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Hexapotassium μ -Oxo-bis[(citrate)-dioxomolybdenum] Dihydrate

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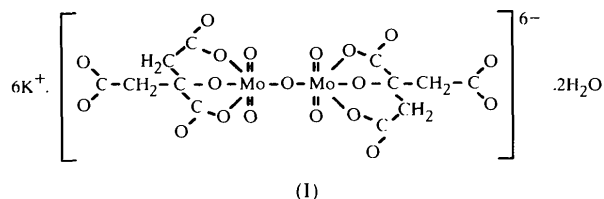
Abstract

In the title compound, hexapotassium μ -oxo-bis{dioxo[2-hydroxy- κ O-1,2,3-propanetricarboxylato(4-)- κ^2 O¹,O²]molybdenum(VI)} dihydrate, $K_6\{[MoO_2(C_6H_4O_7)]_2\} \cdot 2H_2O$, the citrate, as a tridentate ligand, is coordinated to molybdenum through the deprotonated hydroxy group, the α -carboxylate group and also through one β -carboxylate group. The coordination polyhedron of the Mo atom is distorted octahedral, containing one $[Mo_2O_5]^{2+}$ core. Principal dimensions are: Mo—O_r = 1.715 (av), Mo—O_b = 1.915 (2), Mo—O_{hydroxy} = 1.952 (3), Mo—O _{α -carboxy} = 2.216 (4), Mo—O _{β -carboxy} = 2.261 (4) Å and Mo—O_b—Mo = 137.1 (4)°.

Comment

There is at present a growing interest in the chemistry of the coordination compounds of molybdenum,

particularly because of their possible relationship to redox-active molybdoenzymes (Chan *et al.*, 1993; Russ, 1996). However, structural studies on oxomolybdenum complexes containing a citrate ligand are rare. One complex, $K_2Na_4[(MoO_2)_2O(cit)_2] \cdot 5H_2O$ (cit = citrate), has been structurally characterized by X-ray diffraction (Zhou *et al.*, 1997), and the title complex, (I), was considered to be isomorphous with this and to have the same coordination mode. Structure analysis shows that the dimeric anion of (I) consists of the common oxo-bridged $[Mo_2O_5]^{2+}$ entity, which is non-centrosymmetric. Each Mo atom is six-coordinate,



with approximately octahedral geometry. The terminal and bridging oxo groups adopt a *fac* stereochemistry. Other coordination positions are occupied by a fully deprotonated tridentate citrate ligand, which forms both five-membered and six-membered chelate rings. The O1—Mo1—O5 and O1—Mo1—O6 bond angles are 73.86 (13) and 79.68 (14)°, respectively. A comparison of the title compound with two related compounds, namely, $K_2Na_4[(MoO_2)_2O(cit)_2] \cdot 5H_2O$ (Zhou *et al.*, 1997) and $Na_6[W_2O_5(cit)_2] \cdot 10H_2O$ (Llopis *et al.*, 1993), indicates that both reported structures, as well as the present one, have almost the same structural features. The corresponding bond distances and angles to *M* (*M* = Mo or W) are similar, except for the *M*—O _{β -carboxy} distance and the *M*—O_b—*M* angle of the title compound being different to those of $Na_6[W_2O_5(cit)_2] \cdot 10H_2O$ (Llopis *et al.*, 1993) {*M*—O _{β -carboxy} = 2.261 (4) Å and *M*—O_b—*M* = 137.1 (4)° for (I), and 2.289 (2) Å and 180° for $Na_6[W_2O_5(cit)_2] \cdot 10H_2O$ }.

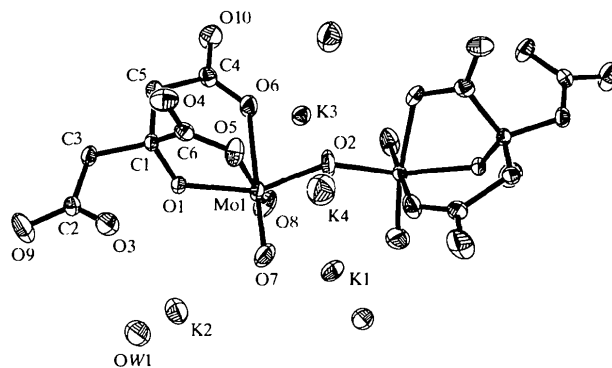


Fig. 1. A view of the title complex showing displacement ellipsoids drawn at the 50% probability level and the atom-labelling scheme.

Experimental

The title compound was obtained as light-yellow prismatic crystals from a reaction system of $(\text{NH}_4)_2\text{MoS}_4^{2-}$ and $\text{K}_3\text{cit}\cdot\text{H}_2\text{O}$ (molar ratio 1:2), which was used in an attempt to prepare an S-bridging Mo-citrate compound. The starting materials were reacted, in solution in a mixture of water and MeOH, at room temperature under a nitrogen atmosphere.

