transition we observed, at 3650 Å. or 27,400 cm.$^{-1}$, can be assigned to this transition. Since this band is the only one not having a counterpart in the WCl_6^{2-} compounds, the remaining bands are probably charge-transfer bands, which should be quite similar for the WCl_6^- and WCl_6^{2-} compounds.

Two d–d bands should have been observed for the WCl_6^{2-} compounds, corresponding to the transitions $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$. The value of approximately 19,000 cm.$^{-1}$ which we observed for our WCl_6^{2-} compounds is not unreasonable for the former transition, and the latter probably should be located at somewhat higher energies than the 27,400 cm.$^{-1}$ band observed in WCl_6^-. It is possible that the band at 3200 Å. reported by Peacock[3] corresponds to the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition, or that the d–d transition is hidden under a charge-transfer band in the same region of the spectrum.

The band in the visible region in our M_2WCl_6 compounds appeared at 5200–5250 Å., as opposed to the position reported by Peacock[3] of 5500 Å. Also, he refers to the fact that $WCl_5(OH)^{2-}$ salts exhibit a band at 5100–5200 Å.[10] However, we feel confident that the M_2WCl_6 compounds prepared from $MWCl_6$ are not partially hydrolyzed, on the basis of analysis, of no O–H bands in the infrared, and of the identity of our powder patterns with those of Peacock's compounds.

Acknowledgment.—This work was supported in part by the Advanced Research Projects Agency. S. E. F. acknowledges the support of the American Viscose Corporation.

[10] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 83 (1957).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

The Identification and Characterization by X-Ray Diffraction of a New Binuclear Molybdenum(VI) Oxalate Complex[1]

BY F. A. COTTON, SHEILA M. MOREHOUSE, AND J. S. WOOD

Received June 15, 1964

The crystal and molecular structures of the compound $K_2\{[MoO_2(C_2O_4)(H_2O)]_2O\}$ have been determined by a three-dimensional, single crystal X-ray diffraction study. This compound had previously been formulated as a molybdenum(V) compound, having one less oxygen atom per dimeric anion. An explanation for the discrepancy in stoichiometry is suggested. The centrosymmetric complex anion contains two (distorted) octahedrally coordinated Mo(VI) atoms with a rigorously linear and symmetrical Mo–O–Mo bridge. The various Mo–O bond lengths and O–Mo–O bond angles vary considerably, but all of the variations appear to correlate very well with simple considerations of interatomic repulsions and Mo–O bond orders. The tendency of ligands coordinated *trans* to multiple Mo–O bonds to have abnormally long bonds to the metal is again observed. The Mo–O (terminal) bonds are 1.69 ± 0.02 Å. and the Mo–O (bridge) bonds are 1.876 ± 0.002 Å.

Introduction

Molybdenum in the V and VI oxidation states forms a considerable number of oxo complexes. Few of them have been unequivocally characterized structurally, but it is important to do so in many cases. It is especially important where it appears that the compound is a diamagnetic one containing Mo(V), for this necessarily means that the true molecular formula is some even multiple of the simplest one containing only one molybdenum atom. The point of particular interest in such compounds is the structural arrangement whereby the Mo(V) atoms succeed in pairing their electron spins so as to produce a diamagnetic compound.

The only X-ray structural investigation of a diamagnetic Mo(V) complex which appears to have been reported[2] deals with the diethyl xanthate compound, $[(C_2H_5OCS_2)_2MoO]_2O$, which is found to contain a linear Mo–O–Mo bridge; it was further shown that, by a simple molecular orbital treatment, pairing of the electron spins through this bridge should take place. Each Mo atom is surrounded by a distorted octahedron of ligand atoms.

The structures of two oxo–Mo(VI) complexes have also been reported. The compound diethylenetriaminetrioxomolybdenum(VI) has been shown to have a mononuclear, distorted *cis*-octahedral structure,[3] while the oxalato complex, $NaNH_4[MoO_3(C_2O_4)]\cdot 2H_2O$, has been reported[4] to consist of infinite Mo–O–Mo–O– chains with a distorted octahedron about each Mo atom provided by two oxo oxygen atoms and two oxygen atoms of a chelate oxalate ion. The Mo–O–Mo bridges are bent and unsymmetrical (Mo–O, 2.23, 1.87 Å.) while the two terminal Mo–O bonds are rather long (1.815, 1.850 Å.), in comparison with those in the other two compounds, *viz.*, 1.64 Å. in the xanthate compound and 1.73 Å. in the diethylenetriamine complex.

Another way in which two Mo(V) atoms might be

---

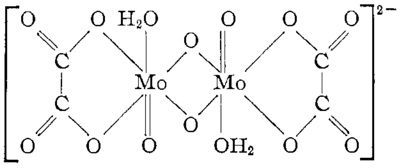
[1] Supported by a grant from the National Institutes of Health.

[2] A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).

[3] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).

[4] L. O. Atomovniyan and G. B. Bokii, *Zh. Strukt. Khim.*, **4**, 576 (1963).

connected in an oxo complex so as to provide the opportunity for pairing of spins is through a double oxygen bridge, that is, by having two octahedra sharing an edge. Our interest in the structure of the compound described in this paper was aroused because a preliminary X-ray study,[5] combined with the reported composition,[6] strongly suggested that such an arrangement would occur. Thus, a substance with the assumed empirical formula $KMoO_2(C_2O_4)H_2O$ which is diamagnetic[7] would probably contain dimers, and the unit cell and space group measurements required two dimers per cell, each lying at a center of symmetry. A seemingly obvious structure, consistent with these facts, would be I, or an isomer thereof. At any rate, a satisfactory structure with a single bridge, Mo–O–Mo, would be impossible to devise.


I

Dr. B. Lucas was kind enough to supply us with the same batch of crystals he used to determine the unit cell and space group. We immediately confirmed his findings, *viz.*, space group $P2_1/c$ and unit cell dimensions in agreement, and proceeded to a full structure determination. The unit cell dimensions of Lucas and Sandor, $a = 7.508$, $b = 14.235$, $c = 6.602$ Å., and $\beta = 94°33'$ were used.

Determination of Structure

From the sample of the crystalline material made available to us by Dr. Lucas, a small equidimensional crystal of maximum dimension *ca.* 0.3 mm. was selected for intensity measurements. Intensities were recorded photographically, using the equi-inclination Weissenberg method and Mo Kα radiation, levels $0kl$ through $7kl$ being obtained by the multiple film technique. All intensities were estimated visually, using a calibration wedge prepared from the same crystal, and measurements were confined to those reflections with $0 < \sin \theta \leqslant 0.4$. This region of reciprocal space gave about 800 independent reflections, of which about 100 were too weak to be measured and were assigned a value one-quarter of the minimum observable value in subsequent calculations. All reflections were corrected for Lorentz-polarization factors in the usual way. No corrections were made for absorption, the linear absorption coefficient being only 24.2 cm.$^{-1}$.

