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Bis[4,4′-bipyridinium(2+)] hexacosaoxooctamolybdate

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The title compound, $(C_{10}H_{10}N_2)_2[Mo_8O_{26}]$, was produced by hydrothermal reaction of an acidified aqueous solution of H_2MoO_4, 4,4′-bipyridine and $NiCl_2\cdot6H_2O$. The structure of the title compound consists of the β-octamolybdate anion having a center of symmetry and protonated 4,4′-bipyridine cations. The distances between Mo and O atoms shared by two or more neighboring {MoO_6} octahedra are in the range 1.750 (2)–2.450 (2) Å and those between Mo and terminal O atoms in the range 1.696 (3)–1.720 (3) Å. The N—H···O hydrogen-bond lengths are in the range 2.722 (4)-2.755 (4) Å.

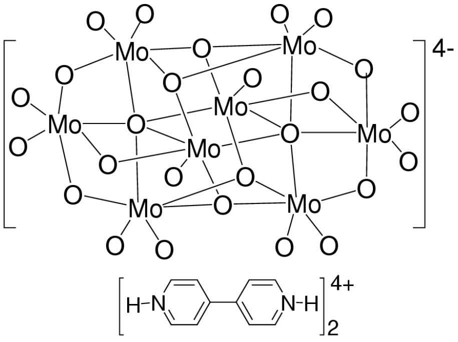
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.022
wR factor = 0.054
Data-to-parameter ratio = 10.1

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

Comment

One of the interesting aspects of octamolybdates, $[Mo_8O_{26}]^{4-}$, is that they exhibit various structural patterns (Xi *et al.*, 1994). Up until now, a series of octamolybdates have been reported in the literature; the structures of the α-, β-, γ, α–γ-, β–γ-, ε- and ξ-$[Mo_8O_{26}]^{4-}$ isomers have been studied in great detail (Day *et al.*, 1977; Hagrman *et al.*, 1999; Lindqvist, 1950; Pope, 1983; Xi *et al.*, 1994; Xu *et al.*, 1999). In the course of our research on the synthesis of 4,4′-bipyridine-bridged heterometallic polymers, the title compound, (I), was obtained as a single crystal.



(I)

As shown in Fig. 1, the octamolybdate anion is built up of eight edge-shared {MoO_6} octahedra. It can also be described as two centrosymmetrically related cyclic {Mo_4O_{13}} units are crosslinked by bridging O atoms. The coordination environment of each Mo atom is a distorted octahedron, with Mo–O distances ranging from 1.696 (3) to 2.450 (2) Å and angles involving the neighboring O atoms ranging from 69.7 (1) to 104.8 (1)°. According to the coordinating mode, the O atoms in the anion can be divided into four different groups, which are terminal O atoms [Mo–O = 1.696 (3)-1.720 (2) Å], μ_2–O atoms [Mo–O = 1.750 (2)-2.299 (3) Å], μ_3–O atoms [Mo–O =

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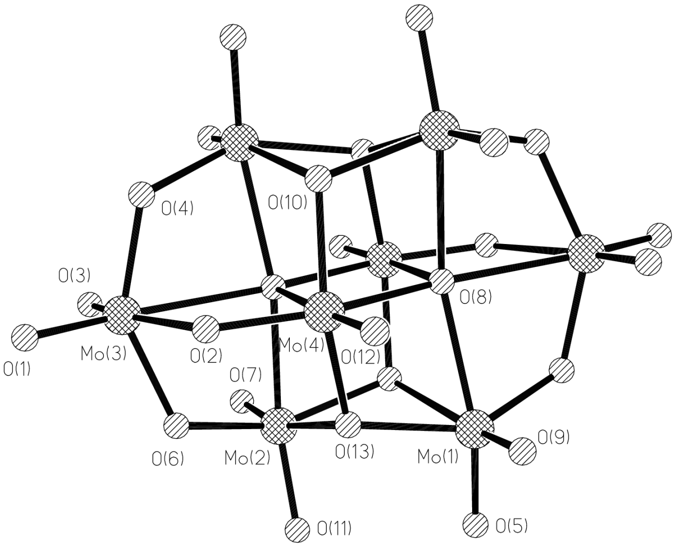

Figure 1
The structure of the β-$[Mo_8O_{26}]^{4-}$ anion.

1.954 (2)-2.388 (2) Å] and μ_5–O atoms [Mo–O = 2.155 (2)-2.450 (2) Å]. N—H···O hydrogen bonding exists in the packing of the title compound (Table 2 and Fig. 2).

