

Studies on Peroxomolybdates

VI. The Crystal Structure of Potassium Oxodiperoxoxalato-
molybdate(VI), $K_2[MoO(O_2)_2(C_2O_4)]^*$

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The crystal structure of $K_2[MoO(O_2)_2(C_2O_4)]$ has been determined from three-dimensional X-ray data, collected by the Weissenberg technique. The yellow crystals are monoclinic, belonging to space group $P2_1/n$, C_{2h}^2 , with $a=13.721$ (2) Å, $b=8.835$ (1) Å, $c=6.885$ (1) Å, $\beta=92.44$ (1)°, $V=833.9$ Å³ and $Z=4$.

Molybdenum is surrounded by seven ligands in the form of a pentagonal bipyramid, the equatorial plane of which consists of the two peroxo groups and one of the oxygen atoms of the oxalate group, while one double-bonded oxygen atom and another oxygen atom of the oxalate group form the apices. The molybdenum atom is displaced 0.35 Å out of the equatorial plane towards the double-bonded oxygen atom. The bond between molybdenum and the oxygen atom *trans* to the double-bonded oxygen atom is weaker than a normal single bond.

Average bond distances are: Mo—O_{peroxo} 1.94 Å, Mo=O_{apical} 1.68 Å, Mo—O_{equatorial} 2.08 Å, Mo—O_{apical} 2.26 Å, (O—O)_{peroxo} 1.46 Å, C—C 1.56 Å, C—O 1.28 Å and C—O 1.21 Å.

Whereas mononuclear peroxochromates containing coordinated organic ligands are easily formed,¹ it is very much more difficult to prepare the analogous compounds of the other group VIb elements. Thus, although $[CrO(O_2)_2py]$ precipitates immediately when a solution of pyridine and hydrogen peroxide is added to a solution of chromium(VI) oxide in water,² for molybdenum only pyridinium salts of peroxomolybdates have been obtained,³ while preliminary attempts to synthesize peroxomolybdates with other simple organic bases coordinated to molybdenum have failed.⁴ At the time this investigation was started, the only known peroxomolybdates containing an organic ligand were the oxalato complexes reported by Rosenheim *et al.*⁵

* Preliminarily reported at the 8th International Congress of Crystallography, Stony Brook, N.Y.

These authors formulated the potassium salts as $K_2C_2O_4 \cdot MoO_5$ and $K_2C_2O_4 \cdot H_2MoO_4 \cdot 2O \cdot H_2O$. As a part of a series of investigations on transition metal peroxo compounds, the structure of the anhydrous potassium peroxoxalato-molybdate has been determined and the results are presented in this paper.

EXPERIMENTAL

Preparation of crystals. $K_2[MoO(O_2)_2(C_2O_4)]$ was prepared according to Rosenheim *et al.*⁵

X-Ray methods. Approximate cell dimensions were obtained from rotation and Weissenberg photographs and more accurate dimensions from X-ray powder photographs taken in a Guinier focusing camera with $CuK\alpha$ radiation, using lead nitrate ($a=7.8566 \text{ \AA}$ at $21^\circ C$)⁶ as an internal standard.

Multiple-film equi-inclination Weissenberg photographs were taken at room temperature for crystals with an approximate thickness of 0.05 mm, with rotation about [001] (layer lines 0–6) and [100] (layer line 0), using $CuK\alpha$ radiation. As these crystals decomposed within 24 h at room temperature, new crystals had to be mounted for each layer line. A total of 1173 independent reflexions were registered. The intensities of the reflexions were estimated visually and corrected for Lorentz and polarisation effects but not for absorption ($\mu R \approx 0.5$) and extinction. $0kl$ -reflexions were registered while rotating the crystal mounted perpendicular to the needle-axis. Since no absorption correction was applied these reflexions were only used to obtain rough scale factors for the zones recorded by rotation about the c -axis. Ultimate scale factors were obtained from the least-squares refinement. This, of course, affects the reliability of the temperature factor values given in Table 2.

Computing methods. All computational work was performed at the Göteborg Universities' Computing Center using an IBM 360/50 computer and the following programmes: POWDER⁷ for indexing powder reflexions and refining cell parameters, DATAP2⁸ for calculation of $|F_o|$ from the measured intensities, DRF⁸ for Fourier summations, LALS⁸ for structure factor least-squares refinement (full-matrix), DISTAN⁸ for calculation of interatomic distances and angles and PLANEFIT⁸ for least-squares determination of the best plane through a set of atoms.

The atomic scattering factors used in the calculation of the structure factors were taken from Volume III of the *International Tables for X-ray Crystallography*, 1962. Dispersion effects were not taken into consideration.

UNIT CELL AND SPACE GROUP

For the crystals of $K_2[MoO(O_2)_2(C_2O_4)]$ which are yellow, needle-shaped and monoclinic, systematic absences were observed for planes of the type $h0l$ with $h+l=2n+1$ and for $0k0$ with $k=2n+1$. Hence, the space group is $P2_1/n, C_{2h}^5$ (No.14).*

The unit cell dimensions at $21^\circ C$, obtained from the measured $\sin^2\theta$ values of the Guinier powder photograph by a least-squares procedure using 46 of the observed lines, are: $a=13.721$ (2) \AA , $b=8.835$ (1) \AA , $c=6.885$ (1) \AA , $\beta=92.44$ (1) $^\circ$ and $V=833.9 \text{ \AA}^3$. Observed and calculated $\sin^2\theta$ values are given in Table 1.