A three-dimensional Patterson synthesis was first computed using the Fourier program[8] ERFR-2. From this synthesis, the location of the double weight Harker peaks, $2x, {}^1/_2, {}^1/_2 + 2z$ and $0, {}^1/_2 - 2y, {}^1/_2$, and the single weight inversion peak, $2x, 2y, 2z$, gave the coordinates of the molybdenum atom which immediately indicated that the anion must be a dimer of some type, the molybdenum being much too close to the origin for the anion to be monomeric. Unambiguous assignment of the coordinates of the potassium ion did not appear possible on the basis of the Patterson map alone, and so the molybdenum atom position was used to derive signs for an initial electron density summation. Analysis of this Fourier synthesis yielded positions for the potassium ion and for all atoms of the oxalate group, and revealed the presence of several peaks around the molybdenum atom at varying distances, three of which were much higher in peak density than the remainder. However, there was no evidence of the expected bridging oxygen atoms (*i.e.*, according to a postulated structure, such as I, discussed in the Introduction) and none of the above three peaks could be assigned to such an atom.

In view of the uncertainty of the location of the various oxygen atoms and the water molecule at this stage, it was thought that one or more of the above-mentioned peaks might be due only to large series termination errors from the molybdenum atom (two of the peaks were *ca.* 1.7–1.8 Å. from the molybdenum) and therefore spurious. Signs for a second three-dimensional electron density map were thus based on the two heavy atoms and the six atoms of the oxalate group.

This second Fourier synthesis confirmed the above atoms and again showed the three peaks around the molybdenum, this time with much greater peak height, almost certainly indicating that they were not spurious. As in the first Fourier map, this electron density map was notable for the absence of the expected bridging oxygen atoms. At this point, least-squares refinement was commenced, using the full matrix least-squares program of Prewitt.[9] In the first cycle, only the positional parameters of the two heavy atoms and the overall scale factor were varied. In subsequent cycles, the atoms of the oxalate group and the two oxygen atoms nearest the molybdenum were included and their positional parameters and eventually their isotropic thermal parameters permitted to vary, along with the positional and thermal parameters of the heavy atoms. From their behavior on refinement, it appeared virtually certain that the two oxygen atoms were genuine. At this stage, a three-dimensional difference Fourier synthesis was calculated, omitting all atoms now considered to be satisfactorily fixed, in order to ascertain the manner in which the two halves of the dimer were linked together. By far the two most prominent features of this map were (1) a high peak lying on the center of symmetry at the origin and (2) the third peak, mentioned earlier, which is more distant from the molybdenum atom than the two already accepted as oxygen atoms. These, together with the other four atoms, completed a distorted octahedron around the metal atom.

It thus seemed clear that the more distant of the

---

[5] B. Lucas and E. Sandor, *Acta Cryst.*, **16**, 854 (1963).

[6] H. M. Spittle and W. Wardlaw, *J. Chem. Soc.*, 2742 (1928).

[7] C. M. French and J. H. Garside, *ibid.*, 2006 (1962).

[8] W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two and Three Dimensional Fourier Program for the IBM 709/7090," 1962.

[9] C. T. Prewitt, "A Full Matrix Least Squares Refinement Program for the IBM 709/7090 Computer," 1962.

TABLE I

FINAL ATOM PARAMETERS AND THEIR STANDARD DEVIATIONS

Atom	x	y	z	B, Å.^{2}	σ_x	σ_y	σ_z	σ_B
Mo	0.1011	0.1077	0.1254	0.73	0.0003	0.0001	0.0003	0.08
C_1	0.4603	0.1800	0.2637	0.5	0.0036	0.0016	0.0034	0.4
C_2	0.4842	0.0673	0.2546	0.7	0.0041	0.0017	0.0037	0.5
O_1	0.3053	0.2051	0.1993	1.1	0.0026	0.0011	0.0024	0.3
O_2	0.3478	0.0269	0.1784	0.8	0.0026	0.0011	0.0023	0.3
O_3	0.5812	0.2271	0.3225	1.7	0.0028	0.0012	0.0026	0.4
O_4	0.6260	0.0353	0.3179	1.9	0.0031	0.0013	0.0028	0.4
O_5	0.0360	0.1959	0.0369	2.3	0.0030	0.0013	0.0028	0.4
O_6	0.0573	0.0893	0.3697	2.0	0.0030	0.0013	0.0028	0.4
O_7	0.2228	0.1172	−0.1878	1.6	0.0028	0.0012	0.0026	0.4
O_8	0.0	0.0	0.0	1.9				0.5
K	0.8061	0.3260	0.1392	0.92	0.0008	0.0004	0.0008	0.13

three peaks was the oxygen atom of the water molecule and that the dimer contained one bridging and four terminal oxygen atoms and was thus incorrectly described by the formula assumed by Lucas and Sandor. The low peak height, and thus apparent absence of the bridging oxygen atom in the three-dimensional electron density summations, can be ascribed to series termination errors in the electron density distributions of the molybdenum atoms. Refinement was thus continued using the full matrix least-squares method and permitting all positional parameters (except those of the bridging oxygen) and an isotropic thermal parameter per atom to vary. Separate scale factors for each equi-inclination level were also used, two for each upper level, since these were divided according to whether spots were extended or compacted on the corresponding Weissenberg photograph. The number of variables refined was sixty.

Three cycles of refinement in this way lowered the residual (defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$) from 0.18 to 0.11, at which point the shifts in the majority of parameters were less than their corresponding standard errors. One further cycle of refinement was carried out, using the weighting scheme recommended by Cruickshank[10] and giving greater weight to the intermediate reflections, for which the errors were adjudged to be smaller. This final cycle produced a few minor changes and it was obvious that convergence of all parameters to their final values had now been reached, the final residual, R, being 0.105. The final positional and thermal parameters of all atoms, together with their standard deviations, are listed in Table I, the B_i being the isotropic temperature factors in the expression $\exp -(B_i \sin^2 \theta/\lambda^2)$. Table II lists the observed and the calculated structure factors based on these parameters. The standard deviations are obtained from the usual least-squares formula $\sigma^2(j) = a_{jj}(\Sigma \omega\Delta^2)/(m - n)$, where a_{jj} is the appropriate element of the matrix inverse to the normal equation matrix. Because the Weissenberg data were collected about only one axis and separate scale factors were used for each layer, the B_i values lack direct physical significance.

The atomic scattering factors used in this analysis were: for molybdenum, that tabulated by Thomas and Umeda[11] corrected for the real part, $\Delta f'$, of anomalous dispersion[12]; for potassium, that tabulated by Berghuis, *et al.*[13]; for carbon and oxygen, those tabulated by Hoerni and Ibers.[14]

Discussion

Formula of the Compound.—The structure determination demonstrates unequivocally that the stoichiometric formula initially assumed for the compound, $K_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$, is wrong, and that the correct stoichiometric formula is $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$. The presence of an additional oxygen atom is compatible with the observed[5] crystal density, 2.59 g. cm.$^{-3}$; the density now calculated is 2.63 g. cm.$^{-3}$. It also makes very little change in the C and H analyses used by Lucas and Sandor as a criterion of identity. Without the additional oxygen atom the calculated analytical figures are: C, 8.86; H, 0.37. With the additional oxygen atom the corresponding figures are: C, 8.61; H, 0.36.