Experimental

The title compound, (I), was prepared by hydrothermal synthesis from a mixture of H_2MoO_4 (0.10 g, 0.62 mmol), $NiCl_2\cdot6H_2O$ (0.10 g, 0.42 mmol), 4,4′-bipyridine·$2H_2O$ (0.05 g, 0.26 mmol) and 65%wt HNO_3 (0.1 ml, 1.5 mmol) in H_2O (18 ml) heated at 443 K for 6 d under autogeneous pressure. After the reaction mixture had been slowly cooled to room temperature, colorless crystals of (I) appeared.

Crystal data

$(C_{10}H_{10}N_2)[Mo_8O_{26}]$
M_r = 1499.92
Monoclinic, $P2_1/n$
a = 10.7493 (2) Å
b = 15.2255 (1) Å
c = 10.7828 (2) Å
β = 93.840 (1)°
V = 1760.79 (5) $Å^3$
Z = 2
D_x = 2.829 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5475 reflections
θ = 2.3–25.0°
μ = 2.86 mm^{-1}
T = 293 (2) K
Prism, colorless
0.39 × 0.32 × 0.28 mm

Data collection

SMART CCD diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.329, T_{max} = 0.449
6344 measured reflections
3065 independent reflections

2781 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 25.0°
$h = -12 \rightarrow 12$
$k = -18 \rightarrow 14$
$l = -10 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.054
S = 1.09
3065 reflections
303 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 2.4922P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.46 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.67 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00224 (12)

Table 1
Selected geometric parameters (Å, °).

Mo1—O9	1.700 (3)	Mo3—O3	1.699 (3)
Mo1—O5	1.705 (3)	Mo3—O1	1.718 (3)
Mo1—O4^{i}	1.898 (2)	Mo3—O4	1.912 (2)
Mo1—O13	2.009 (2)	Mo3—O6	1.927 (2)
Mo1—O8	2.341 (2)	Mo3—O2	2.299 (3)
Mo1—O10^{i}	2.388 (2)	Mo3—O8^{i}	2.450 (2)
Mo2—O11	1.707 (2)	Mo4—O12	1.696 (3)
Mo2—O7	1.720 (3)	Mo4—O2	1.750 (2)
Mo2—O6	1.898 (2)	Mo4—O13	1.954 (2)
Mo2—O10^{i}	1.987 (2)	Mo4—O10	1.957 (2)
Mo2—O13	2.297 (2)	Mo4—O8	2.155 (2)
Mo2—O8^{i}	2.338 (2)	Mo4—O8^{i}	2.396 (2)

