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Bis[2-(4-pyridinio)-1*H*-benzimidazolium] hexacosaoxooctamolybdate(VI)

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Key indicators

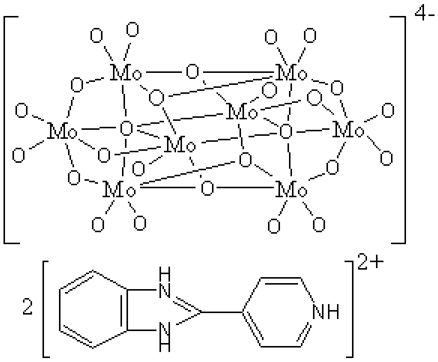
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.043
wR factor = 0.114
Data-to-parameter ratio = 15.0

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

The title compound, $(C_{12}H_{11}N_3)_2[Mo_8O_{26}]$, was prepared by the hydrothermal method. The centrosymmetric β-octamolybdate anions are linked to form a three-dimensional structure by the 2-(4-pyridinio)benzimidazolium cations through N—H···O hydrogen bonds.

Comment

The rapid progress in exploring inorganic/organic hybrid materials has been driven by the interest in their fascinating structural diversity and promising potential applications in chemistry, biology and materials science (Pope & Müller, 1991; Moulton & Zaworotko, 2001). Integration of organic components and polyoxometalate (POM) moieties into a single structure has characterized one fruitful subclass of organic/inorganic hybrid materials (Lü *et al.*, 2004). According to the role of the organic components, the POM-based hybrids may be divided into three groups, namely (i) charge-compensating cations, (ii) ligands bonded directly to the metal oxide scaffolding and (iii) ligands bonded to a secondary metal centre (Hagrman *et al.*, 1999). It is well known that POM building blocks may be linked into extended structural topologies *via* coordination bonds, π–π stacking and hydrogen bonds, and combinations of these (Luo *et al.*, 2003; Randy *et al.*, 2003; Chen *et al.*, 2004). We report here the synthesis and crystal structure of the title compound, (I), in which the organic component acts as a charge-compensating cation.



(I)

Compound (I) consists of centrosymmetric β-octamolybdate anions and doubly protonated 2-(4-pyridinio)benzimidazole cations. The $[Mo_8O_{26}]^{4-}$ anion is built up of eight edge-sharing MoO_6 octahedra and displays the characteristic β-octamolybdate arrangement, which contains two μ_5-O atoms, O11 and O11^{i} [symmetry code (i) $-x, -y, -z$]. Extensive bond-valence sum calculations (Brown & Altermatt, 1985;

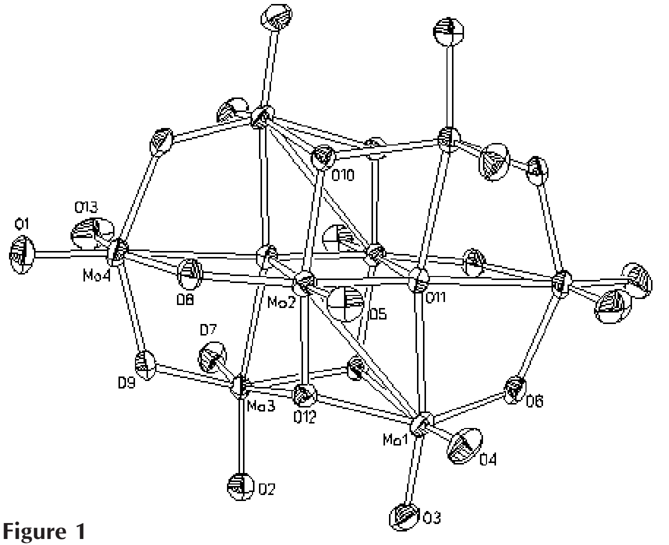


Figure 1
Structure of the β-$[Mo_8O_{26}]^{4-}$ anion, showing 30% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by ($-x$, $-y$, $-z$).

Brese & O'Keeffe, 1991) indicate the valences of Mo and O atoms to be +6 and −2, respectively. Each Mo atom is coordinated octahedrally by six O atoms, which can be divided into four groups: (i) Mo—O(t) bonds, 1.679 (4)–1.709 (4) Å; (ii) Mo—O(μ_2-O), 1.757 (4)–2.253 (4) Å; (iii) Mo—O(μ_3-O), 1.932 (4)–2.360 (4) Å; (iv) Mo—O(μ_5-O), 2.118 (3)–2.492 (3) Å. The β-octamolybdate anions and the 2-(4-pyridinio)benzimidazolium cations are linked to form a three-dimensional structure *via* N—H···O hydrogen bonds (Fig. 2 and Table 2). There is a short C11···O2($x, \frac{1}{2} - y, z - \frac{1}{2}$) contact of 2.967 (9) Å. However, it is not a C—H···O interaction, the H11A···O2 distance being 3.05 Å.