The compound whose structure has been determined is thus a binuclear complex of Mo(VI) and not of Mo(V). The question naturally arises: Where did the error in assigning the formula and hence the incorrect assignment of oxidation state to the molybdenum first occur? According to Spittle and Wardlaw,[6] there are four related oxalato complexes of Mo(V), *viz.*, $KMoO_2(C_2O_4)\cdot nH_2O$, with n = 3.5, 2.5, 1.5, and 1.0, and the substance measured by French and Garside[7] is supposed to have been the last one. This compound is described[6,7] as being red, and we have found that when the directions of Spittle and Wardlaw[6] for obtaining $KMoO_2(C_2O_4)H_2O$ are followed a red compound is indeed obtained.[15] Now, the crystals we received from Dr. Lucas have only a pale reddish tan color, quite unlike the deep red color of the compound which, according to Spittle and Wardlaw, is $KMoO_2(C_2O_4)\cdot H_2O$, and we therefore suggest the following tentative[15] explanation

---

(10) D. W. J. Cruickshank and D. E. Pilling, *et al.*, in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961.

(11) L. F. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 239 (1957).

(12) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(13) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(14) J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

(15) Variations in color among the four compounds are rather remarkable if due solely to variation in content of presumably uncoordinated (to Mo) water molecules. It seems possible that not *all* of the compounds of Spittle and Wardlaw are Mo(V) compounds. Analytically, replacement of $0.5H_2O$ by 0.5O would be very difficult to detect. We are reinvestigating the entire series of compounds.