* General equivalent positions:

$$\pm (x, y, z); \pm (\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$$

Table 1. Powder diffraction data for $K_2[MoO(O_2)_2(C_2O_4)]$ (Guinier camera, $CuK\alpha$ radiation, $\lambda(CuK\alpha_1)=1.54051 \text{ \AA}$, internal standard $Pb(NO_3)_2$, $a=7.8566 \text{ \AA}$ at $21^\circ C$).

hkl	$\sin^2\theta_{obs} \times 10^5$	$\sin^2\theta_{calc} \times 10^5$	I_{obs}	d_{obs}
110	1077	1076	w	7.421
200	1265	1263	w	6.847
$\bar{1}01$	1513	1516	m	6.262
101	1620	1623	m	6.052
210	2023	2023	st	5.416
$\bar{1}11$	2275	2276	m	5.107
111	2380	2383	w	4.993
020	3040	3040	m	4.418
$\bar{2}11$	3170	3170	w	4.326
120	3358	3356	w	4.203
211	3376	3384	vw	4.192
310	3398	3602	w	4.061
021	4294	4294	w	3.717
$\bar{1}21$	4561	4556	st	3.607
121	4660	4663	m	3.568
$\bar{3}11$	4685	4695	st	3.559
002		{5015		
$\bar{3}11$	5010	{5016	vst	3.441
221	5443	5450	st	3.301
221	5662	5664	m	3.237
410	5805	5811	st	3.197
$\bar{2}12$	6828	6824	vw	2.948
$\bar{3}21$	6963	6975	w	2.919
130	7146	7156	m+	2.881
$\bar{4}11$		{7279		
$\bar{3}21$	7290	{7296	m	2.853
022	8053	8055	w	2.714
420	8090	8092	w	2.708
$\bar{1}31$	8342	8357	vw	2.667
131	8454	8464	vw	2.649
$\bar{5}01$	8872	8879	w	2.586
312	8942	8938	vw	2.576
$\bar{2}31$	9246	9250	m	2.533
$\bar{2}31$	9465	9464	m	2.504
402	9636	9638	w	2.481
$\bar{4}12$	10400	10399	vw	2.388
331	10771	10775	vw	2.347
520	10938	10933	m+	2.329
600	11368	11366	m	2.284
$\bar{1}32$	12064	12065	vw	2.218
$\bar{1}13$	12192	12199	vw	2.206
132	12280	12279	vw	2.198
140	12473	12477	m	2.181
$\bar{6}11$	13056	13058	vw	2.132
$\bar{2}40$	13432	13424	w	2.102
611	13722	13700	vw	2.080
141	13793	13784	vw	2.074
$\bar{3}13$		{14404		
$\bar{6}20$	14412	{14406	m	2.028
$\bar{1}23$	14476	14480	w	2.024
530	14735	14734	m	2.006
123	14801	14801	w	2.002

The density of the crystals, as determined by weighing a sample in air and in benzene, is 2.68 g/cm³. The density calculated for a unit cell containing four formula units is 2.725 g/cm³.

STRUCTURE DETERMINATION

The expected Patterson peaks due to the Mo–Mo vectors corresponding to molybdenum atoms occupying the general four-fold position of space group $P2_1/n$ are:

u	v	w	Relative peak height
0	0	0	4
$\pm[2x]$	$\pm 2y$	$2z]$	1
$\pm[\frac{1}{2}-2x]$	$\frac{1}{2}$	$\frac{1}{2}-2z]$	2
$\pm[\frac{1}{2}]$	$\frac{1}{2}-2y$	$\frac{1}{2}]$	2

The largest maxima in the Patterson function appeared at:

u	v	w	Relative peak height
0	0	0	999
$\pm[0.3405]$	± 0.4145	$0.5090]$	187
$\pm[0.1623]$	$\frac{1}{2}$	$0.9795]$	336
$\pm[\frac{1}{2}]$	0.0965	$\frac{1}{2}]$	325

It is obvious that molybdenum occupies the four-fold position $4c$ of space group $P2_1/n$, with the approximate coordinates (0.169₆, 0.204₅, 0.257₄). These agree well with the final parameters (Table 2a).

Although it was possible to identify the Mo–K vectors in the Patterson function, the coordinates of the potassium atoms were instead derived from the first electron density map calculated with the signs based on the molybdenum position only. Both the potassium atoms in the asymmetric unit also occupy general positions. When these positions were included in the structure factor calculation, an R value of 0.28 was obtained and a subsequent Fourier summation revealed all the light atom positions. A structure factor calculation based on all the atomic positions, thus obtained, yielded an R value of 0.18.

The structure was refined by the least-squares method. In the initial cycles, positional parameters, isotropic temperature factors, and a scale factor for each layer were refined. In the final cycles an overall scale factor, positional parameters, anisotropic temperature parameters for molybdenum and potassium and isotropic temperature factors for all light atoms were refined. A total of 11 cycles of refinement were performed. In the last cycle the maximum shift was less than one third of the estimated standard deviation. Each reflexion was given the weight $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$, according to Cruickshank, with $a = 4.0$, $c = 0.010$, and $d = 0.0003$. The final R value was 0.112. The correctness of the proposed structure was checked by difference electron density calculations, the height of the largest peak in the difference map being one third the height of an oxygen atom peak.

