$_2$O$_2$)$_2$] and final atomic positional and thermal parameters for all the hydrogen atoms and for the phosphorus, nitrogen, and carbon atoms of the [(C$_6$H$_5$)$_6$P$_2$N]$^+$ cation (33 pages). Ordering information is given on any current masthead page.

---

(12) (a) Maury, F.; Gleizes, A. *Inorg. Chim. Acta* **1980**, *41*, 185. (b) Gleizes, A.; Maury, F.; Cassoux, P.; Galy, J. *Z. Kristallogr.* **1981**, *155*, 293.

(13) Seiler, P.; Dobler, M.; Dunitz, J. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2744.

(14) Riche, C. *J. Chem. Soc., Chem. Commun.* **1977**, 183.

(15) Guy, J. J.; Sheldrick, G. M. *Acta. Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1718.

(16) (a) Bloomquist, D. R.; Hansen, J. J.; Landee, C. P.; Willett, R. D.; Buder, R. *Inorg. Chem.* **1981**, *20*, 3308. (b) Viswamita, M. A. *J. Chem. Phys.* **1962**, *37*, 1408.

(17) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 395.

(18) Coucouvanis, D.; Hollander, F. J.; Caffery, M. L. *Inorg. Chem.* **1976**, *15*, 1853.

(19) Forrester, J. D.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1964**, *3*, 1507.

(20) Coucouvanis, D. *Transition Met. Chem.* (*Weinheim, Ger.*) **1981**, *6*, 59.

(21) "Tables of Interatomic Distances and Configurations in Molecules and Ions"; The Chemical Society: London, 1960.