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# Tetrakis(4,4′-bipyridinium) octamolybdate 4,4′-bipyridine solvate sesquihydrate

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The title compound, $(C_{10}H_9N_2)_4[Mo_8O_{26}]\cdot C_{10}H_8N_2\cdot 1.5H_2O$ or $[4,4'\text{-Hbipy}]_4[Mo_8O_{26}]\cdot 4,4'\text{-bipy}\cdot 1.5H_2O$ (4,4′-bipy is 4,4′-bipyridine), has been prepared under hydrothermal conditions. The anions are held together in an extended one-dimensional chain *via* O—H···O hydrogen bonds and the 4,4′-bipyridine groups are packed together through $\pi$–$\pi$ stacking interactions. Through these hydrogen-bond contacts and $\pi$–$\pi$ interactions, an extended three-dimensional supramolecular architecture is formed.

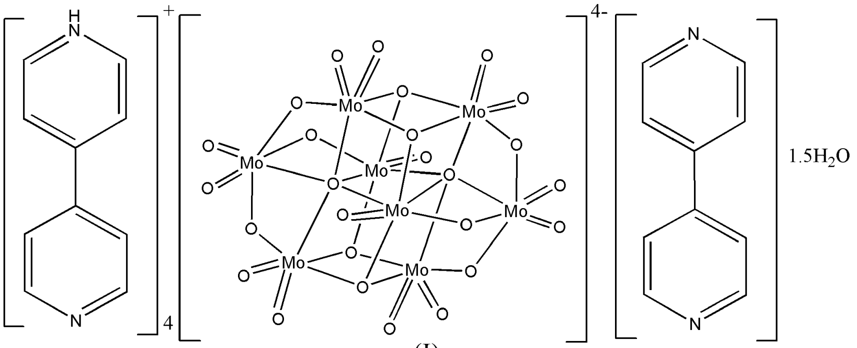
**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.015 Å
H-atom completeness 92%
Disorder in solvent or counterion
$R$ factor = 0.045
$wR$ factor = 0.102
Data-to-parameter ratio = 12.5

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

## Comment

The design of templated molybdenum oxides has been an important advance in the field of organic–inorganic hybrid materials (Hagrman *et al.*, 1997; Xu *et al.* 2003; Xiao *et al.*, 2004). In contrast with extensive reports on molybdenum oxides modified structurally by incorporating transition metal complexes, examples of hybrid materials containing of only molybdenum oxide building blocks have rarely been reported (Range & Fässler, 1990; Zapf *et al.*, 1997). Therefore, we have been investigating the assembly of molybdenum oxides in the presence of organic amines. Here, we present the title new hybrid solid, $[4,4'\text{-Hbipy}]_4[Mo_8O_{26}][4,4'\text{-bipy}]\cdot 1.5H_2O$, (I), containing $[Mo_8O_{26}]^{4-}$ cluster anions in the presence of 4,4′-bipyridine molecules.



(I)

The octamolybdate unit $[Mo_8O_{26}]^{4-}$ of (I) exists in the typical $\beta$-form (Inoue & Yamase, 1995; Hagrman *et al.*, 1999; Wu *et al.*, 2002) (Fig. 1), which contains eight edge-sharing $MoO_6$ octahedra with 14 O($t$), six O($\mu_2$), four O($\mu_3$) and two O($\mu_5$) atoms. The $MoO_6$ octahedra are all distorted, the Mo—O($t$), Mo—O($\mu_2$), Mo—O($\mu_3$) and Mo—O($\mu_5$) bond lengths being in the ranges 1.690 (4)–1.715 (5), 1.748 (5)–2.281 (5), 1.945 (4)–2.386 (4) and 2.141 (4)–2.482 (4) Å, respectively. These distances are comparable with the corresponding ones in $(C_6H_{16}N_4)[Mo_8O_{26}]\cdot 2H_2O$ (Fun *et al.*, 1996). The average