Table 2a. Atomic coordinates, expressed in fractions of the cell edges, for $K_2[MoO(O_2)_2(C_2O_4)]$. Space group $P2_1/n$. $Z=4$. All atoms occupy general positions (4e). The numbers in parentheses are the standard deviations of the last significant figures.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Mo	0.1691 (1)	0.2023 (1)	0.2602 (2)	
K ₁	0.4777 (3)	0.3527 (4)	0.2613 (7)	
K ₂	0.2270 (3)	0.4307 (4)	0.7390 (5)	
O ₁	0.1477 (11)	0.2077 (18)	-0.0214 (24)	3.72 (29)
O ₂	0.1667 (10)	0.0538 (17)	0.0538 (21)	3.30 (25)
O ₃	0.1415 (13)	0.1727 (22)	0.5351 (27)	4.58 (35)
O ₄	0.1669 (9)	0.0341 (16)	0.4399 (19)	2.92 (23)
O ₅	0.2853 (10)	0.2617 (16)	0.2799 (21)	3.06 (24)
O ₆	0.1100 (10)	0.4186 (16)	0.2703 (21)	3.12 (25)
O ₇	-0.0220 (11)	0.5576 (19)	0.2566 (22)	3.65 (28)
O ₈	0.0061 (8)	0.1652 (14)	0.2412 (17)	2.10 (20)
O ₉	-0.1319 (12)	0.2937 (17)	0.2541 (23)	3.62 (28)
C ₁	0.0168 (14)	0.4350 (22)	0.2640 (29)	2.69 (32)
C ₂	-0.0437 (12)	0.2854 (18)	0.2496 (26)	1.94 (26)

Table 2b. Anisotropic temperature parameters β_{ii} and the standard deviations of the last significant figures in parentheses.

The expression used is $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.00358 (9)	0.00325 (17)	0.00785 (40)	-0.00042 (14)	0.00090 (21)	-0.00017 (26)
K ₁	0.00412 (24)	0.00347 (43)	0.02422 (126)	0.00210 (45)	0.00232 (78)	-0.00077 (94)
K ₂	0.00427 (22)	0.00436 (38)	0.00949 (92)	0.00014 (42)	0.00049 (62)	-0.00055 (80)

The atomic parameters obtained in the last cycle are given in Table 2 and observed and calculated structure factors in Table 3.

DESCRIPTION AND DISCUSSION

The crystals of $K_2[MoO(O_2)_2(C_2O_4)]$ contain potassium ions and mononuclear oxodiperoxooxalatomolybdate(VI) ions arranged as shown in the projection of the unit cell in Fig. 1. The complex ion is shown in Fig. 2. Bond distances are given in Table 4 and the cation environment in Table 5.

Molybdenum is 7-coordinated. The oxygen atom, O₆, of the oxalate group and the four oxygen atoms, O₁–O₄, of the two peroxy groups constitute the equatorial plane, while the oxygen atom, O₈, of the oxalate group and the oxygen atom, O₅, occupy the apical positions of a pentagonal bipyramid of the kind hitherto found in most 7-coordinated transition metal diperoxo complexes.

The distances between the molybdenum atom and the four oxygen atoms of the two peroxy groups are all 1.93–1.96 Å and are identical within the

Table 3. Observed and calculated structure factors for $K_2[MoO(O_2)_2(C_2O_4)]$. The columns are successively h , $|F_o|$, and F_c .

