K$_2$[Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·3H$_2$O

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The crystal and molecular structure of dipotassium di-μ-oxo-bis[aqua(oxalato-O^1,O^2)oxomolybdenum(III)] trihydrate, K$_2$-[Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·3H$_2$O, has been determined from X-ray diffraction data. In the dimeric anion, which has approximate twofold symmetry, each Mo atom is in a distorted octahedral coordination, being bonded to one terminal oxo-O atom, two bridging O atoms, two O atoms from the oxalato ligand and one from the water molecule. Bond lengths *trans* to the multiple-bonded terminal oxo ligand are larger than those in the *cis* position, confirming the *trans* influence as a generally valid rule.

Comment

Although the *trans* repulsive influence of the terminal oxo ligand is generally accepted (Spivack & Dori, 1975), there are a few structural examples in which such an influence is not observed. In particular, it has been emphasized that the oxalato complexes of molybdenum(V), *e.g.* Ba[Mo$_2$O$_4$-(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·3H$_2$O (Cotton & Morehouse, 1965) and Cs$_2$[Mo$_2$O$_2$S$_2$(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·H$_2$O (McDonald, 1978), do not show any lengthening of the bonds *trans* to the oxo ligand. However, redetermination of the structure of the barium salt and the determination of Cs$_2$[Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·H$_2$O (Kamenar *et al.*, 1991) and H(pyH)$_3$[Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·-2H$_2$O (Rongsheng & Xiufen, 1985; py = pyridine) show that in all oxalato complexes in which two octahedrally coordinated Mo atoms are doubly bridged through two O atoms there is an obvious *trans* influence of the terminal oxo-O atom. In order to provide additional experimental support for the *trans* repulsive influence of the terminal oxo group, the title

(I)
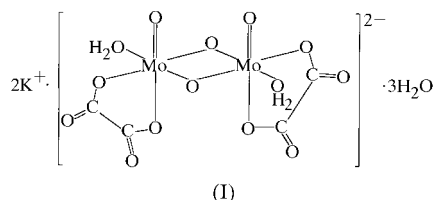
complex, (I), has been prepared and structurally characterized and the results are presented here.
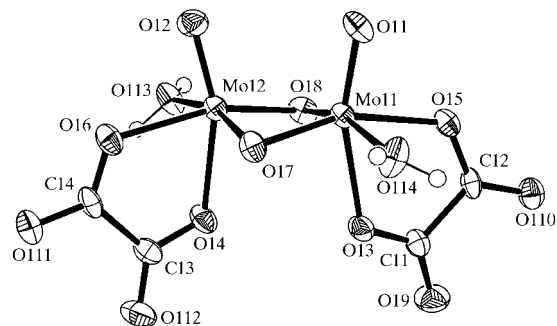

Figure 1
View of the anion of (I) showing the atom-labelling scheme for one of the crystallographically independent anions. The other independent anions have essentially the same features and analogous labelling schemes. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