Crystal data

$\text{K}_6[\text{Mo}_2\text{O}_5(\text{C}_6\text{H}_4\text{O}_7)_2]\cdot 2\text{H}_2\text{O}$
 $M_r = 918.70$
 Monoclinic
 $C2/c$
 $a = 10.167(2) \text{ \AA}$
 $b = 14.499(3) \text{ \AA}$
 $c = 17.860(4) \text{ \AA}$
 $\beta = 92.50(3)^\circ$
 $V = 2630.3(9) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.160 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 50 reflections
 $\theta = 4.78\text{--}12.52^\circ$
 $\mu = 1 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism
 $0.40 \times 0.12 \times 0.10 \text{ mm}$
 Light yellow

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: empirical via ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.610$, $T_{\max} = 0.905$
 3316 measured reflections
 2566 independent reflections
 2191 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 27.99^\circ$
 $h = -1 \rightarrow 8$
 $k = -1 \rightarrow 19$
 $l = -23 \rightarrow 23$
 3 standard reflections every 97 reflections
 intensity decay: 5.51%

Refinement

Refinement on F^2
 $R(F) = 0.040$
 $wR(F^2) = 0.102$
 $S = 1.103$
 2565 reflections
 187 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 21.2206P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.747 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.217 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Mo1	0.36547 (5)	0.24026 (3)	0.31071 (2)	0.0197 (2)
K1	1/2	0.48002 (11)	1/4	0.0332 (4)
K2	0	0.26369 (12)	1/4	0.0348 (4)
K3	0.70099 (13)	0.31232 (8)	0.41658 (6)	0.0279 (3)
K4	0.3070 (2)	0.06365 (12)	0.15294 (8)	0.0530 (4)
O1	0.2420 (4)	0.2227 (2)	0.3902 (2)	0.0196 (7)
O2	1/2	0.1919 (4)	1/4	0.0367 (14)
O3	-0.0276 (4)	0.1186 (3)	0.3414 (2)	0.0303 (9)
O4	0.2070 (4)	-0.0177 (2)	0.3650 (2)	0.0312 (9)
O5	0.2967 (4)	0.0956 (3)	0.3011 (2)	0.0300 (9)

O6	0.4981 (4)	0.1704 (3)	0.3984 (2)	0.0295 (9)
O7	0.2607 (5)	0.2760 (3)	0.2390 (2)	0.0411 (11)
O8	0.4350 (5)	0.3417 (3)	0.3428 (2)	0.0411 (11)
O9	-0.1322 (4)	0.1582 (4)	0.4419 (2)	0.0423 (11)
O10	0.5650 (4)	0.1190 (3)	0.5094 (2)	0.0422 (11)
OW1	-0.0048 (5)	0.4225 (3)	0.3456 (2)	0.0459 (11)
C1	0.2253 (5)	0.1338 (3)	0.4216 (2)	0.0173 (10)
C2	-0.0309 (5)	0.1359 (3)	0.4100 (3)	0.0204 (11)
C3	0.0940 (5)	0.1262 (3)	0.4591 (2)	0.0219 (11)
C4	0.4747 (6)	0.1369 (4)	0.4625 (3)	0.0243 (12)
C5	0.3358 (5)	0.1154 (3)	0.4824 (2)	0.0215 (11)
C6	0.2395 (5)	0.0633 (3)	0.3579 (3)	0.0214 (11)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo1—O7	1.710 (4)	O1—C1	1.419 (5)
Mo1—O8	1.719 (4)	O2—Mo1 ⁱ	1.915 (2)
Mo1—O2	1.915 (2)	O3—C2	1.252 (6)
Mo1—O1	1.952 (3)	O4—C6	1.229 (6)
Mo1—O5	2.216 (4)	O5—C6	1.280 (6)
Mo1—O6	2.261 (4)	O6—C4	1.276 (6)
O7—Mo1—O8	102.9 (2)	O1—Mo1—O5	73.86 (13)
O7—Mo1—O2	97.1 (2)	O1—Mo1—O6	79.68 (14)
O8—Mo1—O1	97.9 (2)	Mo1—O2—Mo1 ⁱⁱ	137.1 (4)
O2—Mo1—O1	149.5 (2)		

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. Non-H atoms were refined anisotropically to convergence. The citrate H atoms were treated using a riding model.

Data collection: *P4 Diffractometer Control Program* (Siemens, 1994a). Cell refinement: *P4 Diffractometer Control Program* and *XSCANS* (Siemens, 1994b). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1274). Services for accessing these data are described at the back of the journal.

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