H 0 0	1 109 -94	2 68 -62	14 14 -12	-9 21 23	3 - -5	H 6 2
2 54 -53	2 53 46	1 71 -66	13 19 17	-10 16 -15	2 37 -41	12 20 -19
4 8 7	3 40 -31	0 - -5	12 20 -22	-11 28 28	1 28 -21	11 20 -20
6 185 204	4 13 -13	-1 84 -88	11 15 -12	10 53 55	0 113 111	10 - -4
8 - -10	5 98 94	-2 49 72	10 53 55	H 9 1	-1 30 26	9 - -8
10 27 -31	6 58 55	-3 119 143	9 23 22	10 - 26	-2 38 -34	8 - -9
12 44 51	7 88 -91	-4 45 -45	8 59 -84	9 26 -35	-3 - -6	7 69 85
14 20 -23	8 - -7	-5 - -11	7 38 -42	8 12 -15	-4 48 -57	6 61 -40
16 24 -26	9 - -9	-6 68 70	6 - -2	7 32 37	-5 76 90	5 52 -45
	10 - -5	-7 65 -70	5 24 22	6 - 14	-6 90 107	4 - -7
	11 39 38	-8 40 36	4 73 71	5 28 32	-7 32 -33	3 - -5
H 1 0	12 15 16	-9 75 92	3 29 -27	4 14 16	-8 47 -54	2 43 -38
2 140 -153	13 42 -42	-10 20 18	2 114 -101	3 36 -32	-9 30 38	1 51 51
3 68 -65	14 - -9	H 2 1	0 0 -11	2 10 -19	-10 22 -28	0 - -5
4 157 161		13 39 34	-1 35 -30	1 61 53	-11 39 46	-1 44 -43
5 39 38	H 7 0	12 42 -41	-2 134 113	0 - -1	-12 36 39	-2 41 -43
6 38 34	1 70 0	11 22 -22	-3 16 -12	-1 61 53		-3 38 -38
7 42 67	2 50 -51	10 13 15	-4 67 -64	-2 21 19	H 3 2	-4 - -14
8 56 -63	3 120 104	9 9 -12	-5 - -3	-3 38 -35	12 27 -24	-5 53 59
9 65 -74	4 59 55	8 41 41	-6 18 -14	-4 29 -24	11 56 49	-6 52 -52
10 44 79	5 - -1	7 45 70	-7 34 -34	-5 33 36	10 34 40	-7 60 -60
11 34 38	6 - -9	6 45 70	-8 49 73	-6 17 -14	8 32 -28	-8 19 16
12 - -6	7 17 -20	5 36 -40	-9 31 33	-7 35 35	8 64 -63	
13 3 - 3	8 24 -28	4 17 -26	-10 55 -56	-8 18 19	7 28 30	H 6 2
14 37 -37	9 89 79	3 4 - -4	-11 15 -15	-9 37 -36	6 - -12	0 - -7
15 - -4	10 24 25	2 78 -72	-12 14 14	-10 24 -29	5 118 119	-4 - -4
16 39 33	11 38 -37	1 122 125	H 4 1	H 10 1	4 49 46	-11 23 24
17 - -0	12 - -1	0 125 115	14 21 22	8 10 10	2 - -9	-13 33 -33
	13 - -8	0 58 -54	13 16 -18	5 32 44	1 114 96	-14 - -10
H 2 0	0 115 -126	-1 147 -132	12 43 -45	4 24 25	0 146 -20	H 7 2
1 59 -60	0 107 -93	-2 120 117	11 18 18	3 18 18	-1 104 99	13 - 0
2 26 27	1 34 32	-3 80 80	10 12 9	2 0 -6	-2 29 33	12 - 8
3 16 -16	2 52 50	-4 8 11	9 13 -13	1 46 -49	-3 22 -24	11 35 33
4 72 70	3 25 19	-5 34 -34	8 7 7	0 18 -4	-4 52 -52	10 18 -19
5 161 158	4 21 18	-6 44 -72	7 36 -35	-1 49 45	-5 91 104	9 175 -68
6 97 -98	5 26 -23	-7 33 33	6 76 -79	-2 - -8	-6 - -24	8 9 - 6
7 52 -53	6 45 -39	-8 9 - 4	5 28 -23	-3 - -15	-7 30 37	7 8 - 6
8 35 35	7 62 59	-9 18 15	4 6 - 1	-4 32 30	-8 67 70	6 43 -32
9 24 26	8 - -15	-10 36 30	3 35 31	-5 43 -51	-9 29 -40	5 6 23 21
10 29 27	9 15 15	2 45 41	2 45 41	-6 12 -13	-10 62 -75	4 - -1
11 85 66	10 16 16	1 125 115	0 143 -118	-7 18 21	-11 19 20	3 77 -78
12 30 -24	11 12 -10	0 28 28	-1 32 31	H 11 1	-12 19 20	2 - 17
13 - -9	12 22 -24	15 29 -26	-2 44 44	3 - -46	-13 - -18	1 48 -35
14 16 14	H 9 0	14 29 26	13 11 17	2 - 0	-14 37 -38	0 - -9
15 18 18	1 1 0	12 28 28	12 28 28	1 - -35	-15 - -9	-1 - -10
16 - -4	2 46 40	11 - -1	-15 25 22	0 - -3	-2 21 -19	-2 21 -19
H 3 0	3 45 -39	10 23 -24	14 25 -24	1 29 -38	-3 81 -83	0 64 68
1 124 -133	4 18 -44	9 22 -25	13 17 -3	-2 - -1	12 - -4	-4 34 28
2 - -9	5 20 16	8 77 80	12 17 -3	-3 - -47	11 36 26	-5 - -4
3 24 27	6 26 27	7 10 9	-9 30 26	H 0 2	10 - -12	-6 - -9
4 28 -29	7 - -8	6 24 27	-10 17 19	6 136 -94	9 0 - 9	-7 25 17
5 107 -104	8 31 32	5 65 69	-11 - -1	4 76 -104	8 45 41	-8 - -15
6 34 -34	9 - -4	4 48 -47	-12 - -51	4 76 -104	7 66 -61	-9 62 -64
7 51 -58	10 - -8	3 43 -41	H 7 1	4 76 -104	6 - -1	-10 - -10
8 61 69	H 10 0	2 108 94	13 7 7	4 76 -104	5 48 43	-11 32 35
9 21 22	0 23 24	1 81 66	12 19 -24	-4 84 -94	4 36 34	H 8 2
10 67 -68	1 24 -27	0 - -2	11 18 -24	-6 61 -75	3 37 32	7 57 -56
11 27 -28	2 43 -43	-1 74 60	10 31 -33	-8 14 -18	2 13 62	6 28 24
12 19 17	3 - -9	-2 122 -106	9 14 -11	-10 - -10	1 165 -151	5 26 26
13 17 -19	4 62 -53	-4 37 34	8 13 10	-12 30 -35	0 - -1	4 - -2
14 - -8	5 4 - -5	-5 76 72	7 35 -35	-14 20 25	-1 147 133	3 - -2
15 32 26	6 33 33	-6 30 -30	6 77 -81	-16 30 23	-2 50 44	2 - -3
16 - -4	7 - -0	-7 23 19	5 45 47	H 1 2	-3 12 -13	2 39 -43
H 4 0	H 11 0	4 73 -81	4 77 81	10 74 -70	-4 41 43	1 38 -38
1 27 28	1 - -8	-8 73 -81	3 45 47	9 35 30	-5 44 -54	0 64 68
2 154 161	2 29 -37	-10 23 21	2 72 71	8 15 13	-6 - -4	-1 49 39
3 82 -80	3 - -3	-11 - -3	1 17 -15	7 21 -19	-7 48 51	-2 38 -36
4 58 -57	H 0 1	-12 34 -30	-2 43 -59	6 24 22	-8 15 20	-3 19 25
5 57 -59	1 5 5	-3 55 43	-3 55 43	5 - -7	-9 6 - -6	-4 - -6
6 24 24	14 28 -25	-4 93 94	-4 93 94	4 66 -93	-10 18 10	-5 32 -31
7 32 36	13 43 -73	-5 28 -24	3 57 -55	3 57 -55	-11 43 -42	-6 26 26
8 39 -41	11 17 18	-6 13 -14	2 24 26	-13 33 41	-12 - -7	-7 59 58
9 17 16	9 12 14	-7 21 -18	1 32 35	-10 18 10	-9 - -11	-8 - -15
10 19 -23	7 107 -133	-8 14 -13	0 19 26	-11 43 -42	-10 - -14	-9 - -14
11 34 -30	5 86 111	-9 23 21	1 21 23	11 45 -38	-11 16 -14	H 9 2
12 - -14	3 33 -29	-10 39 41	-2 32 -43	10 43 34	9 9 10	8 18 -26
13 28 25	1 83 -112	-11 18 -18	-3 31 -31	9 34 33	8 - -7	7 - -9
14 - -4	-3 56 52	-12 28 26	-4 75 92	8 - -7	6 32 29	6 26 -31
15 - -2	-5 90 -102	H 8 1	-6 - -3	6 32 29	5 87 -78	5 28 -23
16 - -3	7 126 133	11 24 -28	-7 22 -25	4 14 10	3 95 85	4 52 53
H 5 0	H 10 1	10 9 -10	-8 23 -26	2 12 12	2 12 12	3 51 47
1 71 73	17 20 -25	9 15 -13	-9 35 36	1 36 -28	2 60 -54	2 - -2
2 51 -43	16 9 9	8 13 -13	-10 63 74	0 19 26	1 36 -28	1 - -1
3 130 -127	15 25 22	7 36 40	-11 23 -26	1 21 23	11 45 -38	0 - -1
4 - -5	-1 61 48	6 37 39	-12 - -5	0 - -1	10 43 34	0 - -1
5 67 69	-2 7 - 8	5 37 39	-13 - -8	-1 57 -55	9 34 33	0 - -1
6 41 -38	-3 48 -57	4 59 -59	-14 31 -34	-2 14 -19	8 - -7	-1 - -7
7 28 28	-4 52 -89	3 15 16	-15 31 -34	-3 76 77	-4 26 -27	-2 67 58
8 31 -27	-5 54 -51	2 18 -12	-16 34 33	-4 26 -27	-5 49 -49	-3 42 40
9 38 -47	-6 82 91	1 22 21	-17 - -4	-5 49 -49	-6 28 -27	-4 43 -40
10 29 -24	-7 47 -45	0 62 55	H 2 2	-7 - -16	-7 27 -28	-5 24 24
11 31 28	-8 47 -45	-1 18 -17	11 47 -42	-8 - -9	-8 27 -28	-6 24 24
12 - -12	-9 76 89	-2 36 -26	10 - -11	-9 36 37	-9 36 37	-7 - -1
13 23 29	-10 29 -27	-3 21 -17	9 45 -42	-10 36 -38	-10 36 -38	-8 31 34
14 33 -30	-11 46 -41	-4 - -2	8 49 -65	-11 27 -28	-11 27 -28	-9 - -11
15 33 -36	-12 63 60	-5 62 63	7 26 27	-12 - -9	-12 - -9	H 10 2
	13 - 0	-6 48 44	6 96 103	-13 21 -25	-13 21 -25	7 - -1
H 6 0	4 61 65	-7 40 -42	5 66 -60	-14 15 -19	-14 15 -19	6 - -33
1 6 - 6	3 117 138	-8 27 -22	4 43 -40	-15 33 36	-15 33 36	