Table II
Observed and Calculated Structure Factors

H	K	L	FOBS	FCAL
0	4	0	142.07	-141.51
0	6	0	53.54	-50.69
0	8	0	99.04	87.00
0	10	0	96.69	90.86
0	12	0	66.35	-54.72
0	14	0	61.19	-56.36
0	3	1	29.57	-20.34
0	4	1	62.84	-56.70
0	5	1	38.75	-34.66
0	6	1	72.72	-61.10
0	7	1	18.36	-14.13
0	8	1	83.94	80.63
0	9	1	81.64	79.16
0	10	1	8.29	-16.28
0	11	1	58.00	53.34
0	12	1	80.94	-81.99
0	13	1	59.21	-61.47
0	14	1	10.13	-14.82
0	0	2	98.22	-98.24
0	1	2	99.55	-105.97
0	2	2	5.42	-3.71
0	3	2	108.80	-109.04
0	4	2	8.60	6.30
0	5	2	89.17	83.83
0	6	2	15.36	12.67
0	7	2	76.35	84.14
0	8	2	7.71	2.90
0	9	2	8.16	-14.49
0	10	2	8.60	10.11
0	11	2	83.88	-83.48
0	12	2	9.50	15.10
0	13	2	9.94	-15.54
0	1	3	33.27	-25.84
0	2	3	59.34	-53.15
0	3	3	6.76	6.21
0	4	3	46.40	-43.70
0	5	3	76.16	74.99
0	6	3	66.28	66.42
0	7	3	13.38	12.30
0	8	3	72.47	70.95
0	9	3	69.15	-64.90
0	10	3	26.51	-21.35
0	11	3	47.93	-41.53
0	12	3	62.91	-66.93
0	0	4	116.76	-128.58
0	1	4	16.83	-13.62
0	2	4	31.10	-25.81
0	3	4	7.78	0.83
0	4	4	109.94	131.35
0	5	4	8.16	-11.74
0	6	4	61.19	59.71
0	7	4	8.73	9.06
0	8	4	94.33	-92.05
0	9	4	9.37	10.09
0	10	4	51.37	-45.86
0	11	4	10.07	1.12
0	1	5	22.18	-26.05
0	2	5	23.39	27.58
0	3	5	16.38	14.07
0	4	5	54.37	52.88
0	5	5	55.51	56.45
0	6	5	32.63	-21.00
0	7	5	9.56	11.01
0	8	5	57.93	-56.49
0	9	5	32.50	-36.71
0	0	6	46.02	38.63
0	1	6	60.36	61.47
0	2	6	9.69	5.57
0	3	6	77.63	86.62
0	4	6	9.88	1.00
0	5	6	40.15	-42.18
0	6	6	10.20	7.02
1	4	0	138.42	-157.09
1	5	0	19.99	-16.26
1	6	0	59.83	-51.04
1	7	0	71.19	65.71
1	8	0	83.97	77.73
1	9	0	62.36	56.07
1	10	0	92.80	86.71
1	11	0	84.23	-73.37
1	12	0	17.39	-12.61
1	13	0	51.78	-53.37
1	14	0	49.32	-45.38
1	3	1	31.34	28.18
1	4	1	60.87	-56.44
1	5	1	21.03	13.32
1	6	1	135.04	142.92
1	7	1	33.61	-27.31
1	8	1	82.09	79.80
1	9	1	28.94	26.87
1	10	1	53.15	-53.71
1	11	1	23.10	22.62
1	12	1	79.88	-75.50
1	13	1	14.02	-20.39
1	14	1	10.38	6.36
1	0	2	56.20	42.81
1	1	2	68.79	-69.25
1	2	2	38.68	-31.21
1	3	2	65.93	-64.66
1	4	2	8.89	14.78
1	5	2	36.86	30.97
1	6	2	71.97	62.67
1	7	2	85.72	81.55
1	8	2	26.67	-25.50
1	9	2	25.76	-18.16
1	10	2	56.91	-54.16
1	11	2	46.66	-44.11
1	12	2	9.67	6.48
1	13	2	14.34	-18.16
1	1	3	76.25	-79.80
1	2	3	34.20	23.49
1	3	3	63.60	53.01
1	4	3	17.65	-19.38
1	5	3	116.42	128.05
1	6	3	22.78	-19.65
1	7	3	21.60	-13.20
1	8	3	47.18	40.89
1	9	3	81.38	-85.00
1	10	3	56.46	51.43
1	11	3	9.73	-5.99
1	12	3	27.13	-27.95
1	0	4	91.56	-92.00
1	1	4	7.79	10.87
1	2	4	22.91	-17.62
1	3	4	46.46	42.22
1	4	4	127.00	147.46
1	5	4	28.23	19.99
1	6	4	55.94	58.26
1	7	4	57.82	-55.01
1	8	4	59.83	-54.86
1	9	4	25.70	-22.15
1	10	4	39.78	-40.37
1	11	4	30.11	33.87
1	1	5	29.72	24.99
1	2	5	75.41	73.60
1	3	5	12.72	-18.63
1	4	5	50.62	45.17
1	5	5	9.34	6.05
1	6	5	83.65	-84.06
1	7	5	21.87	23.62
1	8	5	61.13	-58.91
1	9	5	10.38	-6.69
1	0	6	26.35	24.87
1	1	6	44.32	42.16
1	2	6	14.02	16.09
1	3	6	60.80	57.08
1	4	6	49.19	-46.76
1	5	6	34.65	-32.72
-1	3	1	125.18	-94.94
-1	4	1	33.66	-24.21
-1	5	1	61.75	-56.20
-1	6	1	36.83	33.16
-1	7	1	17.02	10.96
-1	8	1	59.16	52.85
-1	9	1	99.74	98.87
-1	10	1	52.82	43.22
-1	11	1	32.82	30.63
-1	12	1	31.52	-32.99
-1	13	1	57.22	-60.44
-1	14	1	19.29	-9.12
-1	0	2	117.61	142.25
-1	1	2	114.63	-117.77
-1	2	2	33.07	24.58
-1	3	2	84.60	-66.72
-1	4	2	89.97	64.49
-1	5	2	43.30	35.87
-1	6	2	38.51	-32.19
-1	7	2	77.22	74.65
-1	8	2	26.34	-18.30
-1	9	2	11.72	10.78
-1	10	2	75.99	75.37
-1	11	2	79.94	-77.93
-1	12	2	9.64	-7.15
-1	13	2	26.99	-23.03
-1	1	3	39.29	31.64
-1	2	3	188.67	-214.98
-1	3	3	16.63	-12.04
-1	4	3	39.03	-32.46
-1	5	3	7.38	-9.60
-1	6	3	66.93	56.47
-1	7	3	40.58	36.56
-1	8	3	66.93	62.79
-1	9	3	8.80	-5.89
-1	10	3	73.27	-68.34
-1	11	3	9.64	-10.44
-1	12	3	73.01	-72.67
-1	0	4	114.56	-123.57
-1	1	4	10.74	-5.97
-1	2	4	25.83	-20.39
-1	3	4	49.64	-46.51
-1	4	4	57.41	57.01
-1	5	4	8.22	-11.98
-1	6	4	56.44	53.17
-1	7	4	51.20	44.23
-1	8	4	12.88	-17.34
-1	9	4	44.08	45.41
-1	10	4	56.31	-55.04
-1	11	4	58.45	-52.47
-1	1	5	75.47	-74.74
-1	2	5	29.39	20.86
-1	3	5	57.15	53.53
-1	4	5	30.23	25.44
-1	5	5	88.28	93.51
-1	6	5	9.39	8.57
-1	7	5	25.83	-27.57
-1	8	5	31.91	-26.77
-1	9	5	64.98	-68.53
-1	0	6	9.71	-6.68
-1	1	6	32.62	26.18
-1	2	6	9.77	-11.93
-1	3	6	56.44	58.73
-1	4	6	10.16	16.37
-1	5	6	10.16	-15.18
-1	6	6	34.76	39.46
2	4	0	28.00	-21.77
2	5	0	22.99	-20.04
2	6	0	49.79	-41.59
2	7	0	128.70	131.72
2	8	0	29.62	-28.95
2	9	0	31.66	31.22
2	10	0	55.22	47.88
2	11	0	76.66	-69.66
2	12	0	34.20	29.59
2	13	0	62.20	-59.94
2	14	0	34.56	-33.02
2	3	1	19.11	19.53
2	4	1	51.06	-40.98
2	5	1	90.41	97.21
2	6	1	135.26	159.72
2	7	1	19.82	15.47
2	8	1	59.66	56.23
2	9	1	53.03	-49.44
2	10	1	51.27	-41.96
2	11	1	9.73	-0.32
2	12	1	39.63	-38.32
2	13	1	15.30	16.95
2	0	2	39.56	19.11
2	1	2	29.20	20.05
