Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

$(C_6H_{16}N_2)_2[Mo_8O_{26}]$: a new *β*-octamolybdate salt

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Received 10 March 2005
Accepted 15 March 2005
Online 25 March 2005

Crystals of the title compound, 2,5-dimethylpiperazinediium *β*-octamolybdate, were grown under mild hydrothermal conditions. The anion and cations lie on inversion centers. A network of N—H···O bonds helps to stabilize the crystal packing.

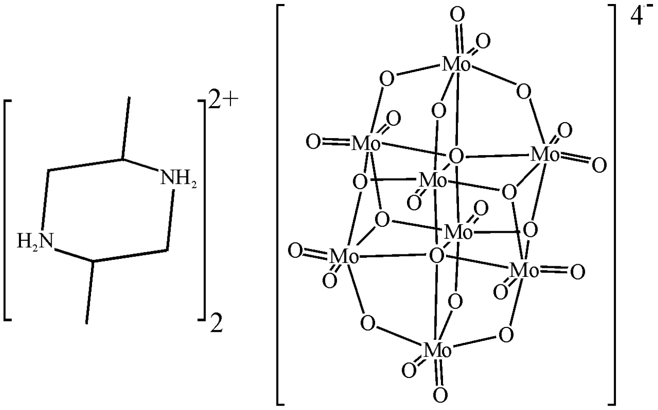
Key indicators

Single-crystal X-ray study
T = 153 K
Mean *σ*(C–C) = 0.014 Å
R factor = 0.043
wR factor = 0.095
Data-to-parameter ratio = 12.4

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

Comment

Interest in octamolybdate anions has spanned several decades, from the initial report of Lindqvist (1950) to more recent times (Yan *et al.*, 2003). The octamolybdate anion can adopt several structures, with the *α* (Hsieh *et al.*, 1987), *β* (Harrison *et al.*, 1993), *δ* (Rarig & Zubieta, 2001) and *γ* (Niven *et al.*, 1991) forms being the most common. The continued interest in such compounds has stemmed from their diversity and ability to interconvert (Wang *et al.*, 1993). Our interest in these materials is focused upon molybdate reactions in the presence of concentrated sulfuric acid, and the associated structural effects.



(I)

The *β*-octamolybdate anions present in the title compound, (I) (Fig. 1), are similar to previously reported species. Four crystallographically distinct molybdenum centers are observed and the complete anion is generated by inversion symmetry. Each Mo^{6+} cation resides near to the center of a coordination octahedron. Distinct distortions from the centers of these octahedra are observed, a result of the second-order Jahn–Teller activity of Mo^{6+} (Pearson, 1969; Wheeler *et al.*, 1986; Kunz & Brown, 1995; Halasyamani, 2004). Both bridging (O_b) and terminal (O_t) oxide ions are observed. The Mo—O_t bonds [1.690 (6)–1.720 (6) Å] are shorter than the Mo—O_b bonds [1.760 (6)–2.460 (6) Å] (Table 1). Eight $[MoO_6]$ octahedra share both edges and vertices, forming the well known *β*-octamolybdate anion.

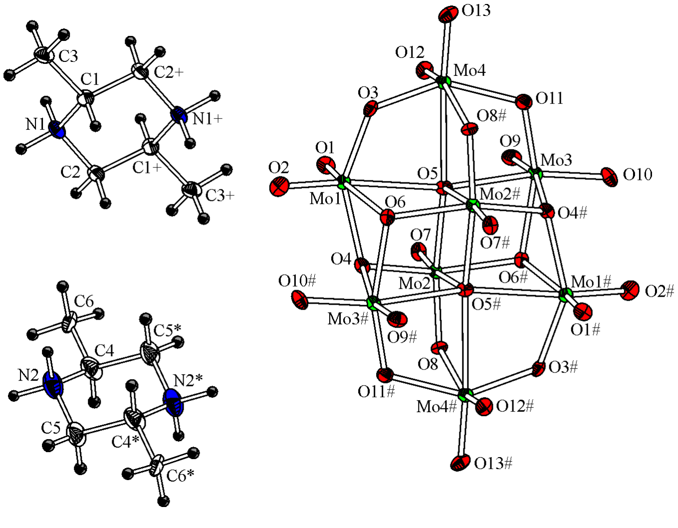


Figure 1
View of (I), showing 50% displacement ellipsoids (abritrary spheres for the H atoms). Atoms labeled with the suffixes hash (#), plus (+) and asterisk (*) are generated by the symmetry codes $(-x, -y, 2-z)$, $(-x-1, -y, 2-z)$ and $(-x, -y-1, 2-z)$, respectively.

The three-dimensional structure of (I) consists of the $[Mo_8O_{26}]^{4-}$ anions and 2,5-dimethylpiperazinediium cations. There are two distinct cations, both generated by inversion symmetry from the atoms of the respective asymmetric unit (Fig. 1). The $[Mo_8O_{26}]^{4-}$ anions are arranged in a pseudo-body-centered geometry, with anions centered at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, as shown in Fig. 2. The $C_6H_{16}N_2^{2+}$ cations reside between anions and interact with them by way of N—H···O hydrogen bonds (Table 2).