Table 3. Continued.

5	-	7	4	83	69	-12	37	36	3	-	1	-4	-	-6	-8	-	1	-4	15	12		
4	43	42	3	79	64	-13	15	-13	11	36	39	-4	32	-30	-9	17	-17	-5	24	25		
3	-	-10	2	117	-73	-14	11	-19	10	52	52	-5	53	52	-10	15	21	-6	-	-6		
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13	63	55	-10	21	-23	3	31	-30	-2	77	94								6	44	42	
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-4	14	-11	H																			

Table 3. Continued.

-1	-	-5	-10	44	38		H 2 6	9	-	-11	5	-	13	0	-	-1	-8	-	12	
-2	14	-11	-12	36	-37	11	16	-22	8	25	-21	4	-	16	-1	44	-44	-9	-	-11
-3	20	-23				10		-2	7		-5	3	34	30	-2	17	-14			
-4	14	-14		H 1 6		9	19	-19	6	-	1	2	31	28	-3	54	48	H 7 6		
-5	45	53	12		-12	8	36	-35	5	51	57	1	63	-78	-4	-	-3	6	13	14
-6	22	26	11	23	-26	7	27	24	4	21	19	0	14	-12	-5	18	-14	5	-	9
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-8	-	-8	9	19	24	5	25	-27	2	14	13	-2	14	12	-7	35	-28	3	36	-39
			8	-	10	4	-	-6	1	22	24	-3	-	6	-8	-	-6	2	18	17
	H 9 5		7	19	-18	3	-	-5	0	26	-26	-4	28	26	-9	30	29	1	25	-22
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0	-	-12	3	-	-2	-1	10	-7	-4	23	-22	-8	-	5				-3	52	-50
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-4	14	-15	-1	17	-18	-5	58	63	-8	37	39	-12	-	-10	5	29	-27	-7	22	26
			-2	40	-55	-6	51	50	-9	36	-25				4	-	-5			
	H 0 6		-3	28	23	-7	32	-30	-10	28	-31		H 5 6		3	-	-19		H 8 6	6
12	20	-19	-4	46	51	-8	-	-15	-11	-	10	10	-	12	2	-	-12	3	-	6
10	17	-14	-5	-	-7	-	-	-	-12	-	7	9	26	21	1	51	46	2	26	-35
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4	21	-23	-8	35	-34	-12	18	19		H 4 6		6	19	17	-2	26	-19	-1	20	17
2	32	44	-9	34	32	-13	-	-7	11	10	-	5	62	-56	-3	38	-35	-2	22	-17
-2	-	9	-10	41	37				9	24	16	4	20	-15	-4	-	21			
-4	-	5	-11	14	-14		H 3 6		8	28	27	3	59	57	-5	50	52	-3	22	23
-6	52	-50	-12	-	7		11	24	7	45	-38	2	-	14	-6	34	-31			
-8	-	-8	-13	-	2		10	33	6	-	-12	1	-	-9	-7	44	-44			