2	2	2	26.38	-27.76
2	3	2	22.00	-18.39
2	4	2	94.99	94.99
2	5	2	7.33	6.55
2	6	2	86.53	87.46
2	7	2	11.64	16.93
2	8	2	29.27	-24.74
2	9	2	30.82	24.71
2	10	2	70.10	-67.26
2	11	2	29.55	-27.77
2	12	2	21.65	-14.68
2	13	2	22.71	-27.15
2	1	3	74.96	-72.76
2	2	3	49.65	45.63
2	3	3	69.46	65.67
2	4	3	16.22	12.24
2	5	3	111.50	118.68
2	6	3	85.40	-81.42
2	7	3	49.65	-42.30
2	8	3	28.84	-25.89
2	9	3	59.31	-56.10
2	10	3	10.23	-3.12
2	11	3	10.65	-1.84
2	12	3	18.69	22.15
2	0	4	43.51	-36.62
2	1	4	31.66	30.78
2	2	4	17.63	-15.95
2	3	4	89.63	88.03
2	4	4	9.03	-3.96
2	5	4	9.24	-3.59
2	6	4	43.94	37.89
2	7	4	94.57	-92.30
2	8	4	22.71	-17.86
2	9	4	38.93	-37.51
2	10	4	22.28	-26.92
2	1	5	41.04	39.67
2	2	5	99.72	101.27
2	3	5	18.55	-22.71
2	4	5	31.03	27.63
2	5	5	37.94	-41.07
2	6	5	74.47	-69.72
2	7	5	10.79	5.20
2	8	5	35.54	-36.97
2	9	5	33.15	28.44
2	0	6	48.03	49.07
2	1	6	10.86	-0.95
2	2	6	10.93	15.57
2	3	6	11.00	6.44
2	4	6	20.87	-24.60
-2	3	1	96.15	-79.53
-2	4	1	17.46	10.15
-2	5	1	108.79	-106.06
-2	6	1	57.50	-49.07
-2	7	1	45.88	41.27
-2	8	1	35.04	-23.99
-2	9	1	82.36	85.49
-2	10	1	13.18	18.76
-2	11	1	8.31	-1.75
-2	12	1	35.34	37.01
-2	13	1	37.15	-36.78
-2	0	2	52.80	42.85
-2	1	2	26.67	18.05
-2	2	2	20.29	14.22
-2	3	2	18.66	-13.21
-2	4	2	107.59	-94.36
-2	5	2	13.55	-14.30
-2	6	2	53.22	-49.23
-2	7	2	41.66	36.82
-2	8	2	61.77	60.24
-2	9	2	25.95	22.66
-2	10	2	90.49	102.13
-2	11	2	28.78	-27.70
-2	12	2	16.80	-17.54
-2	13	2	28.96	-28.39
-2	1	3	86.69	84.21
-2	2	3	115.59	-116.39
-2	3	3	38.17	-34.77
-2	4	3	6.56	-0.65
-2	5	3	37.69	-29.80
-2	6	3	128.60	129.42
-2	7	3	23.00	-25.50
-2	8	3	56.83	54.78
-2	9	3	65.14	59.90
-2	10	3	43.23	-40.01
-2	11	3	33.11	35.51
-2	12	3	47.20	-45.77
-2	0	4	67.19	64.06
-2	1	4	78.27	-88.61
-2	2	4	7.10	2.53
-2	3	4	63.15	-59.34
-2	4	4	23.84	24.71
-2	5	4	7.65	-4.20
-2	6	4	47.92	44.11
-2	7	4	65.02	64.72
-2	8	4	8.49	2.93
-2	9	4	42.62	47.03
-2	10	4	40.52	-40.44
-2	11	4	62.97	-68.67
-2	1	5	86.75	-92.20
-2	2	5	31.13	-34.55
-2	3	5	73.87	81.36
-2	4	5	8.37	-13.04
-2	5	5	70.08	76.97
-2	6	5	23.36	-20.51
-2	7	5	8.97	-7.31
-2	8	5	20.59	22.93
-2	9	5	60.51	-68.93
-2	10	5	9.81	-11.15
-2	0	6	83.99	-93.27
-2	1	6	8.97	2.35
-2	2	6	9.03	-15.54
-2	3	6	9.15	-2.88
-2	4	6	56.17	59.07
-2	5	6	21.01	23.24
3	4	0	107.50	119.57
3	5	0	63.72	54.14
3	6	0	35.46	25.74
3	7	0	97.45	98.72
3	8	0	60.94	-46.57
3	9	0	9.15	11.65
3	10	0	9.75	10.53
3	11	0	54.65	-50.53
3	12	0	10.87	7.44
3	2	1	59.82	-67.02
3	3	1	15.82	12.91
3	4	1	32.83	-27.10
3	5	1	128.19	150.42
3	6	1	27.36	25.38
3	7	1	18.44	19.13
3	9	1	74.66	-69.12
3	10	1	72.26	-60.09
3	11	1	69.57	-67.44
3	12	1	37.18	-31.38
3	13	1	70.39	62.42
3	0	2	98.13	-119.60
3	1	2	36.43	33.06
3	2	2	34.26	-27.81
3	3	2	67.77	64.07
3	4	2	71.44	78.77
3	5	2	53.00	-49.06
3	6	2	56.07	50.75
3	7	2	44.75	-32.98
3	8	2	86.81	-85.86
3	9	2	9.82	11.40
3	10	2	52.32	-45.79
3	11	2	10.87	1.09
3	12	2	55.25	44.16
3	1	3	38.68	-37.78
3	2	3	40.93	36.75
3	3	3	30.73	28.07
3	4	3	49.78	41.30
3	5	3	47.15	39.92
3	6	3	13.12	-20.27
3	7	3	9.67	-8.17
3	8	3	66.87	-62.28
3	9	3	48.58	-36.91
3	10	3	50.75	42.61
3	11	3	11.47	8.77
3	0	4	80.43	79.41
3	1	4	73.69	68.58
3	2	4	9.37	-4.51
3	3	4	88.23	86.16
3	4	4	47.08	-42.84
3	5	4	29.09	-21.50
3	6	4	10.27	2.43
3	7	4	84.26	-81.22
3	8	4	60.64	57.29
3	9	4	11.32	-11.82
3	1	5	55.55	55.77
3	2	5	70.09	68.58
3	3	5	10.72	-15.24
3	4	5	10.87	12.48
3	5	5	55.92	-52.37
3	6	5	41.83	-40.60
3	7	5	16.42	-20.34
3	0	6	85.01	85.65
3	1	6	37.63	-35.38
-3	4	1	82.16	57.80
-3	5	1	62.19	-54.66
-3	6	1	67.90	-53.87
-3	7	1	28.64	22.40
-3	8	1	86.24	-80.87
-3	9	1	47.11	40.36
-3	10	1	8.23	-2.38
-3	11	1	35.18	32.08
-3	12	1	60.87	67.01
-3	13	1	32.47	-31.12
-3	0	2	135.68	164.88
-3	1	2	56.91	43.29
-3	2	2	20.98	15.36
-3	3	2	79.84	61.11
-3	4	2	122.68	-120.95
-3	5	2	31.91	-26.90
-3	6	2	53.71	-44.56
-3	7	2	64.82	-62.20
-3	8	2	90.33	86.52
-3	9	2	32.60	30.82
-3	10	2	54.08	50.86
-3	11	2	18.28	16.57
-3	12	2	19.22	-24.88
-3	1	3	71.11	56.89
-3	2	3	60.55	-44.26
-3	3	3	6.53	2.08
-3	4	3	9.61	-13.08
-3	5	3	97.93	-88.30
-3	6	3	7.41	5.05
-3	7	3	34.61	-30.67
-3	8	3	28.71	22.50
-3	9	3	81.78	81.78
-3	10	3	8.98	-9.98
-3	11	3	51.95	54.01
-3	0	4	21.23	19.56
-3	1	4	76.51	-71.12
-3	2	4	7.41	-6.08
-3	3	4	86.43	-100.38
-3	4	4	45.04	-44.58
-3	5	4	40.64	42.98
-3	6	4	8.23	5.76
-3	7	4	81.53	91.45
-3	8	4	34.11	30.67
-3	9	4	9.23	0.78
-3	10	4	9.55	18.38
-3	1	5	20.48	-19.71
-3	2	5	34.05	-38.21
-3	3	5	8.54	11.96
-3	4	5	12.31	-15.54
-3	5	5	61.87	59.89
-3	6	5	45.98	46.05
-3	7	5	9.36	-2.71
-3	8	5	68.34	74.17
-3	0	6	62.69	-65.48
-3	1	6	54.59	-54.57
-3	2	6	9.42	10.79
-3	3	6	30.65	-22.90
-3	4	6	76.88	90.03
4	4	0	47.70	46.29
4	5	0	20.22	21.17
4	6	0	54.97	50.50
4	7	0	71.60	69.27
4	8	0	58.73	-51.04
4	9	0	30.16	-24.03