Experimental

A mixture of MoO_3, $ZnSO_4{\cdot}7H_2O$, 2-(4-pyridyl)benzimidazole and water in the molar ratio 1.0:1.2:1.0:1835 was sealed in a Teflon-lined stainless steel reactor and heated for 3 d at 453 K and autogeneous pressure. After allowing the reaction mixture to cool to room temperature, yellow crystals of (I) were collected, washed with water and air-dried (yield *ca* 34%).

Crystal data

$(C_{12}H_{11}N_3)_2[Mo_8O_{26}]$
M_r = 1578.00
Monoclinic, $P2_1/c$
a = 11.304 (3) Å
b = 9.485 (3) Å
c = 17.835 (5) Å
β = 97.434 (2)°
V = 1896.1 (9) Å^3
Z = 2

D_x = 2.764 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5270 reflections
θ = 2.0–27.5°
μ = 2.66 mm^{-1}
T = 293 (2) K
Prism, yellow
0.20 × 0.10 × 0.10 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scan
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
T_{min} = 0.683, T_{max} = 0.766
14 344 measured reflections

4335 independent reflections
3867 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 27.5°
$h = -13 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 22$

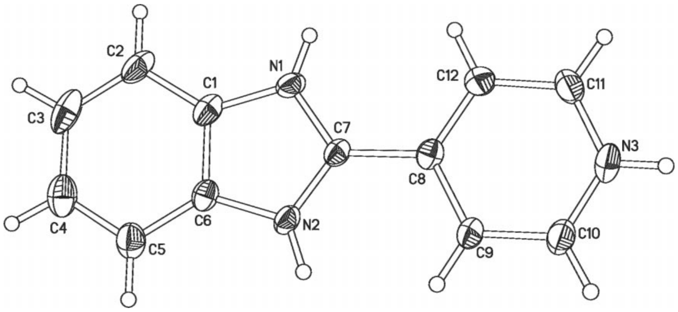


Figure 2
Structure of the 2-(4-pyridinio)benzimidazolium cation, showing 30% probability displacement ellipsoids.

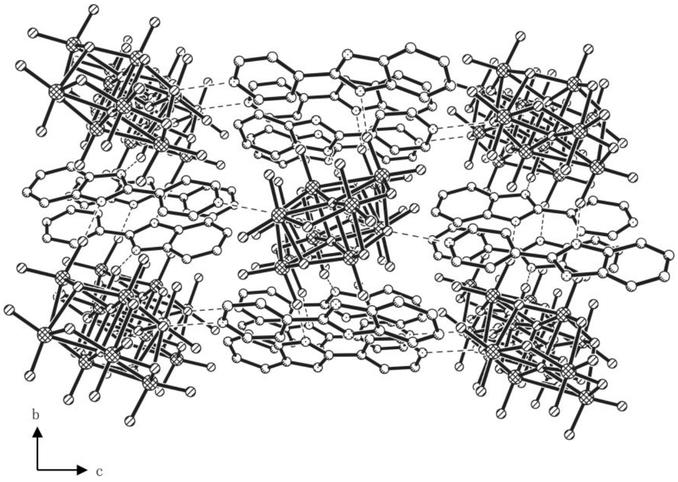


Figure 3
Packing diagram of (I). Broken lines indicate hydrogen bonds. All H atoms have been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.114
S = 1.09
4335 reflections
289 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 5.8052P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.87 e Å^{-3}
$\Delta\rho_{min}$ = −2.90 e Å^{-3}

Table 1
Selected bond distances (Å).

Mo1—O3	1.695 (4)	Mo3—O7	1.687 (4)
Mo1—O4	1.709 (4)	Mo3—O2	1.689 (4)
Mo1—O6	1.893 (4)	Mo3—O9	1.909 (4)
Mo1—O12	1.993 (4)	Mo3—O10^{i}	2.018 (4)
Mo1—O11	2.321 (3)	Mo3—O11^{i}	2.333 (4)
Mo1—O10^{i}	2.338 (4)	Mo3—O12	2.360 (4)
Mo2—O5	1.679 (4)	Mo4—O13	1.705 (6)
Mo2—O8	1.757 (4)	Mo4—O1	1.698 (5)
Mo2—O12	1.932 (4)	Mo4—O9	1.904 (4)
Mo2—O10	1.980 (4)	Mo4—O6^{i}	1.941 (4)
Mo2—O11	2.118 (3)	Mo4—O8	2.253 (4)
Mo2—O11^{i}	2.374 (4)	Mo4—O11^{i}	2.492 (3)

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

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

	D—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O13^{ii}	0.86	2.07	2.764 (7)	138
N2—H2*B*···O4^{iii}	0.86	1.85	2.674 (7)	160
N3—H3*B*···O10	0.86	1.95	2.794 (6)	168

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

H atoms bound to N atoms were located in difference density maps, but, after refinement, N—H bond distances were a little shorter than normal. All H atoms were positioned geometrically, with C—H = 0.93 Å and N—H = 0.86 Å, and allowed to ride with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom).

Data collection: *CrystalClear* (Rigaku Corporation, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXTL*.

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