Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Redetermination of dipotassium μ-oxo-bis[aqua(oxalato-κ^2O,O')dioxomolybdate(VI)] at 150 K

Luís Cunha-Silva, Bernardo Monteiro, Martyn Pillinger, Isabel S. Gonçalves, João Rocha and Filipe A. Almeida Paz*

Department of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal

Correspondence e-mail: fpaz@dq.ua.pt

Received 11 December 2006
Accepted 22 December 2006

Key indicators

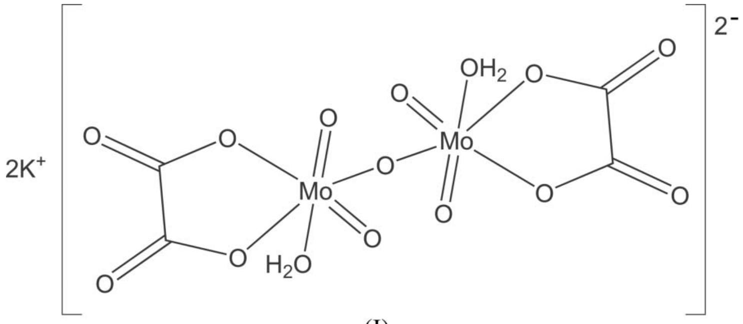
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.020
wR factor = 0.064
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of title compound, $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$, originally determined by Cotton, Morehouse & Wood [(1964). *Inorg. Chem.* pp. 1603–1608], has been redetermined to higher precision and the hydrogen-bonding network elucidated. The anionic $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ complex ion is centrosymmetric with the μ_2-bridging O atom located at the inversion centre.

Comment

Dioxomolybdenum(VI) complexes represent an important class of catalysts or catalyst precursors for O-atom transfer reactions in chemical and biological systems (Kühn *et al.*, 2002, and references therein). In particular, molybdenum(VI) forms a variety of binuclear dioxomolybdenum(VI) oxalate complexes (Modec *et al.*, 2005, and references therein). The structure of $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ was first reported by Cotton *et al.* (1964), but no H-atom positions were established. Later, Cindrić *et al.* (2000) described the isostructural $A_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ (A = Rb^+ and NH_4^+). As part of our ongoing research into these types of compounds, we now report the synthesis and structure of the title compound, (I), which is isostructural with its rubidium and ammonium analogues. Cindrić *et al.* (2000) described their structures in the non-standard space group $P2_1/a$, with the a and c unit-cell parameters switched compared to (I).



(I)

Compound (I) contains a dimeric dioxomolybdenum(VI) oxalate complex anion, $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$, composed of two Mo^{VI} centres, in a distorted octahedral coordination geometry, and connected *via* a μ_2-bridging O atom (O2). Since this atom lies at a crystallographic centre of inversion, the asymmetric unit is composed of only half of the anionic complex plus one K^+ cation, as depicted in Fig. 1. Moreover, this linear Mo1—O2—Mo1^i [symmetry code: (i) $1 - x$, $-y$, $2 - z$] oxo bridge has an Mo1···Mo1^i separation of 3.7544 (3) Å. The MoO_6 coordination environment is signifi-

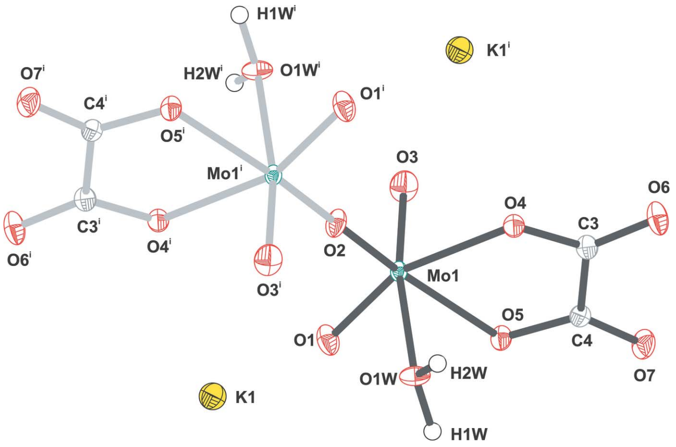


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $1 - x$, $-y$, $2 - z$.]

cantly distorted, with the *cis* and *trans* O—Mo—O angles found within the ranges 74.39 (8)–104.30 (12)° and 155.00 (6)–169.61 (10)°, respectively. The longer Mo—O distances are those involving the water molecule O1*W* and the Mo—O$_{oxalate}$ bonds (Table 1) as a consequence of the strong *trans* influence of the two short, formal, Mo=O bonds.