4	10	0	53.30	-45.93
4	11	0	56.39	-43.10
4	12	0	30.08	21.18
4	2	1	58.90	72.79
4	3	1	31.24	24.30
4	4	1	7.44	9.22
4	5	1	84.21	96.50
4	6	1	40.18	-35.93
4	7	1	31.50	31.14
4	8	1	9.94	1.07
4	9	1	101.25	-97.45
4	10	1	51.88	45.89
4	11	1	39.85	-36.96
4	0	2	71.18	-84.85
4	1	2	59.98	65.52
4	2	2	7.69	-2.38
4	3	2	64.41	68.63
4	4	2	94.99	107.85
4	5	2	9.02	-13.96
4	6	2	13.45	13.19
4	7	2	73.02	-74.30
4	8	2	58.65	-48.85
4	9	2	11.11	-12.33
4	10	2	16.54	-16.66
4	11	2	74.60	69.37
4	1	3	31.91	25.94
4	2	3	67.17	61.46
4	3	3	24.48	-21.04
4	4	3	39.43	34.46
4	5	3	10.11	-2.04
4	6	3	30.66	-25.27
4	7	3	24.48	22.10
4	8	3	63.24	-62.26
4	9	3	26.65	21.42
4	10	3	12.45	8.26
4	0	4	109.77	115.38
4	1	4	66.17	62.28
4	2	4	19.88	18.91
4	3	4	61.90	56.27
4	4	4	63.24	-60.97
4	5	4	33.00	-26.42
4	6	4	21.80	-21.71
4	7	4	46.28	-43.66
4	8	4	33.25	30.08
4	1	5	68.25	65.39
4	2	5	44.36	-43.00
4	3	5	32.50	-23.06
4	4	5	12.36	-4.21
4	5	5	57.98	-54.17
-4	4	1	75.66	68.50
-4	5	1	58.15	44.94
-4	6	1	63.59	-57.82
-4	7	1	47.83	-42.42
-4	8	1	51.33	-51.85
-4	9	1	21.98	15.95
-4	10	1	58.09	58.26
-4	11	1	8.45	9.65
-4	12	1	70.89	87.94
-4	0	2	96.80	105.43
-4	1	2	30.13	23.90
-4	2	2	30.37	25.39
-4	3	2	110.14	104.02
-4	4	2	59.48	-55.37
-4	5	2	34.96	-29.14
-4	6	2	6.52	14.05
-4	7	2	79.65	-84.28
-4	8	2	66.61	64.70
-4	9	2	17.45	-17.59
-4	10	2	27.78	20.99
-4	11	2	43.84	48.67
-4	1	3	82.13	72.25
-4	2	3	70.23	54.38
-4	3	3	21.20	-17.49
-4	4	3	13.35	11.39
-4	5	3	81.16	-84.78
-4	6	3	62.62	-56.61
-4	7	3	7.55	-1.55
-4	8	3	7.91	-8.88
-4	9	3	57.00	62.56
-4	10	3	14.61	12.42
-4	0	4	61.59	59.39
-4	1	4	73.61	-72.45
-4	2	4	26.33	23.41
-4	3	4	76.03	-75.59
-4	4	4	39.49	-42.12
-4	5	4	40.70	41.23
-4	6	4	50.54	-55.62
-4	7	4	47.28	49.16
-4	8	4	30.07	31.55
-4	9	4	8.88	-3.51
-4	1	5	19.75	21.38
-4	2	5	77.60	-81.95
-4	3	5	26.45	-23.09
-4	4	5	35.39	-37.48
-4	5	5	22.95	-26.46
-4	6	5	51.15	51.40
-4	0	6	52.54	-59.85
-4	1	6	9.00	-15.41
5	4	0	61.76	61.52
5	5	0	9.53	12.15
5	6	0	75.96	73.44
5	7	0	11.40	8.04
5	8	0	12.23	-9.13
5	9	0	13.06	3.54
5	10	0	91.81	-88.02
5	2	1	96.58	128.76
5	3	1	52.33	47.08
5	4	1	9.43	19.64
5	5	1	70.16	69.55
5	6	1	73.06	-64.46
5	7	1	11.81	-0.72
5	8	1	46.53	-36.95
5	9	1	45.08	-35.16
5	10	1	37.93	30.50
5	0	2	42.28	33.69
5	1	2	63.83	63.19
5	2	2	22.18	19.32
5	3	2	64.77	66.23
5	4	2	10.78	11.13
5	5	2	11.50	5.18
5	6	2	12.02	0.31
5	7	2	72.85	-69.41
5	8	2	29.95	-22.10
5	9	2	54.20	-46.00
5	1	3	76.79	75.86
5	2	3	54.30	52.05
5	3	3	60.73	-56.31
5	4	3	12.44	5.56
5	5	3	37.41	-31.70
5	6	3	64.66	-65.29
5	7	3	13.89	13.82
5	8	3	42.18	-41.05
5	0	4	44.87	35.84
5	1	4	13.37	-10.39
5	2	4	13.47	6.07
5	3	4	13.68	12.25
5	4	4	53.89	-45.70
5	5	4	24.15	-16.16
-5	4	1	19.44	16.43
-5	5	1	63.53	65.32
-5	6	1	83.37	-82.43
-5	7	1	25.86	-25.30
-5	8	1	42.17	-41.87
-5	9	1	67.31	-70.68
-5	10	1	28.84	29.99
-5	0	2	27.31	-23.28
-5	1	2	38.07	33.17
-5	2	2	22.25	-20.55
-5	3	2	61.61	56.17
-5	4	2	14.22	11.62
-5	5	2	21.85	23.02
-5	6	2	8.76	7.29
-5	7	2	89.16	-84.56
-5	8	2	16.71	-12.34
-5	9	2	19.68	-23.97
-5	10	2	15.66	0.39
-5	1	3	76.39	71.97
-5	2	3	77.51	76.66
-5	3	3	35.50	-37.57
-5	4	3	48.51	44.15
-5	5	3	50.76	-50.21
-5	6	3	58.39	-60.07
-5	7	3	10.12	16.34
-5	8	3	15.02	-13.46
-5	9	3	61.61	66.19
-5	0	4	62.09	65.22
-5	1	4	15.82	-15.26
-5	2	4	52.77	47.48
-5	3	4	9.72	5.92
-5	4	4	42.17	-45.77
-5	5	4	10.28	-12.28
-5	6	4	47.23	-48.36
-5	7	4	11.00	4.44
-5	1	5	54.38	54.88
-5	2	5	65.94	-70.02
-5	3	5	35.42	-30.58
-5	4	5	11.24	-10.97
6	4	0	54.09	58.02
6	5	0	30.64	-32.30
6	6	0	60.70	59.63
6	7	0	28.99	-27.26
6	8	0	39.20	-35.58
6	2	1	61.19	74.87
6	3	1	20.43	19.40
6	4	1	16.93	18.05
6	5	1	45.33	39.59
6	6	1	64.20	-58.31
6	7	1	41.83	-34.16
6	8	1	87.74	-77.10
6	0	2	67.22	81.29
6	1	2	9.34	7.40
6	2	2	9.61	-10.44
6	3	2	50.29	47.52
6	4	2	69.26	-74.67
6	5	2	10.99	-9.91
6	6	2	28.40	-26.35
6	7	2	67.61	-62.49
6	1	3	49.61	45.70
6	2	3	52.33	48.03
6	3	3	35.80	-27.99
6	4	3	11.96	6.10
6	5	3	81.91	-76.95
-6	4	1	5.49	-4.02
-6	5	1	72.20	73.80
-6	6	1	53.20	-40.26
-6	7	1	13.57	11.69
-6	8	1	7.76	9.86
-6	0	2	67.68	-91.09
-6	1	2	25.47	23.42
-6	2	2	5.37	-1.41
-6	3	2	54.56	49.77
-6	4	2	85.33	83.05
-6	5	2	12.41	-9.48
-6	6	2	32.90	26.89
-6	7	2	48.29	-44.91
-6	8	2	39.24	-35.33
-6	1	3	33.94	30.87
-6	2	3	68.65	66.17
-6	3	3	30.19	-30.82
-6	4	3	40.66	39.81
-6	5	3	30.12	-26.17
-6	6	3	50.48	-48.97
-6	0	4	72.40	64.36
-6	1	4	49.19	46.74
-6	2	4	7.69	7.76
-6	3	4	47.83	49.61
-6	4	4	58.89	-56.22
7	4	0	44.41	44.19
7	5	0	45.30	-46.53
7	6	0	11.74	9.95
7	2	1	42.39	45.38
7	3	1	9.96	-4.07
7	4	1	49.66	53.86
7	5	1	46.87	-39.89
7	0	2	105.15	106.85
7	1	2	42.73	34.12
7	2	2	38.37	31.52
-7	4	1	6.82	8.87
-7	5	1	73.12	60.19
-7	0	2	69.15	-85.97
-7	3	2	20.54	21.61
-7	4	2	85.17	78.44
-7	1	3	43.85	-33.25

