metal-organic papers

Tetrakis[4-amino-N-(2-hydroxyethyl)-pyridinium] hexacosaoxooctamolybdate

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The title compound, $(C_7H_{11}N_2O)_4[Mo_8O_{26}]$, was synthesized by hydrothermal reaction of an acidified aqueous solution of $Na_2Mo_2O_4 \cdot 2H_2O$, N-(2-hydroxyethyl)-4-aminopyridine sulfate and $Zn(CH_3COO)_2 \cdot 4H_2O$. Single X-ray crystal analysis reveals that the structure of the title compound consists of a centrosymmetric β-octamolybdate anion and N-(2-hydroxy-ethyl)-4-aminopyridinium cations. The Mo—O bond lengths are in the range 1.687 (4)–1.708 (4) Å for terminal Mo—O bonds and 1.759 (4)–2.437 (4) Å for the Mo—O bonds shared by two or more neighboring $\{MoO_6\}$ octahedra. The O—H···O hydrogen-bond lengths are 2.677 (8)–2.804 (8) Å, and the N—H···N hydrogen-bond lengths are 2.905 (8)–3.033 (7) Å.

Comment

In the past few decades, a series of octamolybdates, $[Mo_8O_{26}]^{4-}$, has been reported in the literature. At the same time, there has been much research (Day *et al.*, 1977; Hagrman *et al.*, 1999; Lindqvist, 1950; Pope, 1983; Rarig & Zubieta, 2001; Xi *et al.*, 1994; Xu *et al.*, 1999) on the structures of $[Mo_8O_{26}]^{4-}$ isomers, showing that there are several types of octamolybdate structures, *viz.* the α-, β-, γ-, ξ- and the ε-, α-γ-, β-γ- forms, *etc.* The various structural patterns of octamolybdates have aroused considerable interest over recent years. As part of our research on the synthesis of heterometallic polymers, the title compound, (I), was obtained as single crystals.
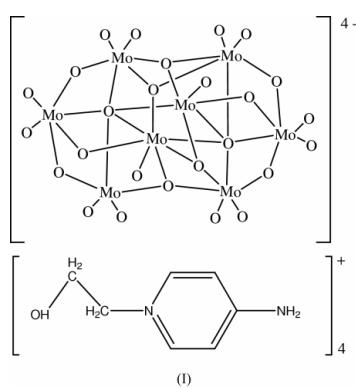
As shown in Fig. 1, the octamolybdate anion is constructed of eight edge-shared $\{MoO_6\}$ octahedra. It can also be described as two centrosymmetrically related cyclic $\{Mo_4O_{13}\}$ units cross-linked by bridging O atoms. In each $\{MoO_6\}$ octahedron, the Mo—O bond lengths vary from 1.687 (4) to 2.437 (4) Å and the O—Mo—O angles involving neighboring O atoms from 71.4 (1) to 105.2 (2)°, which means that the $\{MoO_6\}$ octahedron is distorted. According to the coordinating mode, the O atoms in the anion can be divided into four different groups (Wu *et al.*, 2001), *viz.* terminal O atoms
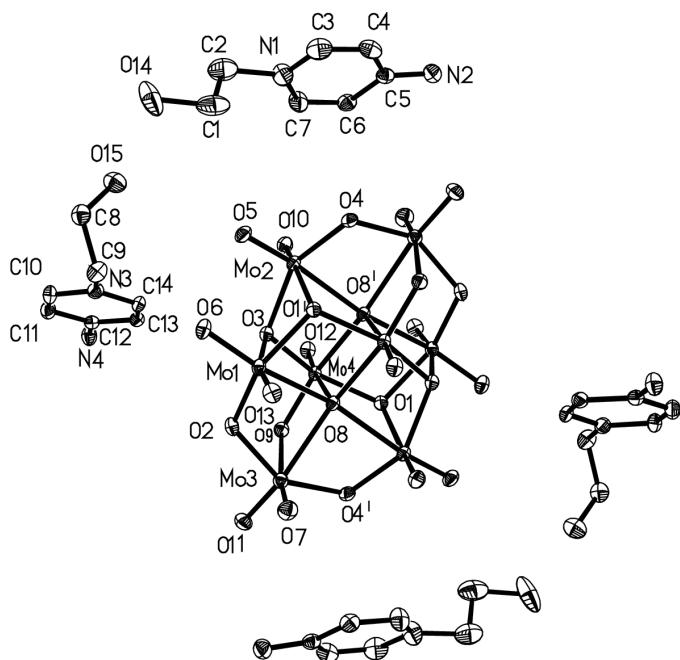
Figure 1