In the crystal structure, neighbouring complex anions interact through a series of rather strong and highly directional O—H···O hydrogen bonds between coordinated water molecules and O5 and O6 (belonging to adjacent complexes) (Fig. 2*a*; Table 2). This leads to a three-dimensional hydrogen-bonded network exhibiting channels running parallel to the crystallographic *c* axis, which are occupied by the 10-coordinate potassium cations (Fig. 2*b*).

Experimental

Molybdenum(VI) oxide (2.93 g; 20 mmol) was refluxed with oxalic acid (2.52 g, 20 mmol) and KCl (1.50 g, 20 mmol) in water (approximately 20 cm^3) for five hours. The resulting solution was then filtered and evaporated to dryness under reduced pressure. Suitable crystals of (I) for X-ray structure analysis were grown by slow evaporation of an aqueous solution. Yield 4.83 g (86%). Analysis

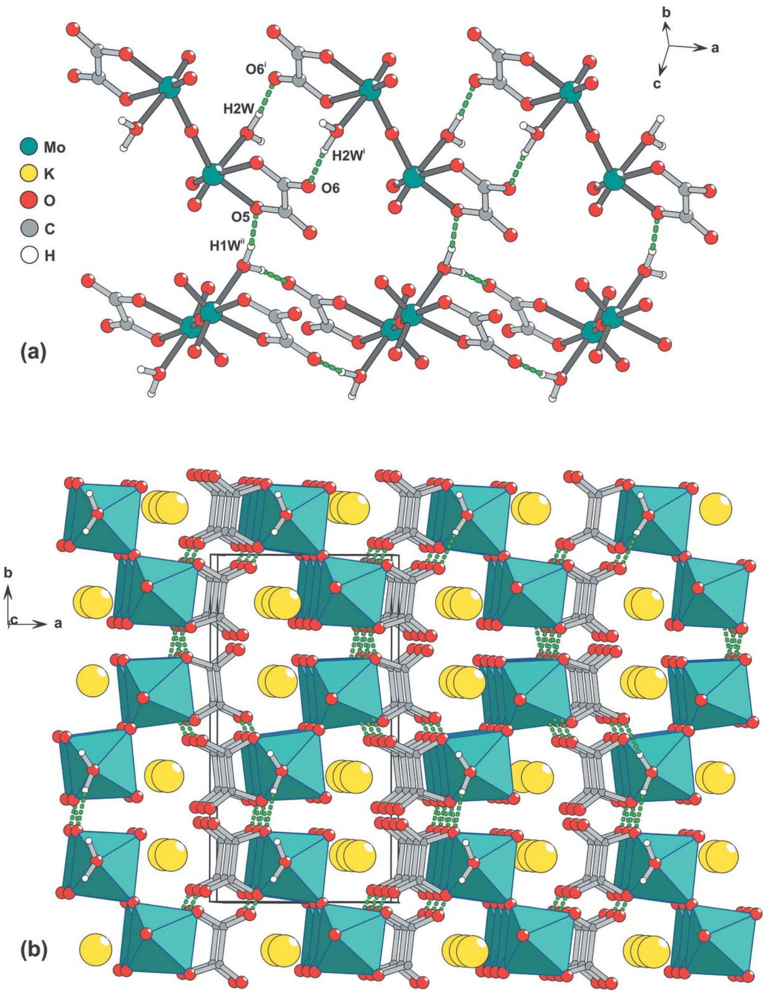


Figure 2
(*a*) Schematic representation showing the O—H···O hydrogen-bonding interactions (dashed lines) connecting adjacent $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ anions. (*b*) Crystal packing arrangement viewed along the [001] direction, with the $\{Mo_2O_6\}$ cores represented as octahedra and the O—H···O hydrogen bonds as dashed green lines. For hydrogen bonding geometry see Table 2. [Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