of the discrepancy. Lucas and Sandor prepared the crystals[5,16] by slowly cooling an aqueous solution, open to the air through a 0.2-mm. capillary tube, of the putative $KMoO_2(C_2O_4) \cdot H_2O$ for a period of 12 days. We believe that air oxidation to the Mo(VI) compound could easily have occurred. Thus the compound $KMoO_2(C_2O_4) \cdot H_2O$ may well be genuine and correctly formulated as a Mo(V) compound, but it is not the one which ultimately crystallized from the solution. A comparison of the infrared spectra of the two compounds in the region of the metal–oxygen stretch confirms this. We have actually observed that on heating a solution of the presumed red monohydrate in air, the red color fades almost completely over a period of 24 hr. We have not, however, succeeded in obtaining crystals from such a solution.

Discussion of the Structure.—Figure 1 shows the contents of the unit cell viewed down the z axis. Figure 2 shows a perspective view of the binuclear anion $[MoO_2(C_2O_4)(H_2O)]_2O$, with the atoms numbered as in Tables I, III, and IV. The bond lengths and interbond angles for all bonds to molybdenum are given, with their standard deviations, in Table III. Since the bridging oxygen atom lies at a crystallographic center of symmetry, the Mo–O–Mo bridge is rigorously linear and symmetrical.[17] The array of six oxygen

---

(16) B. Lucas, private communication.

(17) A referee has suggested that the Mo–O–Mo group might be bent with the O atom disordered. This cannot be positively ruled out, but the difference Fourier map showed only a strong, sharp, symmetrical peak, and the idea seems to us far-fetched.

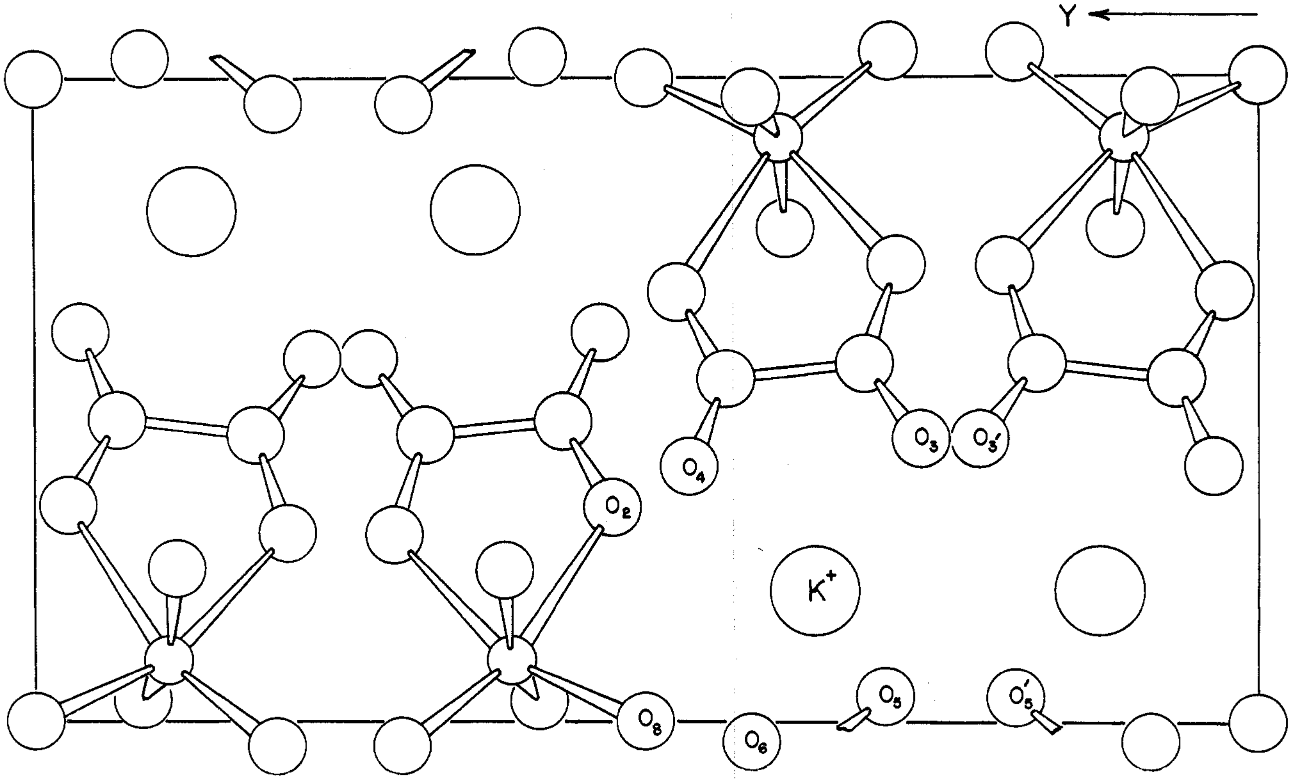


Fig. 1.—The contents of one unit cell viewed down the *z* axis with atoms referred to in Table V indicated.

TABLE III

BOND LENGTHS AND ANGLES AROUND THE MOLYBDENUM ATOM

Bond lengths, Å.			
Mo–O_1	2.087 ± 0.018	Mo–O_6	1.680 ± 0.019
Mo–O_2	2.186 ± 0.018	Mo–O_7	2.330 ± 0.018
Mo–O_5	1.700 ± 0.020	Mo–O_8	1.876 ± 0.002
Interbond angles, deg.			
O_1–Mo–O_2	73.77 ± 0.62	O_2–Mo–O_8	87.00 ± 0.45
O_1–Mo–O_5	89.93 ± 0.77	O_5–Mo–O_6	106.51 ± 1.03
O_1–Mo–O_6	94.29 ± 0.91	O_5–Mo–O_7	85.50 ± 0.81
O_1–Mo–O_7	80.74 ± 0.62	O_5–Mo–O_8	103.95 ± 0.68
O_2–Mo–O_6	89.56 ± 0.77	O_6–Mo–O_8	100.95 ± 0.75
O_2–Mo–O_7	77.62 ± 0.66	O_7–Mo–O_8	80.18 ± 0.49

TABLE IV

MOLECULAR DIMENSIONS OF THE OXALATE GROUP[a]

Bond lengths, Å.		Bond angles, deg.	
C_1–O_1	1.27 ± 0.03	O_1–C_1–O_3	129 ± 2
C_1–O_3	1.17 ± 0.03	O_1–C_1–C_2	112 ± 2
C_2–O_2	1.25 ± 0.03	O_3–C_1–C_2	120 ± 2
C_2–O_4	1.20 ± 0.04	O_2–C_2–O_4	130 ± 2
C_1–C_2	1.61 ± 0.03	O_2–C_2–C_1	113 ± 2
		O_4–C_2–C_1	117 ± 2
		Mo–O_1–C_1	122 ± 2
		Mo–O_2–C_2	119 ± 2

[a] Equation of the best plane[b] through atoms O_1, O_2, O_3, O_4, C_1, and C_2: $-0.3840X - 0.0814Y + 0.9197Z = 0.1107$. Distances of atoms from the above plane (Å.): O_1, 0.023; O_2, −0.029; O_3, −0.033; O_4, 0.032; C_1, 0.002; C_2, 0.008; Mo, 0.257. [b] $X = ax + c(\cos\beta)z$; $Y = by$; $Z = c(\sin\beta)z$.

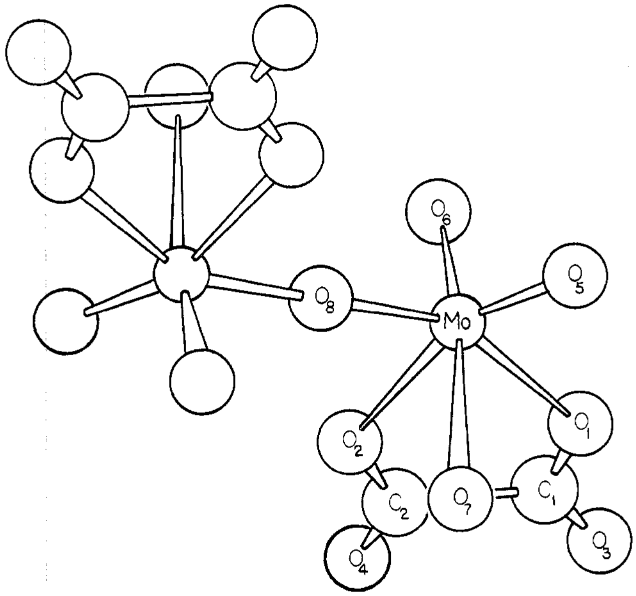


Fig. 2.—A perspective view of the $\{[MoO_2(C_2O_4)(H_2O)]_2O\}^{2-}$ anion, with the atoms numbered to correspond with Tables I, III, and IV.

atoms about each molybdenum atom forms a distorted octahedron.