A perspective view of (I). Displacement ellipsoids are drawn at the 30% probability level. For clarity, H atoms are omitted. [Symmetry code: (i) $2 - x, 2 - y, -1 - z$.]
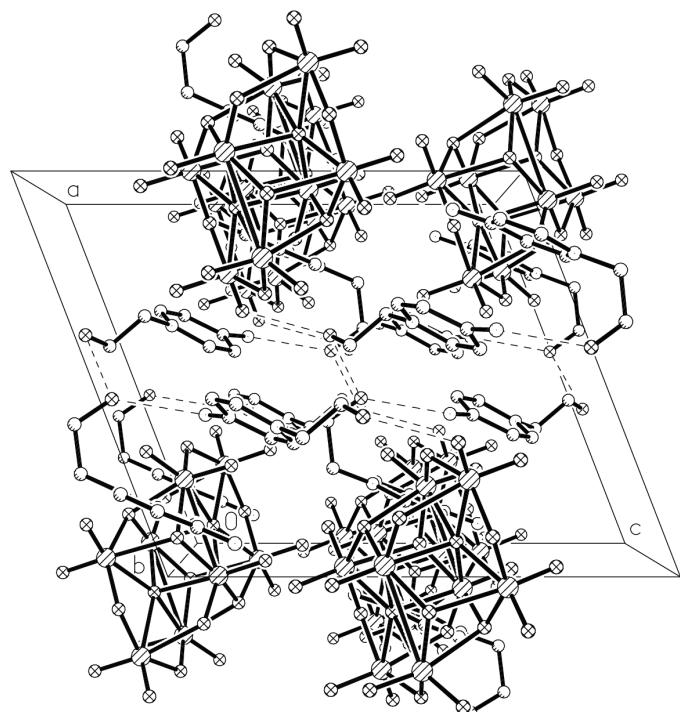
Figure 2

Cell packing diagram, viewed down the *b* axis. Hydrogen bonding is indicated by dashed lines. For clarity, H atoms are omitted.

Table 1
Selected geometric parameters (Å, °).

Mo1—O6	1.687 (4)	Mo3—O7	1.696 (5)
Mo1—O13	1.708 (4)	Mo3—O11	1.705 (4)
Mo1—O2	1.904 (4)	Mo3—O4^i	1.916 (4)
Mo1—O1^i	1.996 (4)	Mo3—O2	1.931 (4)
Mo1—O8	2.321 (4)	Mo3—O9	2.309 (4)
Mo1—O3	2.386 (4)	Mo3—O8	2.437 (4)
Mo2—O10	1.704 (4)	Mo4—O12	1.687 (4)
Mo2—O5	1.706 (4)	Mo4—O9	1.758 (4)
Mo2—O4	1.901 (4)	Mo4—O3	1.948 (4)
Mo2—O3	1.995 (4)	Mo4—O1	1.956 (4)
Mo2—O8^i	2.311 (4)	Mo4—O8^i	2.187 (4)
Mo2—O1^i	2.369 (4)	Mo4—O8	2.413 (4)
O6—Mo1—O13	105.2 (2)	O7—Mo3—O11	104.8 (2)
O6—Mo1—O2	101.9 (2)	O7—Mo3—O4^i	99.7 (2)
O13—Mo1—O2	103.0 (2)	O11—Mo3—O4^i	102.3 (2)
O6—Mo1—O1^i	98.8 (2)	O7—Mo3—O2	98.4 (2)
O13—Mo1—O1^i	97.4 (2)	O11—Mo3—O2	102.3 (2)
O2—Mo1—O1^i	145.9 (2)	O4^i—Mo3—O2	144.5 (2)
O6—Mo1—O8	159.7 (2)	O7—Mo3—O9	168.0 (2)
O13—Mo1—O8	94.7 (2)	O11—Mo3—O9	87.2 (2)
O2—Mo1—O8	77.2 (2)	O4^i—Mo3—O9	78.2 (2)
O1^i—Mo1—O8	74.1 (1)	O2—Mo3—O9	77.9 (2)
O6—Mo1—O3	87.8 (2)	O7—Mo3—O8	97.2 (2)
O13—Mo1—O3	164.3 (2)	O11—Mo3—O8	158.0 (2)
O2—Mo1—O3	82.5 (2)	O4^i—Mo3—O8	73.8 (2)
O1^i—Mo1—O3	71.4 (1)	O2—Mo3—O8	73.9 (2)
O8—Mo1—O3	72.0 (1)	O9—Mo3—O8	70.8 (1)
O10—Mo2—O5	103.6 (2)	O12—Mo4—O9	104.7 (2)
O10—Mo2—O4	101.9 (2)	O12—Mo4—O3	102.5 (2)
O5—Mo2—O4	101.0 (2)	O9—Mo4—O3	97.6 (2)
O10—Mo2—O3	97.9 (2)	O12—Mo4—O1	100.6 (2)
O5—Mo2—O3	99.8 (2)	O9—Mo4—O1	96.4 (2)
O4—Mo2—O3	146.9 (2)	O3—Mo4—O1	148.8 (2)
O10—Mo2—O8^i	96.6 (2)	O12—Mo4—O8^i	98.3 (2)
O5—Mo2—O8^i	159.6 (2)	O9—Mo4—O8^i	156.9 (2)
O4—Mo2—O8^i	77.1 (2)	O3—Mo4—O8^i	78.2 (2)
O3—Mo2—O8^i	74.4 (2)	O1—Mo4—O8^i	78.0 (2)
O10—Mo2—O1^i	166.0 (2)	O12—Mo4—O8	174.2 (2)
O5—Mo2—O1^i	87.8 (2)	O9—Mo4—O8	80.9 (2)
O4—Mo2—O1^i	83.5 (2)	O3—Mo4—O8	77.9 (1)
O3—Mo2—O1^i	71.8 (1)	O1—Mo4—O8	77.0 (1)
O8^i—Mo2—O1^i	71.8 (1)	O8^i—Mo4—O8	76.1 (1)