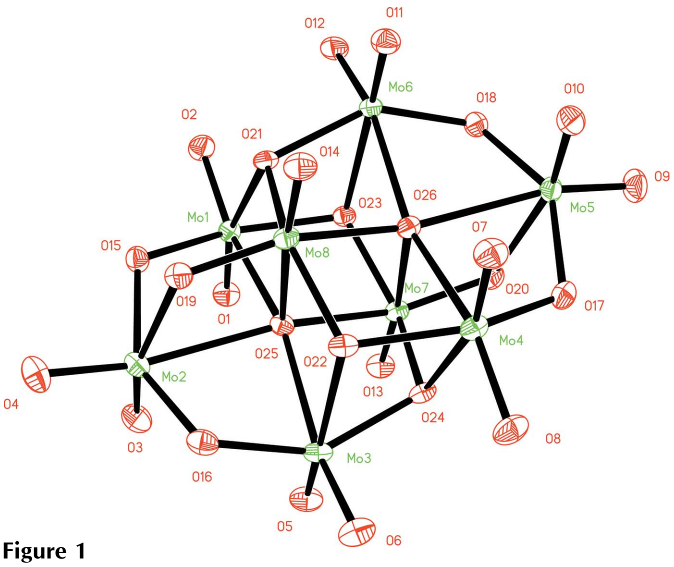


**Figure 1**
The structure of the octamolybdate anion of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

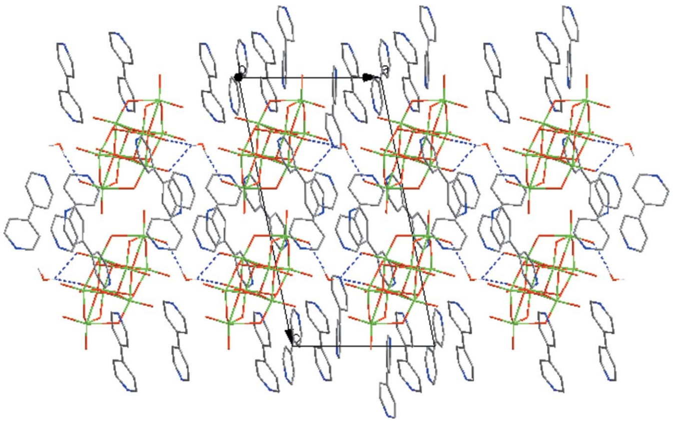


**Figure 2**
A packing diagram for (I), viewed along the *b* axis. Dashed lines indicate the O1*W*···O hydrogen bonds. H atoms attached to C atoms have been omitted.

Mo—O bond lengths are similar around all eight Mo atoms (1.980–2.006 Å).

There are hydrogen bonds between the water molecule (O1*W*) and the terminal O atoms (O5, O10 and O13) of the anions. The anions are held together *via* O—H···O hydrogen bonds to form an infinite one-dimensional chain. The O1*W*···O distances range from 2.919 (8) to 3.031 (7) Å. At the same time, all the 4,4′-bipy groups are packed together through $\pi$–$\pi$ stacking interactions. The closest contact distance between adjacent aromatic rings is 3.423 (12) Å. These hydrogen-bond contacts and $\pi$–$\pi$ interactions play an important role in stabilizing the crystal structure, such that discrete molecules are extended into a three-dimensional supramolecular architecture (Fig. 2).

The bond-valence sum (Brown & Altermatt, 1985) values for all Mo atoms are in the range 5.86–5.96, consistent with the +6 oxidation state. Charge balance requires four protons, which are assumed to be bound to 4,4′-bipy molecules. Bond-valence sums for all N atoms further confirm that four 4,4′-bipyridine molecules are each monoprotonated.

## Experimental

All reagents were purchased from commercial sources and used without further purification. Compound (I) was prepared by a hydrothermal method from a mixture of $(NH_4)_2Ce(NO_3)_6$ (1.0 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.5 mmol), $Mn(CH_3COO)_2\cdot 4H_2O$ (0.5 mmol), $MnSO_4\cdot H_2O$ (0.5 mmol), 4,4′-bipyridine (0.3 mmol) and $H_2O$ (833.4 mmol) in the molar ratio of 2:1:1:1:0.6:1667. The mixture was heated in a 30 ml Teflon-lined acid digestion bomb inside a programmable electric furnace at 433 K for 3 d, with a starting pH of 5.26 adjusted by NaOH solution (2 *M*). The autoclave was then cooled to room temperature over 2 d and yellow crystals were obtained.

*Crystal data*

$(C_{10}H_9N_2)_4[Mo_8O_{26}]\cdot C_{10}H_8N_2\cdot$-$1.5H_2O$
$M_r = 1995.50$
Triclinic, $P\overline{1}$
$a = 10.2290\ (18)$ Å
$b = 17.016\ (3)$ Å
$c = 18.874\ (3)$ Å
$\alpha = 86.296\ (2)^\circ$
$\beta = 78.076\ (2)^\circ$
$\gamma = 72.520\ (2)^\circ$
$V = 3065.9\ (9)$ Å$^3$
$Z = 2$
$D_x = 2.162$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 1.68$ mm$^{-1}$
$T = 293\ (2)$ K
Block, yellow
$0.26 \times 0.18 \times 0.15$ mm

*Data collection*

Bruker APEXII CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.670$, $T_{max} = 0.787$
22446 measured reflections
10700 independent reflections
7820 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0^\circ$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.102$
$S = 1.07$
10700 reflections
859 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 24.0938P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.95$ e Å$^{-3}$
$\Delta\rho_{min} = -0.79$ e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Mo2—O3 | 1.715 (5) | Mo7—O20 | 1.748 (5) |
| Mo2—O25 | 2.482 (4) | Mo8—O14 | 1.690 (4) |
| Mo4—O24 | 2.386 (4) | Mo8—O22 | 1.945 (4) |
| Mo5—O20 | 2.281 (5) | Mo8—O26 | 2.141 (4) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*WA*···O5$^{i}$ | 0.85 | 2.09 | 2.925 | 166 |
| O1*W*—H1*WA*···O13$^{i}$ | 0.85 | 2.63 | 3.031 | 111 |
| O1*W*—H1*WB*···O10 | 0.85 | 2.11 | 2.919 | 159 |

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

H atoms attached to C atoms were included in the refinement in calculated positions in the riding-model approximation, with C—H =

0.93 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) for C$sp^2$. The H atoms of the water molecules were included in the refinement in calculated positions in the riding-model approximation, with O—H = 0.85 Å and $U_{iso}$(H) = 1.5$U_{eq}$(O).

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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