O9—Mo1—O5	104.8 (1)	O4—Mo3—O8^{i}	73.8 (1)
O9—Mo1—O4^{i}	103.0 (1)	O6—Mo3—O8^{i}	73.8 (1)
O5—Mo1—O4^{i}	101.7 (1)	O2—Mo3—O8^{i}	69.7 (1)
O9—Mo1—O13	96.6 (1)	O12—Mo4—O2	104.4 (1)
O5—Mo1—O13	100.4 (1)	O12—Mo4—O13	101.3 (1)
O9—Mo1—O8	95.9 (1)	O2—Mo4—O13	97.1 (1)
O4^{i}—Mo1—O8	76.7 (1)	O12—Mo4—O10	101.8 (1)
O13—Mo1—O8	73.1 (1)	O2—Mo4—O10	96.0 (1)
O5—Mo1—O10^{i}	87.6 (1)	O12—Mo4—O8	98.9 (1)
O4^{i}—Mo1—O10^{i}	84.4 (1)	O13—Mo4—O8	78.5 (1)
O13—Mo1—O10^{i}	70.4 (1)	O10—Mo4—O8	78.7 (1)
O8—Mo1—O10^{i}	71.4 (1)	O2—Mo4—O8^{i}	80.2 (1)
O11—Mo2—O7	104.8 (1)	O13—Mo4—O8^{i}	77.5 (1)
O11—Mo2—O6	100.4 (1)	O10—Mo4—O8^{i}	78.0 (1)
O7—Mo2—O6	100.6 (1)	O8—Mo4—O8^{i}	76.5 (1)
O11—Mo2—O10^{i}	102.2 (1)	Mo4—O2—Mo3	118.1 (1)
O7—Mo2—O10^{i}	96.6 (1)	Mo1^{i}—O4—Mo3	118.6 (1)
O11—Mo2—O13	88.4 (1)	Mo2—O6—Mo3	117.8 (1)
O6—Mo2—O13	84.1 (1)	Mo4—O8—Mo2^{i}	91.9 (1)
O10^{i}—Mo2—O13	72.8 (1)	Mo4—O8—Mo1	91.7 (1)
O7—Mo2—O8^{i}	94.3 (1)	Mo4—O8—Mo4^{i}	103.5 (1)
O6—Mo2—O8^{i}	77.0 (1)	Mo2^{i}—O8—Mo4^{i}	96.0 (1)
O10^{i}—Mo2—O8^{i}	73.8 (1)	Mo1—O8—Mo4^{i}	97.8 (1)
O13—Mo2—O8^{i}	72.5 (1)	Mo2^{i}—O8—Mo3^{i}	86.3 (1)
O3—Mo3—O1	104.6 (1)	Mo1—O8—Mo3^{i}	86.3 (1)
O3—Mo3—O4	100.2 (1)	Mo4^{i}—O8—Mo3^{i}	91.9 (1)
O1—Mo3—O4	100.8 (1)	Mo4—O10—Mo2^{i}	110.0 (1)
O3—Mo3—O6	97.4 (1)	Mo4—O10—Mo1^{i}	110.1 (1)
O1—Mo3—O6	104.2 (1)	Mo2^{i}—O10—Mo1^{i}	102.4 (1)
O1—Mo3—O2	89.0 (1)	Mo4—O13—Mo1	109.1 (1)
O4—Mo3—O2	78.4 (1)	Mo4—O13—Mo2	111.5 (1)
O6—Mo3—O2	77.3 (1)	Mo1—O13—Mo2	105.0 (1)
O3—Mo3—O8^{i}	96.8 (1)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.93 (4)	1.79 (5)	2.722 (4)	174 (4)
N2—H2A···O7^{i}	0.88 (5)	1.91 (5)	2.755 (4)	161 (5)

Symmetry code: (i) $\frac{5}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

H atoms were clearly visible in the difference maps. All of the H atoms were refined isotropically. The C—H and N—H bond-length ranges are 0.86 (4)–1.02 (6) and 0.88 (5)-0.93 (4) Å, respectively. The highest residual peak (0.46 e $Å^{-3}$) is located at (0.2010, 0.8171, 0.6423), 0.81 Å from O1; the deepest hole (−0.67 e $Å^{-3}$) is located at (0.2088, 0.3951, 0.8263), 0.78 Å from Mo3.

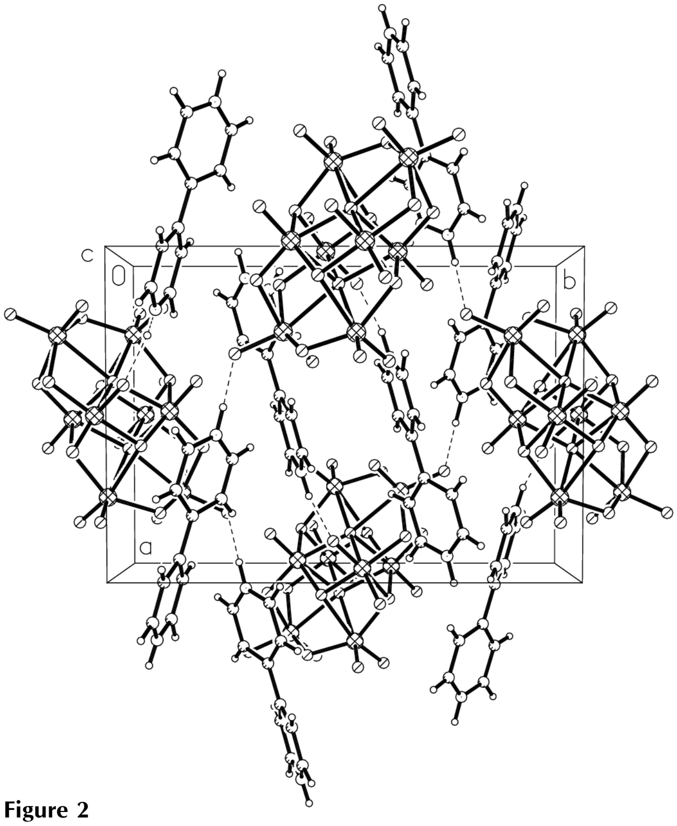

Figure 2
Packing diagram viewed down the c axis. Hydrogen bonding is indicated by dashed lines.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *SMART* and *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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