Symmetry code: (i) $2 - x, 2 - y, -1 - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O14—H14$B\cdots$O11^i	0.82	1.99	2.804 (8)	174.3
O15—H15$A\cdots$O14	0.82	1.86	2.677 (8)	178.3
N2—H2$A\cdots$O15^{ii}	0.86	2.13	2.905 (8)	150.2
N2—H2$B\cdots$O10^{ii}	0.86	2.18	3.017 (7)	165.4
N4—H4$A\cdots$O13^{iii}	0.86	2.22	3.033 (7)	158.2
N4—H4$B\cdots$O2^{iv}	0.86	2.18	3.028 (7)	169.0

Symmetry codes: (i) $1 + x, y, z$; (ii) $3 - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $2 - x, 1 - y, -1 - z$.

lengths are 2.905 (8)–3.033 (7) Å (Fig. 2 and Table 2).

Experimental

The pH of a mixture of Na$_2$MoO$_4$·2H$_2$O(0.242 g 1 mmol), Zn(CH$_3$COO)$_2$·2H$_2$O (0.11 g 0.5 mmol) and *N*-(2-hydroxy)ethyl-4-aminopyridine sulfate (0.08 g 0.19 mmol) in 18 ml water was adjusted to 2.13 by adding 10% HNO$_3$. The mixture was then heated at 443 K for two days under autogeneous pressure. Colorless crystals were

[Mo—O = 1.687 (4)–1.708 (4) Å], μ_2–O atoms [Mo—O = 1.759 (4)–2.309 (4) Å], μ_3–O atoms [Mo—O = 1.956 (4)–2.369 (4) Å] and μ_5–O atoms [Mo—O = 2.187 (4)–2.437 (4) Å]. The O—H$\cdots$O hydrogen-bond lengths are 2.677 (8)–2.804 (8) Å, and the N—H$\cdots$N hydrogen-bond

isolated after the reaction solution was cooled gradually to room temperature.

Crystal data
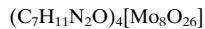
$(C_7H_{11}N_2O)_4[Mo_8O_{26}]$
$M_r = 1740.23$
Monoclinic, $P2_1/c$
$a = 12.657 (3)$ Å
$b = 13.816 (3)$ Å
$c = 14.892 (3)$ Å
$\beta = 111.15 (1)°$
$V = 2428.8 (9)$ Å^3
$Z = 2$

$D_x = 2.380$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4440
 reflections
$\theta = 2.1–25.1°$
$\mu = 2.10$ mm^{-1}
$T = 293 (2)$ K
Prism, colorless
$0.47 \times 0.38 \times 0.27$ mm

Data collection

Bruker SMART CCD
 diffractometer
φ and ω scans
Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
$T_{min} = 0.363$, $T_{max} = 0.568$
7194 measured reflections

4280 independent reflections
3561 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.1°$
$h = -4 \rightarrow 15$
$k = -14 \rightarrow 16$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.104$
$S = 1.09$
4280 reflections
335 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 9.0016P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.10$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}
Extinction correction: SHELXL
Extinction coefficient: 0.00024 (1)

H atoms were positioned geometrically and included in the refinement as riding. The highest residual peak is located 1.05 Å from Mo4 and the deepest hole is located 0.89 Å from Mo3.

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXL97; software used to prepare material for publication: SHELXL97.

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