

Fig. 1. The complex anion viewed down *a*.

There is no clear difference (in the limits of 3σ) between the bonds C—O(endocyclic) (single-numbered O atoms in Table 2) and C—O(exocyclic) (double-numbered O atoms in Table 2). The oxalate ligands are not planar. The —C—C(=O)—O⁻ groups are planar and twist angles as defined by Siems & Lohn (1972) range from 6.0 to 7.4°. The C—C lengths are comparable to those found in oxalic acid dihydrate (Sabine & Cox, 1969), [Mn(C₂O₄)]·2H₂O (Deyrieux, Berro & Peneloux, 1973) and Cs₂[Mn₂(C₂O₄)₃]·3H₂O (Siems & Lohn, 1972). Three water molecules are distributed in the crystal lattice in such a way that the crystal packing is similar to that in K₃[Cr(ox)₃]·3H₂O and K₃[Al(ox)₃]·3H₂O (Taylor, 1978). Each of the K(1), K(2) and K(3) cations is surrounded by six O atoms at

distances varying from 2.63 (1) to 2.99 (1) Å. The problem of cooperative disordering of K(3)—K(33) and H₂O(3)—H₂O(33) seems to be of the same nature as in K₃[Cr(ox)₃]·3H₂O or K₃[Al(ox)₃]·3H₂O (Taylor, 1978).

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Potassium Formate

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Abstract. CHO₂⁻.K⁺, orthorhombic, *Cmcm*, *Z* = 4, *a* = 5.887 (1), *b* = 6.791 (2), *c* = 7.024 (2) Å, *V* = 280.8 (1) Å³ at 295 K, *D_c* = 1.99 Mg m⁻³, *μ* = 1.57 mm⁻¹; 576 non-equivalent diffractometer data up to *sin θ/λ* = 0.97 Å⁻¹; final *R(F)* = 0.026, *R_w(F)* = 0.027. The K atom has an eightfold coordination of O atoms. Four K—O bonds of 3.0025 (7) Å form a chelate-like structure, while the other four with the shorter distance of 2.8195 (6) Å interconnect different formate groups.

Introduction. K formate was prepared by neutralizing a solution of formic acid in methanol with K carbonate. Because the solution contains water, evaporation will

normally not result in the crystallization of K formate. However, by drying the solution in a desiccator over P₂O₅, large prismatic crystals of K formate appeared. Because of their deliquescent nature the crystals had to be handled with considerable care. A specimen 0.5 × 0.6 × 0.6 mm was cut from a large crystal and sealed in a capillary, partly filled with P₂O₅.

Precession photographs showed the space group to be *Cmc2₁*, *C2cm*, or *Cmcm*. Data were collected on a Syntex P2₁ diffractometer with Nb-filtered Mo K α radiation. Reflections were measured in two quadrants ($-h, k, \pm l$ and $h, k, \pm l$) up to *sin θ/λ* = 0.90 and 0.97 Å⁻¹ respectively, yielding 2789 reflections. Coinci-

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
K	0	0	0	0.0261 (1)	0.0311 (1)	0.0237 (1)	0	0	0.0001 (1)
C	0	0.40095 (13)	0.25	0.0237 (3)	0.0203 (3)	0.0398 (4)	0	0	0
O	0.1888 (1)	0.31911 (9)	0.25	0.0224 (2)	0.0307 (2)	0.0482 (3)	0.0026 (2)	0	0
H	0	0.546 (5)	0.25	0.044 (6)					

dence losses of the detector were corrected with the method of Chipman (1969) and with an attenuation filter for the very strong reflections. Background corrections were made by profile analysis (Blessing, Coppens & Becker, 1974). Three standard reflections measured after every 50 reflections showed no significant fluctuations. An absorption correction resulted in transmission factors ranging from 0.397 to 0.512. The equivalent reflections were averaged ($R = \sum |I - \langle I \rangle| / \sum I = 0.037$). Of the 591 non-equivalent reflections, 576 had $I > 0$ and were used for the analysis.

The structure was determined by the Patterson method. The position of the H atom was obtained from a difference synthesis. The structure was successfully refined in the centrosymmetric space group *Cmcm*. An isotropic extinction correction was made (Larson, 1969). Anomalous-dispersion factors were applied to K (Cromer & Liberman, 1970). The final $R(F) = 0.026$, $R_w(F) = 0.027$ and $S = [\sum w(F_o - F_c)^2 / (\text{NO} - \text{NV})]^{1/2} = 2.49$. Scattering factors were from *International Tables for X-ray Crystallography* (1974), except for H (Stewart, Davidson & Simpson, 1965).

The calculations were carried out with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on the Univac 1108 computer of the University of Frankfurt. The positional and thermal parameters of the atoms are reported in Table 1, bond lengths and angles in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35226 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances (Å) and angles (°)*

2 × C—O ^(a)	1.2426 (7)	O—C—O	126.86 (8)
1 × C—H	0.99 (3)	O—C—H	116.57 (5)
4 × K—O ^(b)	2.8195 (6)		
4 × K—O ^(c)	3.0025 (7)		

Symmetry codes

(a)	(b)	(c)
<i>x, y, z</i>	$-\frac{1}{2} + x, -\frac{1}{2} + y, z$	<i>x, y, z</i>
$-x, y, z$	$\frac{1}{2} - x, \frac{1}{2} - y, -z$	$-x, -y, -z$
	$\frac{1}{2} - x, -\frac{1}{2} + y, z$	$-x, y, z$
	$-\frac{1}{2} + x, \frac{1}{2} - y, -z$	<i>x, -y, -z</i>

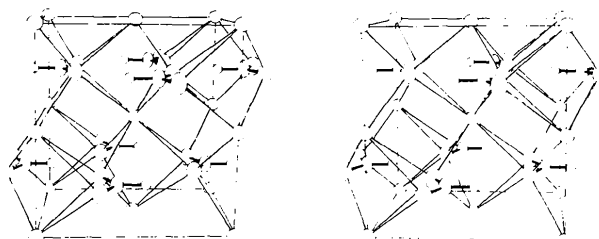


Fig. 1. Stereoscopic view of the structure of K formate along *a*. The thermal ellipsoids are the 50% probability surfaces. The H atoms are on an arbitrary scale.