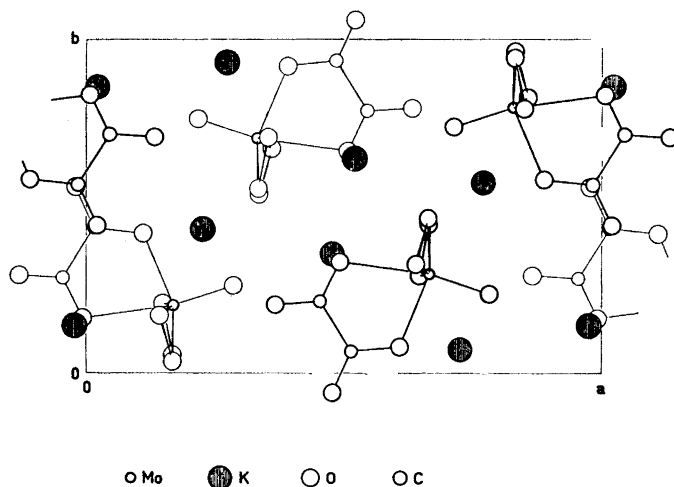


Fig. 1. Projection on (001) of the crystal structure of $K_2[MoO(O_2)_2(C_2O_4)]$.

limits of experimental error. They agree well with Mo-O_{peroxo} distances found in other peroxomolybdates (see Table 6). Furthermore, the values 1.93 and 2.00 Å were observed in $[Zn(NH_3)_4][Mo(O_2)_4]$ ¹⁶ and single bond Mo-O distances in the range 1.91–1.95 Å were found in $K_4[Mo_4O_{12}(O_2)_2]$.¹⁷ The distance between the molybdenum atom and the fifth equatorial oxygen atom, which belongs to the oxalate group, is significantly longer (2.08 Å).

The value 1.68 Å for the bond distance between molybdenum and the double-bonded oxygen atom does not differ significantly from the corresponding values found in other peroxomolybdates (see Table 6). In addition values in the range 1.69–1.71 Å were observed in $K_4[Mo_4O_{12}(O_2)_2]$.¹⁷

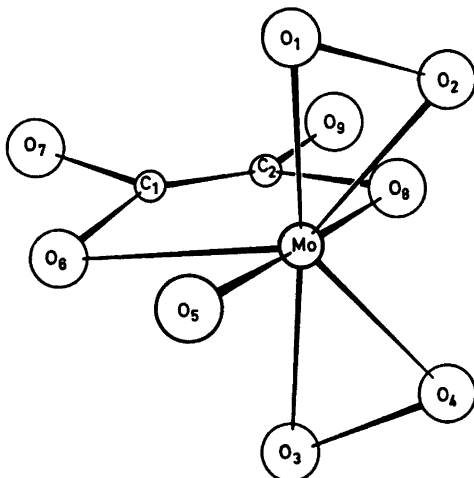
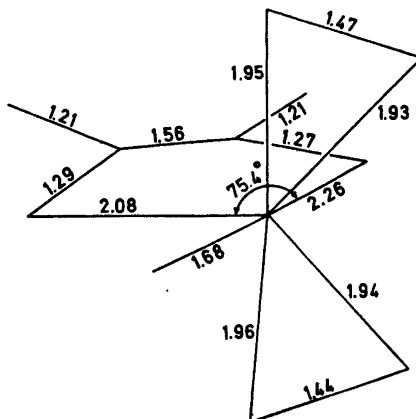
Fig. 2a. The $[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]^{2-}$ ion.Fig. 2b. Bond distances in the $[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]^{2-}$ ion.

Table 4. Bond distances and angles in the oxodiperoxoxalatomolybdate(VI) ion.