Experimental

Compound (I) was synthesized through the addition of MoO_3 (0.492 g, 3.418×10^{-3} mol), H_2SO_4 (0.088 g, 8.98×10^{-3} mol), 2,5-dimethylpiperazine (0.143 g, 1.25×10^{-3} mol) and deionized water (0.994 g, 5.52×10^{-2} mol) to a 23 ml Teflon-lined pressure vessel. The reaction gel was heated at 453 K for 24 h, and then cooled slowly to room temperature over an additional 24 h. Crystals of (I) were recovered by filtration.

Crystal data

$(C_6H_{16}N_2)_2[Mo_8O_{26}]$
$M_r = 1415.92$
Monoclinic, $P2_1/n$
$a = 11.0450\ (11)$ Å
$b = 12.3699\ (11)$ Å
$c = 13.0539\ (15)$ Å
$\beta = 113.148\ (10)^\circ$
$V = 1639.9\ (3)$ Å^3
$Z = 2$

$D_x = 2.867$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3088 reflections
$\theta = 3.9$–33.3°
$\mu = 3.06$ mm^{-1}
$T = 153\ (2)$ K
Plate, colorless
$0.09 \times 0.08 \times 0.02$ mm

Data collection

Oxford Diffraction CrysAlis CCD diffractometer
ω scans
Absorption correction: analytical (multifaceted crystal model; Clark & Reid, 1995)
$T_{min} = 0.636$, $T_{max} = 0.862$
14643 measured reflections

5519 independent reflections
2797 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 33.4^\circ$
$h = -15 \rightarrow 16$
$k = -16 \rightarrow 18$
$l = -19 \rightarrow 18$

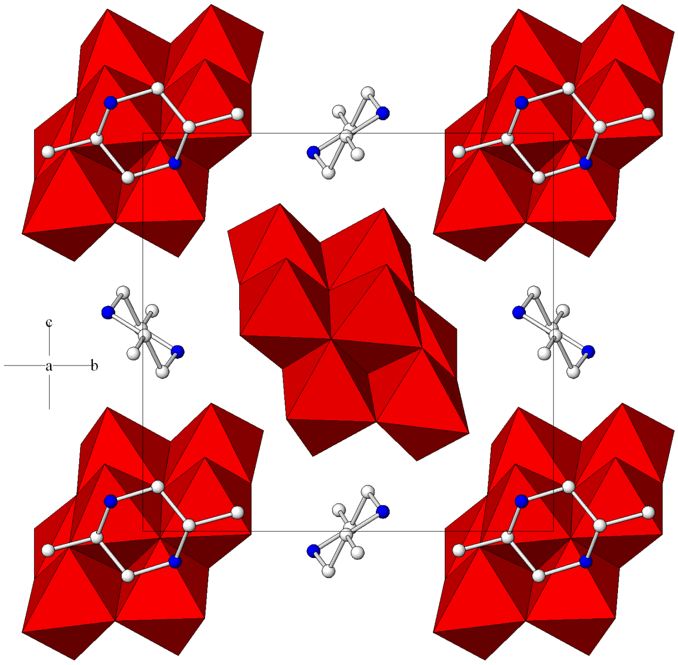


Figure 2
Packing in the unit cell of (I), with the $[Mo_8O_{26}]^{4-}$ anions shown in polyhedral representation. H atoms have been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.095$
$S = 0.85$
2797 reflections
226 parameters
H-atom parameters constrained

Robust weighting scheme (Prince, 1982) fitted by a five-term Chebychev polynomial (Watkin, 1994) with coefficients 12.6, 20.2, 12.3, 5.21 and 1.63
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.41$ e Å^{-3}
$\Delta\rho_{min} = -1.35$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mo1—O1	1.708 (6)	Mo3—O4^i	2.360 (5)
Mo1—O2	1.700 (6)	Mo3—O5	2.301 (6)
Mo1—O3	1.922 (6)	Mo3—O6^i	2.016 (6)
Mo1—O4	2.001 (6)	Mo3—O9	1.712 (6)
Mo1—O5	2.346 (6)	Mo3—O10	1.702 (6)
Mo1—O6	2.347 (6)	Mo3—O11	1.919 (6)
Mo2—O4	1.940 (6)	Mo4—O3	1.897 (6)
Mo2—O5	2.134 (6)	Mo4—O5	2.460 (6)
Mo2—O5^i	2.371 (5)	Mo4—O8^i	2.282 (5)
Mo2—O6^i	1.986 (6)	Mo4—O11	1.929 (6)
Mo2—O7	1.690 (6)	Mo4—O12	1.702 (6)
Mo2—O8	1.760 (6)	Mo4—O13	1.720 (6)

Symmetry code: (i) $-x, -y, 2-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O13^{ii}	1.01	1.83	2.783 (9)	156
N1—H2···O6	1.00	1.92	2.871 (9)	158
N2—H9···O11^i	1.00	1.96	2.929 (11)	164
N2—H10···O12^{iii}	1.02	1.92	2.882 (10)	156

Symmetry codes: (i) $-x, -y, 2-z$; (ii) $-\frac{1}{2}-x, y-\frac{1}{2}, \frac{5}{2}-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{5}{2}-z$.

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H atoms were placed geometrically after each cycle in idealized locations and refined as riding on their carrier atoms. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) was applied in all cases. The highest peak is 1.13 Å from atom N2 and the deepest hole is 1.30 Å from O5.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2002); software used to prepare material for publication: *CRYSTALS*.

The authors acknowledge support from the the Camille and Henry Dreyfus Foundation.

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