The crystal structure of (I), with four molecules in the asymmetric unit, is built up of K$^+$ cations, binuclear [Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$]$^{2-}$ anions and water molecules. Complex anions 1 and 2, as well as 3 and 4, are related by a pseudo-translation of $a/2$ along the x axis. However, the K$^+$ cations and the water molecules are not related in this way. In
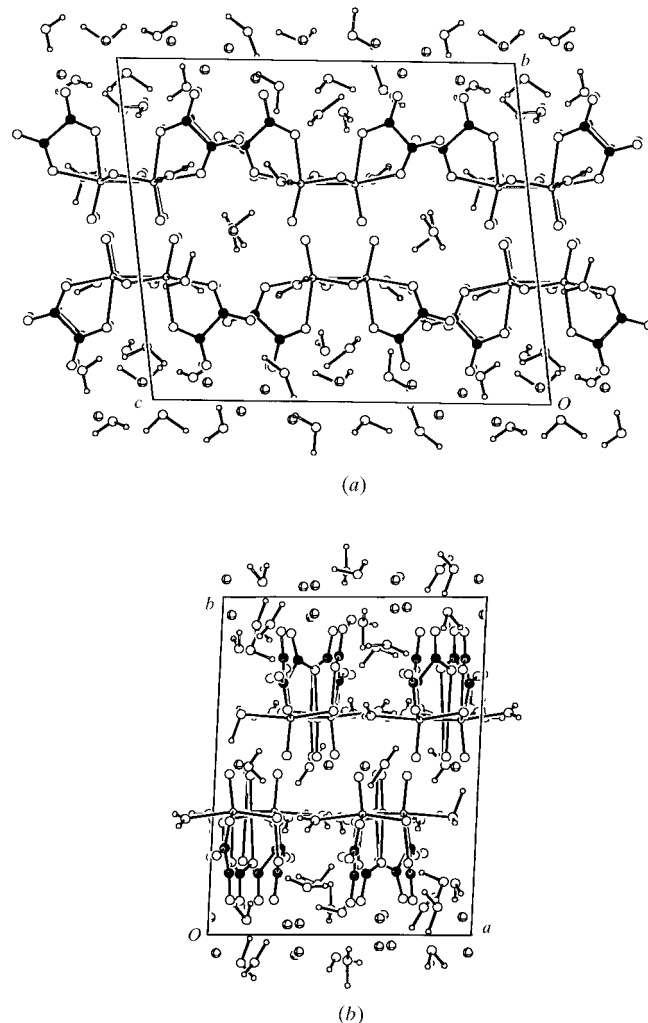

(a)

(b)

Figure 2
View of the unit cell of (I) along (a) the a axis and (b) the c axis.

each binuclear anion with local *C*2 symmetry (Fig. 1), two Mo atoms are coordinated in a distorted octahedral environment by one terminal oxo ligand, two bridging O atoms, two oxalato O atoms and one O atom from the water molecule. The Mo—O distances, as already observed, indicate their dependence upon their position in the structure, *i.e.* *cis* or *trans* to the terminal or bridging O atoms. Bond lengths to the terminal O atom (Mo—O_t) vary from 1.669 (5) to 1.688 (5) Å (average 1.678 Å), while bond lengths to the bridging O atoms (Mo—O_b) vary from 1.916 (5) to 1.958 (4) Å (average 1.938 Å). The Mo—$O_{oxalato}$ bond lengths *trans* to the terminal O atom, which range from 2.192 (5) to 2.250 (5) Å (average 2.227 Å), are significantly longer than the Mo—$O_{oxalato}$ bonds *cis* to the terminal O atom, which range from 2.132 (5) to 2.166 (5) Å (average 2.151 Å), thus showing the *trans* influence of the terminal oxo ligand. The bond lengths involving the O atoms of the water molecules range from 2.115 (5) to 2.185 (5) Å (average 2.144 Å). The Mo—Mo distances, which range from 2.5627 (9) to 2.5695 (10) Å, correspond to a single bond between metal atoms (Cotton, 1965, 1977). The coordination octahedra are significantly distorted, with the angles at the metal atoms ranging from 71.98 (19) to 109.6 (2)°.

The K^+ cations are irregularly and differently surrounded by 8–11 O atoms from the complex anions and water molecules at distances of between 2.608 (6) and 3.419 (7) Å. The K1 and K2 cations and water molecules O*W*2 and O*W*4 are positioned within the channel along the *a* axis which is formed by the terminal O atoms of anions facing each other (Fig. 2). The remaining cations and water molecules in the *ac* plane separate the layers of negatively charged anions. The distances listed in Table 2 show that all H atoms from the water molecules participate in O—H···O hydrogen bonding between binuclear anions and water molecules, thus additionally stabilizing the crystal structure.

Table 1
Selected geometric parameters (Å).