Discussion. Several studies have been made to determine or refine the structures of various formates. Work in our group concerned the structure of the different phases in copper formate tetradeuterate (Burger & Fuess, 1979; Burger, Fuess & Burlet, 1980) and the electron density distribution in α -Ca(HCOO)₂ (Burger, 1979) and NaCO₂H (Bats & Fuess, 1980). Our results seem to indicate an influence of the cation on the electron density distribution of the formate group. To determine the interactions between K and the formate group we decided to undertake the present study. The structure is shown in Fig. 1. The formate groups form layers which are situated in the mirror planes of the space group at $z = 0.25$ and 0.75 . The K atom occupies a center of symmetry and has an eightfold coordination of O atoms. Four K—O bonds of 3.0025 (7) Å form a chelate-like structure, while the four with the shorter distance of 2.8195 (6) Å interconnect different formate groups.

The O—C—O angle of 126.86 (8)° is rather large. Values of 122.9 to 126.3° are reported for other formates (Watanabé & Matsui, 1978). The variety of O—C—O angles has been attributed to the different types of coordination in the various formates.

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Structure of Tetrabutylammonium μ -Oxo- μ -sulfido-bis[(1,2-dithiosquarato-*S,S'*)oxomolybdate(V)]

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Abstract. $C_{40}H_{72}Mo_2N_2O_7S_5$, $[N(C_4H_9)_4]_2[Mo_2O_3S(C_4O_2S_2)_2]$, triclinic, $P\bar{1}$, $a = 13.75$ (3), $b = 18.44$ (4), $c = 10.55$ (2) Å, $\alpha = 80.5$ (1), $\beta = 83.4$ (2), $\gamma = 83.0$ (2)°, $V = 2606.4$ Å³, $Z = 2$, D_m (floatation) = 1.29 (2), $D_x = 1.31$ Mg m⁻³, $F(000) = 1084$. The μ -O- μ -S bridged dimeric complex anion is chelated *trans* to the bridge bonds through S to two 1,2-dithiosquarato dianions. The Mo–Mo distance of 2.700 (1) Å is intermediate between those in the related di- μ -sulfido- and di- μ -oxo-molybdenum(V) dimers. The anion adopts the *syn* configuration.

Introduction. There has been considerable activity in the area of Mo coordination chemistry since it was suggested that Mo has a functional role in various enzymes (Stiefel, 1976; Wentworth, 1976). In particular, the chemistry and structure of complexes with S donor ligands have been studied. Among these ligands we have so far investigated the behavior of the 1,2-dithiooxalate dianion (Mennemann & Mattes, 1979). A very similar ligand is the dianion of 1,2-dithiosquaric acid (dts) (3,4-dimercapto-3-cyclobutene-1,2-dione) (Coucouvani & Hollander, 1974). Its interesting ligand properties have already been shown (Coucouvani, Holah & Hollander, 1975; Hollander & Coucouvani, 1977). The aim of the present work was to study the structure of the complex formed by the reaction of K_2dts with dimeric Mo^V species in aqueous solution, especially with respect to the coordination of Mo, and to study the change in the

molecular geometry of the ligand compared to its free state. Suitable crystals of the title compound could be prepared by adding $[N(C_4H_9)_4]Br$ in excess to an aqueous solution of $MoCl_5$ and K_2dts in the molar ratio 1:5. A yellow-greenish specimen $0.1 \times 0.1 \times 0.06$ mm was used in the data collection performed on a Syntex $P2_1$ diffractometer with graphite-monochromated $Mo K\alpha$ radiation. Using the ω - 2θ scan technique and variable scan speeds (2 – 29.3° min⁻¹), 6423 reflections were collected to $\theta_{max} = 23.5^\circ$. Backgrounds were measured at each end of the scan for a total time equal to the scan time. No absorption correction was applied ($\mu = 0.67$ mm⁻¹). The structure determination was based on 5064 reflections with $I > 3.92\sigma(I)$. The structure was solved using the Syntex *XTL* program system by a combination of Patterson and Fourier methods and refined by full-matrix least-squares calculations.

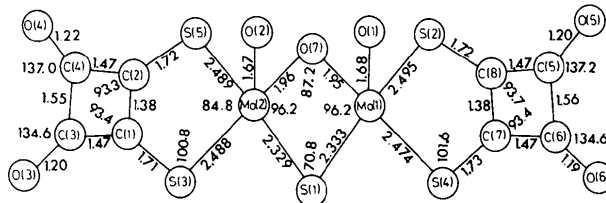


Fig. 1. Distances (Å) and angles (°) in the $[Mo_2O_3S(dts)_2]^{2-}$ ion. Standard deviations are 0.003 Å for Mo–S, 0.007 Å for Mo–O and 0.010 to 0.016 Å for the remaining bonds, and 0.1 to 1.1° for the bond angles.