Distance (Å)	e.s.d. (Å)	Distance (Å)	e.s.d. (Å)		
Mo—O ₁	1.949	0.016	O ₁ —O ₂	1.474	0.022
Mo—O ₂	1.933	0.015	O ₃ —O ₄	1.439	0.024
Mo—O ₃	1.963	0.018	C ₁ —C ₂	1.561	0.025
Mo—O ₄	1.935	0.014	C ₁ —O ₅	1.287	0.023
Mo—O ₅	1.678	0.014	C ₁ —O ₆	1.207	0.025
Mo—O ₆	2.079	0.014	C ₁ —O ₇	1.266	0.020
Mo—O ₇	2.259	0.011	C ₂ —O ₈	1.213	0.023
Angle (°)	e.s.d. (°)	Angle (°)	e.s.d. (°)		
O ₁ —Mo—O ₂	44.6	0.6	O ₄ —Mo—O ₅	83.3	0.5
O ₁ —Mo—O ₃	159.2	0.7	O ₅ —Mo—O ₆	94.6	0.6
O ₁ —Mo—O ₄	130.5	0.6	O ₅ —Mo—O ₇	170.0	0.6
O ₁ —Mo—O ₅	100.1	0.7	O ₆ —Mo—O ₇	75.4	0.5
O ₁ —Mo—O ₆	88.2	0.6	Mo—O ₁ —O ₂	67.1	0.8
O ₁ —Mo—O ₇	80.8	0.5	Mo—O ₂ —O ₁	68.3	0.8
O ₂ —Mo—O ₃	128.3	0.7	Mo—O ₃ —O ₄	67.3	0.9
O ₂ —Mo—O ₄	87.1	0.6	Mo—O ₄ —O ₃	69.4	0.9
O ₂ —Mo—O ₅	105.0	0.6	Mo—O ₅ —C ₁	119.4	1.2
O ₂ —Mo—O ₆	130.9	0.6	Mo—O ₆ —C ₁	114.3	1.0
O ₂ —Mo—O ₇	82.7	0.5	O ₅ —C ₁ —O ₆	122.5	1.8
O ₃ —Mo—O ₄	43.3	0.7	O ₆ —C ₁ —O ₇	115.6	1.6
O ₃ —Mo—O ₅	100.7	0.7	O ₇ —C ₁ —O ₆	121.7	1.7
O ₃ —Mo—O ₆	89.9	0.7	O ₆ —C ₂ —O ₈	126.3	1.6
O ₃ —Mo—O ₇	78.8	0.6	O ₈ —C ₂ —C ₁	115.2	1.4
O ₄ —Mo—O ₅	103.3	0.6	O ₈ —C ₂ —C ₁	118.4	1.5
O ₄ —Mo—O ₆	131.9	0.6			

The apical oxygen atom, O_8 , *trans* to the double-bonded oxygen atom, lies at a distance of 2.26 Å from the molybdenum atom, and is thus considerably less tightly bound than the other oxygen atoms, a phenomenon which has been found to occur in the other 7-coordinated transition-metal peroxo complexes of the type $[MO(O_2)_n \dots]$ ($M = Cr, Mo, W$) hitherto investigated, some examples of which are given in Table 6. In all these compounds the coordinated atom in question is a water oxygen atom or belongs to a bidentate group.

The average O—O distance is 1.46 Å, which does not differ significantly from the value of 1.49 Å found in the peroxide ion or the value of 1.48 Å observed in both $K_2Mo_2O_{11} \cdot 4H_2O^9$ and in $K_4[Mo_4O_{12}(O_2)_2]$.¹⁷ For comparison,

Table 5. Cation environment in $K_2[MoO(O_2)_2(C_2O_4)]$. Distances less than 3.5 Å are included. The number in parenthesis after the atom symbol denotes:

(1)	x	y	z	(6)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$
(2)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	(7)	$-x$	$1-y$	$1-z$
(3)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(8)	x	y	$1+z$
(4)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$				
(5)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$				

$K_1(1)$	$-O_7(2)$	2.68 Å	$K_2(1)$	$-O_4(6)$	2.75 Å
	$-O_5(1)$	2.77		$-O_2(4)$	2.76
	$-O_1(3)$	2.77		$-O_3(7)$	2.76
	$-O_6(4)$	2.77		$-O_8(3)$	2.77
	$-O_3(5)$	2.80		$-O_7(7)$	2.82
	$-O_4(4)$	2.86		$-O_1(8)$	2.82
	$-O_2(4)$	2.99		$-O_5(1)$	2.90
	$-O_6(3)$	3.31		$-O_3(6)$	3.16
	$-O_2(3)$	3.32		$-O_1(4)$	3.38

O—O distances observed in some other transition metal peroxo complexes are given in Table 6. As can be seen from this table rather short O—O bonds have been found in two peroxomolybdates, but even in the peroxochromates O—O distances as short as 1.40 Å have been observed.¹³⁻¹⁵ It is thus obvious that there is a wide spectrum of O—O bonds in transition metal peroxo compounds.

Within the limits of experimental error, all five equatorial oxygen atoms, O_1-O_4 and O_6 , lie in a plane A, determined by the least-squares method, the equation of which is

$$A: 0.9712 X + 0.2269 Y + 0.0792 Z = 2.364$$

X , Y , and Z are the atomic coordinates expressed in Å and refer to an orthogonal coordinate system in which the X and Y axes coincide with the crystallographic a and b axes, respectively. The distances of certain atoms from the plane A are:

A to O_1	-0.02 Å	A to O_4	-0.02 Å	A to O_8	1.90 Å
O_2	0.02	O_5	-2.02	Mo	-0.35
O_3	0.02	O_6	0.00		

Table 6. Comparison between corresponding distances in $K_2[MoO(O_2)_2(C_2O_4)]$ and other 7-coordinated transition metal peroxo complexes of the type $[MO(O_2)_n \dots]$ ($M=Cr, Mo, W$).

Compound	Distances (Å)					Ref.
	M-O _{peroxo}	M=O	M-X (where X is <i>trans</i> to O _{apical})	O-O	M-equa- torial plane	
$K_2[O(MoO(O_2)_2(H_2O))_2](H_2O)_2$ (NH_4) ₂ F[MoO(O ₂)F ₄] $K_2[MoO(O_2)F_4](H_2O)$ $K_2[MoO(O_2)F_4](H_2O)$ $K_2[O(WO(O_2)_2(H_2O))_2](H_2O)_2$ $[Cr(O_2)_2phen]$ $[Cr(O_2)_2dipy]$ (pyH) ₂ [O(MoO(O ₂) ₂ (H_2O)) ₂] (pyH) ₂ [O ₂ MoO(OOH) ₂ MoO(O ₂) ₂] $K_2[MoO(O_2)_2(C_2O_4)]$	1.94-1.98 1.91	1.66	2.42-2.47	1.45-1.52	0.38-0.39	9
	1.94-1.95	1.67	2.03	1.36	0.23	10
	1.81-2.00	1.64	2.02	1.44	0.18	11
	1.80-1.87	1.66-1.71	2.33-2.38	1.46-1.54	0.35	12
	1.78-1.92	1.56	2.26	1.40	0.27	14
	1.96-1.98	1.57	2.23	1.40	0.31	15
	1.92-1.96	1.68	2.43	1.44-1.46	^a	26
	1.93-1.96	1.67	2.39	1.47-1.48	^a	26
		1.68	2.26	1.44-1.47	0.35	This paper

^a Not given.