Mo11—O11	1.679 (5)	Mo31—O31	1.675 (5)
Mo11—O17	1.922 (5)	Mo31—O38	1.944 (5)
Mo11—O18	1.958 (4)	Mo31—O37	1.946 (5)
Mo11—O114	2.117 (5)	Mo31—O314	2.129 (5)
Mo11—O15	2.155 (5)	Mo31—O35	2.149 (5)
Mo11—O13	2.235 (5)	Mo31—O33	2.245 (5)
Mo11—Mo12	2.5686 (10)	Mo31—Mo32	2.5635 (10)
Mo12—O12	1.674 (5)	Mo32—O32	1.672 (5)
Mo12—O18	1.924 (5)	Mo32—O37	1.916 (5)
Mo12—O17	1.941 (5)	Mo32—O38	1.935 (5)
Mo12—O113	2.145 (4)	Mo32—O36	2.132 (5)
Mo12—O16	2.148 (5)	Mo32—O313	2.172 (5)
Mo12—O14	2.212 (5)	Mo32—O34	2.220 (5)
Mo21—O21	1.669 (5)	Mo41—O41	1.678 (5)
Mo21—O27	1.940 (5)	Mo41—O48	1.939 (5)
Mo21—O28	1.955 (4)	Mo41—O47	1.953 (5)
Mo21—O25	2.140 (5)	Mo41—O414	2.115 (5)
Mo21—O214	2.142 (5)	Mo41—O45	2.166 (5)
Mo21—O23	2.250 (5)	Mo41—O43	2.241 (5)
Mo21—Mo22	2.5627 (9)	Mo41—Mo42	2.5695 (10)
Mo22—O22	1.686 (5)	Mo42—O42	1.688 (5)
Mo22—O28	1.924 (5)	Mo42—O47	1.930 (4)
Mo22—O27	1.936 (4)	Mo42—O48	1.943 (4)
Mo22—O26	2.155 (5)	Mo42—O413	2.146 (5)
Mo22—O213	2.185 (5)	Mo42—O46	2.160 (5)
Mo22—O24	2.192 (5)	Mo42—O44	2.217 (5)

Experimental

The title complex was prepared from a mixture of Ba[Mo2O4-(C2O4)2(H2O)2]·3H2O (1.00 g; James & Wardlaw, 1928) and K2SO4 (0.25 g) dissolved in water (5 ml) and heated. The precipitated BaSO4 was filtered off and the resulting orange–red solution was left at room temperature. After two days, transparent red crystals of (I) were isolated.

Crystal data

K2[Mo2O4(C2O4)2(H2O)2]·3H2O	Z = 8
M_r = 600.20	D_x = 2.523 Mg m^{-3}
Triclinic, $P\bar{1}$	Mo *K*α radiation
a = 12.2683 (10) Å	Cell parameters from 30
b = 15.0622 (17) Å	reflections
c = 18.2824 (17) Å	θ = 8–17°
α = 81.818 (9)°	μ = 2.20 mm^{-1}
β = 71.050 (7)°	T = 293 (2) K
γ = 85.001 (9)°	Prism, red
V = 3159.7 (5) Å^3	0.30 × 0.27 × 0.25 mm