All of the main dimensions of the structure seem to be in good accord with reasonable expectations. Let us consider first the twelve bond angles about the metal atom. These vary from 74 to 106°, in good accord with the expected effects of repulsion forces and constraint in the chelate ring. The angle between the two Mo–O bonds in the chelate ring is quite small because the oxygen atoms are held relatively close together within the oxalate ion. The largest O–Mo–O angle is between the two terminal Mo–O bonds, which are the shortest ones. Because of the shortness of these *cis* Mo–O bonds, O · · · O repulsion tends to be large and is at least partially mitigated by expansion of the interbond angle. The same effect was noted in the dien·MoO_3 structure.[3]

The next largest angles are those between each of the Mo–O terminal bonds and the Mo–O bridge bond, the latter being also rather short, though not so much as the terminal ones. Finally, the smallest bond angles, except for those in the chelate ring, are those between the very long Mo–OH_2 bond and its four *cis* neighbors. These range from 78 to 86°. The remaining four bonds are in the range 87–94°.

The six Mo–O bond lengths cover a large range, 2.33–1.68 Å., but the differences are understandable in terms of the different types and orders of the bonds. The Mo–OH_2 bond, at 2.33 Å., is the longest, and seems to be representative for this type of dative bond. Thus, in dien·MoO_3, the Mo–N bonds were also 2.33 Å. The next shortest bonds are those to the oxalate oxygen atoms, 2.09 and 2.19 Å., with the longer one being *trans* to one of the terminal Mo–O bonds. This result can be compared with those previously discussed for the xanthate complex,[2] where it was found that Mo–S bond lengths varied from 2.46 to 2.51 Å. for Mo–S *trans* to Mo–S, through 2.53 Å. for Mo–S *trans* to Mo–O (bridge) to 2.69 Å. for Mo–S *trans* to the multiple Mo–O terminal bond. It was therefore suggested that there may be a general tendency for bonds *trans* to Mo–O multiple bonds to be weakened and hence lengthened. The present results seem to confirm this suggestion very strongly.

The Mo–O (bridge) bonds are 1.876 ± 0.002 Å. in length, which may be compared with the two bridge bond lengths, 1.85 ± 0.03 and 1.87 ± 0.03 Å., found in the xanthate complex. Within the combined uncertainties, 1.88 Å. does not differ significantly from the average of the distances in the xanthate complex, 1.86 Å. In each case, the Mo–O–Mo bridge bonding can be considered in terms of a three-center molecular orbital treatment. In the xanthate complex, a combination of the d_{xz} orbitals of the two metal atoms and the p_x orbital of the oxygen atom produces one bonding, one nonbonding, and one antibonding MO, with four electrons occupying the lower two. In the present case, using the same set of orbitals, only the bonding orbital will be occupied. Thus, in this rough approximation, the difference between the two cases lies solely in the presence or absence of a pair of approximately nonbonding electrons. This would not be expected to have much effect on the strength and, hence, the length, of the Mo–O (bridge) bonds.

The two crystallographically nonequivalent Mo–O (terminal) bonds have lengths of 1.68 and 1.70 Å.; the magnitude of the standard deviations is such that the difference is without significance, so that they may be said to be equal, with a length of 1.69 ± 0.02 Å. This is greater than the mean length of the Mo–O (terminal) bonds in the xanthate complex, 1.65 ± 0.03 Å. (by an amount which is, however, not necessarily significant), and less than the mean length of the Mo–O bonds in dien·MoO_3, 1.74 ± 0.01 Å., by an amount which is probably significant. This progression of lengths with increasing number of terminal oxygen atoms bound to one metal atom is readily explained in terms of the spatial relationship of the oxygen atoms to the metal $d\pi$ orbitals required for π-bonding. When only a single terminal oxygen atom is present, it has access to two $d\pi$ orbitals, one for each of its $p\pi$ electron pairs, and thus the greatest possible amount of $p\pi \rightarrow d\pi$ bonding should occur. When two terminal oxygen atoms are *cis*, each has separate access to one $d\pi$ orbital, but the third $d\pi$ orbital must be shared. When three terminal oxygen atoms occur *cis* to one another, each $d\pi$ orbital is shared by some two of them. Thus the number of $d\pi$ orbitals available to each oxygen atom goes from 2.0 to 1.5 to 1.0 in the sequence MoO, *cis*-MoO_2, *cis*-MoO_3, and the extent of π-bonding may be expected to decrease accordingly. Augmenting this trend is the further effect of the tendency to build up charge on the metal atom through $p\pi \rightarrow d\pi$ bonding, so that the presence of one π-bonded oxygen atom militates against $p\pi \rightarrow d\pi$ bonding by a second oxygen atom and *vice versa*.

The dimensions of the oxalate ion are summarized in Table IV. They are generally in good accord with those previously found in various oxalate compounds.[18] The only oxalate complex for which reliable dimensions of the oxalate ion have been given is the tetraoxalatozirconate(IV) ion.[18] Here the C–O (coordinated) distance is 1.28 Å., the C–O (uncoordinated) distance is 1.22 Å., the C–C distance is 1.55 Å., and the oxalate ion is planar within experimental error. In the present compound, the ion is also found to be flat, within the uncertainties of the atomic coordinates, although the Mo atom lies about 0.26 Å. out of the mean plane of the ion. The two C–O (uncoordinated) distances are 1.17 and 1.20 Å., each with a standard deviation of ~0.035 Å. Thus, they are equal, within the limits of significance, as are the C–O (coordinated) lengths of 1.27 and 1.25 Å., each with a standard deviation of ~0.035 Å. The apparent differences in the lengths of the two bonds of each type, while strictly speaking without significance, are in the expected directions, the longer Mo—O bond going with the shorter C—O bond and the longer C═O bond, and *vice versa*. The C—C bond is surprisingly long, 1.62 Å., but the standard deviation of 0.034 Å. leaves open a reasonable possibility that it is really 0.04–0.06 Å. less than this, *i.e.*, 1.56–1.58 Å.

TABLE V

POTASSIUM–OXYGEN PACKING DISTANCES, Å.

O_2	2.76 ± 0.04	O_5	2.67 ± 0.04
O_3	3.03 ± 0.04	O_5'	3.25 ± 0.04
O_3'	2.88 ± 0.04	O_6	3.22 ± 0.04
O_4	2.95 ± 0.04	O_8	3.24 ± 0.04

Finally, Table V lists the eight potassium ion–oxygen closest approaches. Taking the radius of the potassium ion as 1.33 Å. and the van der Waal's radius of an oxygen atom as *ca.* 1.4 Å., all of these distances appear to be reasonable, within the experimental uncertainties.

---

[18] G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963); see Table III for a summary of structural data.