Table 7. Interatomic distances and angles within the oxalate group.

Compound	Bond (Å)			Angle (°)			Ref.
	C-C	C-O(1)	C-O(2)	O(1)-C-O(2)	C-C-O(1)	C-C-O(2)	
$Li_2C_2O_4$ $K_2C_2O_4 \cdot H_2O$ $(NH_4)_2C_2O_4 \cdot H_2O$ $H_2C_2O_4 \cdot 2H_2O$ $K_2[MoO(O_2)_2(C_2O_4)]$	1.559 (4)	1.257 (3)	1.247 (3)	127.1 (3)	116.4 (3)	116.5 (3)	18
	1.574 (2)	1.260 (2)	1.247 (2)	126.3 (1)	115.8 (1)	118.0 (1)	19 ^a
	1.569 (8)	1.252 (6)	1.263 (6)	126.0 (5)	117.5 (5)	116.5 (5)	22
	1.546 (2)	1.281 (2)	1.207 (2)	127.1 (1)	111.9 (1)	121.0 (1)	23, 24
	1.561 (25)	1.287 (23)	1.207 (25)	122.5 (18)	115.6 (16)	121.7 (17)	} This work
	1.266 (20)	1.213 (23)	126.3 (16)	115.2 (14)	118.4 (15)		

^a Previously investigated by Hendricks²⁰ and Pedersen.²¹

The molybdenum atom is thus displaced 0.35 Å from the equatorial plane in the direction of the apical double-bonded oxygen atom, O₅. The same situation has been found to occur in other transition metal peroxo complexes (see Table 6). As a consequence of the displacement of the metal atom, the distances of the apical atoms from the equatorial plane are almost the same.

The oxalate group is not completely planar, and the planes defined by O₆-C₁-O₇ and O₈-C₂-O₉, the equations of which are $-0.0300 X + 0.0323 Y + 0.9990 Z = 1.934$ and $0.0229 X - 0.0389 Y + 0.9990 Z = 1.601$, respectively, form an angle of 5.1° with each other (this is approximately 5σ). Nor did Hodgson *et al.*¹⁹ find the oxalate anion to be planar in K₂C₂O₄·H₂O, but found it to consist of two parallel O-C-O planes separated by approximately 0.016 Å. The best plane, **B**, through the atoms of the oxalate group has the equation

$$\mathbf{B}: -0.0237 X - 0.0356 Y + 0.9991 Z = 1.652$$

The planes **A** and **B** are almost perpendicular to one another, the angle between them being 87.6°. The distances of selected atoms from the plane **B** are:

B to Mo	0.02 Å	B to O ₇	-0.05 Å	B to C ₁	0.02 Å
O ₅	0.10	O ₈	-0.05	C ₂	-0.01
O ₆	0.04	O ₉	0.05		

From these values it is evident that the molybdenum atom and the oxygen atom O₅ are very close to the plane **B**. The complex has, therefore, almost C_s symmetry.

Distances and angles obtained for the oxalate group in this work and, for comparison, in oxalic acid and some simple oxalates are given in Table 7. The C-C bond distance, 1.56₁ Å, is longer than that found in ethane, 1.536 Å, which is in agreement with that which has been observed in the other oxalates cited. The C-O bonds do not differ appreciably between the different oxalates as can be seen from Table 7. This is contrary to what is found in both oxalic acid and in K₂[MoO(O₂)₂(C₂O₄)], where two of the oxygen atoms are involved in bonding to hydrogen and molybdenum, respectively. The agreement between the corresponding C-O bond distances observed in oxalic acid and in the present work is excellent except for the value found for the C₂-O₈ bond. This shortening by 0.02 Å relative to C₁-O₆, indicating increased bond strength, is readily explained by the fact that O₈ is less tightly bound to molybdenum. This must, of course, influence the strength of the C₂-O₈ bond in the observed direction.

As was mentioned in the introduction, molybdenum does not, in general, form peroxomolybdates with organic ligands as easily as does chromium. There is, *e.g.*, no molybdenum counterpart to [CrO(O₂)₂py].¹³ Quite recently, however, two peroxomolybdates with hexamethylenephosphorus triamide (= HMPT) have been synthesized, *viz.* MoO₅(HMPT)(H₂O) and MoO₅(HMPT)(py). Their structures have been determined by Weiss *et al.*²⁵ in connection with the use of transition metal peroxo complexes as industrial catalysts.

The crystal structures of several transition metal peroxo complexes have now been determined. In these compounds the O₂:M ratio has had the values

1:2, 1:1, 2:1, 3:1, and 4:1. In all complexes hitherto investigated this ratio has determined the geometrical configuration of ligands about the central metal atom. Thus the configuration of the 1:2 complex has been found to be distorted octahedral, that of the 1:1 and 2:1 complexes to be pentagonal pyramidal or bipyramidal, and that of the 3:1 and 4:1 complexes to be dodecahedral.

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