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O113—H11···O27	0.69	2.02	2.683 (6)	163
O113—H12···O310[i]	0.94	1.68	2.615 (7)	173
O114—H13···O311	0.86	1.72	2.566 (7)	165
O114—H14···O28[ii]	0.89	1.80	2.632 (7)	155
O213—H21···O17[iii]	0.77	1.98	2.740 (6)	170
O213—H22···O410[iv]	0.98	1.65	2.612 (7)	168
O214—H23···O412[iii]	0.90	1.72	2.610 (8)	170
O214—H24···O18	0.87	1.88	2.686 (6)	154
O313—H31···O48	0.95	2.04	2.692 (7)	124
O313—H31···O37	0.95	2.39	2.865 (7)	111
O313—H32···O41[v]	1.26	2.15	3.012 (8)	122
O314—H33···O47[iii]	0.85	1.80	2.616 (7)	160
O314—H34···O212[vi]	0.93	1.74	2.630 (7)	158
O413—H41···O110[ii]	0.81	1.81	2.589 (7)	164
O413—H42···O38[ii]	0.78	1.92	2.633 (6)	153
O414—H43···O111[vi]	0.75	1.87	2.598 (8)	163
O414—H44···O37	0.78	1.93	2.650 (7)	153
OW1—H1A···O23[vii]	1.20	2.02	2.912 (8)	128
OW1—H1A···O29[vii]	1.20	2.02	3.192 (8)	165
OW1—H1B···O24[vii]	1.03	2.15	2.913 (7)	129
OW1—H1B···O211[vii]	1.03	2.36	2.886 (8)	111
OW2—H2A···O46	0.93	2.44	3.025 (10)	121
OW2—H2B···O16[viii]	1.01	2.35	3.013 (9)	123
OW3—H3A···O311	1.12	1.76	2.775 (8)	149
OW3—H3B···O211[vii]	1.28	1.79	3.050 (8)	168
OW4—H4A···O26	1.11	2.06	2.921 (9)	132
OW4—H4A···O22	1.11	2.48	3.263 (10)	126
OW4—H4B···O15[ix]	1.19	2.34	3.472 (10)	158
OW5—H5A···O17[iii]	1.23	2.41	3.158 (8)	116
OW5—H5B···OW3[iii]	1.26	1.97	3.094 (10)	146
OW6—H6A···O23	0.93	2.09	3.011 (8)	173
OW6—H6B···O18	1.07	2.18	3.168 (8)	154
OW7—H7A···OW10	1.09	2.31	3.201 (15)	138
OW7—H7B···O44[iii]	1.05	2.26	3.092 (8)	135
OW8—H8A···OW11[x]	0.92	2.14	3.009 (14)	158
OW8—H8B···O411[iii]	1.11	2.08	3.145 (9)	161
OW9—H9A···O310[x]	1.11	1.95	2.786 (9)	129
OW9—H9B···O19	1.09	2.51	3.465 (11)	147
OW10—H10A···O110	0.92	2.11	2.883 (9)	141
OW10—H10B···OW7	1.10	2.52	3.201 (15)	120
OW11—H11A···OW8[x]	1.20	2.20	3.009 (14)	122
OW11—H11A···O43	1.20	2.39	3.074 (10)	113
OW11—H11B···OW12[ii]	1.09	2.47	3.316 (13)	133
OW12—H12A···O411[x]	1.02	1.95	2.788 (12)	137
OW12—H12A···O44[x]	1.02	2.23	3.054 (10)	137
OW12—H12B···O43[x]	1.25	1.93	2.975 (11)	137
OW12—H12B···O49[x]	1.25	2.03	3.124 (12)	143

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 + x, y, z$; (iii) $x - 1, y, z$; (iv) $x - 1, y, z - 1$; (v) $2 - x, 1 - y, 2 - z$; (vi) $x, y, 1 + z$; (vii) $1 - x, -y, 1 - z$; (viii) $2 - x, 1 - y, 1 - z$; (ix) $1 - x, 1 - y, 1 - z$; (x) $1 - x, -y, 2 - z$.

Data collection

Philips PW1100 diffractometer updated by Stoe	$h = -16 \rightarrow 17$
	$k = -20 \rightarrow 21$
ω/θ scans	$l = 0 \rightarrow 25$
18 345 measured reflections	3 standard reflections
18 254 independent reflections	frequency: 90 min
7507 reflections with $I > 2\sigma(I)$	intensity decay: 24.2%
$\theta_{max} = 30.1°$	

Refinement

Refinement on F^2	H-atom parameters not refined
$R(F) = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.934$	$(\Delta/\sigma)_{max} = 0.003$
18 254 reflections	$\Delta\rho_{max} = 1.51$ e Å^{-3}
907 parameters	$\Delta\rho_{min} = -1.14$ e Å^{-3}

The crystal chosen for data collection, which was stable in air, slowly decomposed in the X-ray beam, so data were corrected for decay (24%). 83 reflections with $\Delta/\sigma > 5$ were excluded from the final stages of refinement. The highest residual peak in the difference Fourier map was located 1.39 Å from Mo42 and 0.79 Å from O48.

Data collection: *STADI*4 (Stoe & Cie, 1996); cell refinement: *STADI*4; data reduction: *XRED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON* (Spek, 1982) and *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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