Acta Cryst. (2007). E**63**, m376–m378 Cunha-Silva *et al.* • $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ **m377**

calculated for $C_4H_4K_2Mo_2O_{15}$ (562.14): C 8.55, H 0.72%; found: C 8.31, H 0.50%. Selected FT–IR (KBr, cm^{-1}): 3286 (*br*), 1729 (*vs*), 1675 [(*vs*), $\nu(-CO_2)_{asym}$], 1401 (*vs*), 1240 [(*s*), $\nu(-CO_2)_{sym}$], 960 [(*vs*), $\nu(Mo{=}O)_{sym}$], 921 [(*vs*), $\nu(Mo{=}O)_{asym}$], 854 [(*vs*), (Mo—O—Mo)], 802 [(*vs*), (Mo—O—Mo)].

Crystal data

$K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$
$M_r = 562.15$
Monoclinic, $P2_1/c$
$a = 7.4774$ (2) Å
$b = 14.2242$ (3) Å
$c = 6.5726$ (1) Å
$\beta = 94.284$ (1)°
$V = 697.11$ (3) Å^3

$Z = 2$
$D_x = 2.678$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.48$ mm^{-1}
$T = 150$ (2) K
Prism, colourless
0.40 × 0.27 × 0.20 mm

Data collection

Bruker X8 APEX-II diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.420$, $T_{max} = 0.612$

28523 measured reflections
1582 independent reflections
1566 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.064$
$S = 1.23$
1582 reflections
112 parameters
Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 2.2974P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -1.07$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mo1—O1	1.703 (2)	K1—O6^{iii}	2.818 (2)
Mo1—O2	1.8772 (2)	K1—O7^{iv}	2.860 (2)
Mo1—O3	1.692 (2)	K1—O7^{iii}	2.864 (2)
Mo1—O4	2.184 (2)	K1—O4^{v}	2.887 (2)
Mo1—O5	2.083 (2)	K1—O1	2.930 (2)
Mo1—O1*W*	2.260 (2)	K1—O1*W*	3.162 (3)
K1—O1^{i}	2.733 (2)	K1—O2	3.3036 (7)
K1—O3^{ii}	2.758 (2)	K1—O3^{v}	3.381 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O5^{i}	0.95 (3)	1.784 (11)	2.720 (3)	170 (3)
O1*W*—H2*W*···O6^{vi}	0.95 (3)	1.73 (3)	2.676 (3)	170 (3)

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

The H atoms were located in difference maps and refined with O—H and H···H distances restrained to 0.95 (1) and 1.55 (1) Å, respectively, and $U_{iso}(H) = 1.5U_{eq}(O)$. The deepest residual electron density hole is 0.38 Å from K1.

Data collection: *SMART* (Bruker 2001); cell refinement: *SAINT* (Bruker 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker 2001); program(s) used to refine structure: *SHELXTL* (Bruker 2001); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL*.

We are grateful to Fundação para a Ciência e Tecnologia (FCT, Portugal) for their general financial support under the POCI programme (supported by FEDER) and for the grants SFRH/BPD/14410/2003 and SFRH/BD/24717/2005 (to LCS and BM, respectively).

References

Brandenburg, K. (2006). *DIAMOND*. Version 3.1d. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SHELXTL*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cindrić, M., Strukan, N., Vrdoljak, V., Devčić, M., Veksli, Z. & Kamenar, B. (2000). *Inorg. Chim. Acta*, **304**, 260–267.
Cotton, F. A., Morehouse, S. M. & Wood, J. S. (1964). *Inorg. Chem.* **3**, 1603–1608.
Kühn, F. E., Groarke, M., Bencze, É., Herdtweck, E., Prazeres, A., Santos, A. M., Calhorda, M. J., Romão, C. C., Gonçalves, I. S., Lopes, A. D. & Pillinger, M. (2002). *Chem. Eur. J.* **8**, 2370–2383.
Modec, B., Brenčič, J. V. & Koller, J. (2005). *Eur. J. Inorg. Chem.* pp. 1611–1620.
Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.

m378 Cunha-Silva *et al.* • $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ *Acta Cryst.* (2007). E**63**, m376–m378