

A co-crystal of 2-methylbenzimidazole and ammonium octamolybdate

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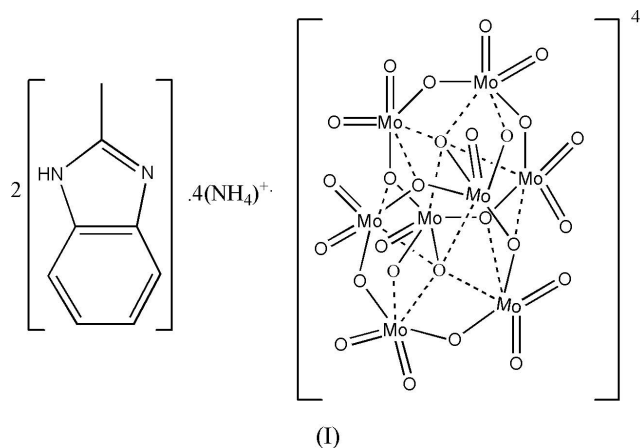
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$
 R factor = 0.032
 wR factor = 0.089
Data-to-parameter ratio = 12.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, tetraammonium octamolybdate bis(2-methylbenzimidazole), $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}] \cdot 2\text{C}_8\text{H}_8\text{N}_2$, the crystal packing is stabilized by $\text{N}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{O}$ intra- and intermolecular hydrogen bonds, as well as $\pi-\pi$ stacking. The anion lies on an inversion center.

Comment

Recently, the synthesis and characterization of polymolybdates linked by coordinated transition metal fragments have attracted much attention (Yaghi & Li, 1996; Yaghi *et al.*, 1998; Stupp & Braun, 1997; Wang *et al.*, 1995; Matsumoto *et al.*, 1999; Carlucci *et al.*, 1995). Many metal complexes containing polymolybdates have been synthesized and characterized (Luo *et al.*, 2003; Wu *et al.*, 2002). During our ongoing studies of related materials, we obtained the title compound, (I) (Fig. 1), and present its crystal structure here.



The most important geometric parameters of (I) are listed in Table 1. The unit cell contains two 2-methylbenzimidazole molecules, an $[\text{Mo}_8\text{O}_{26}]^{4-}$ anion and four NH_4^+ cations. The complete $[\text{Mo}_8\text{O}_{26}]^{4-}$ moiety is generated from the asymmetric unit atoms by inversion symmetry, consists of eight edge-sharing MoO_6 octahedra and displays the characteristic β -octamolybdate arrangement, in which an Mo_6O_6 ring is capped on opposite faces by two MoO_6 octahedra. All the Mo atoms exhibit a +6 oxidation state and possess distorted octahedral geometry. The average $\text{Mo} \cdots \text{Mo}$ separation of $3.2055(8)\text{ \AA}$ in (I) is similar to that seen in related structures [$3.200(1)\text{ \AA}$; Luo *et al.*, 2003]. The 2-methylbenzimidazole molecule appears to play an important role in the crystal packing by linking ammonium cations and β -octamolybdate anions *via* numerous $\text{N}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds and $\text{Csp}^2-\text{H} \cdots \text{O}$ and $\text{Csp}^3-\text{H} \cdots \text{O}$ interactions

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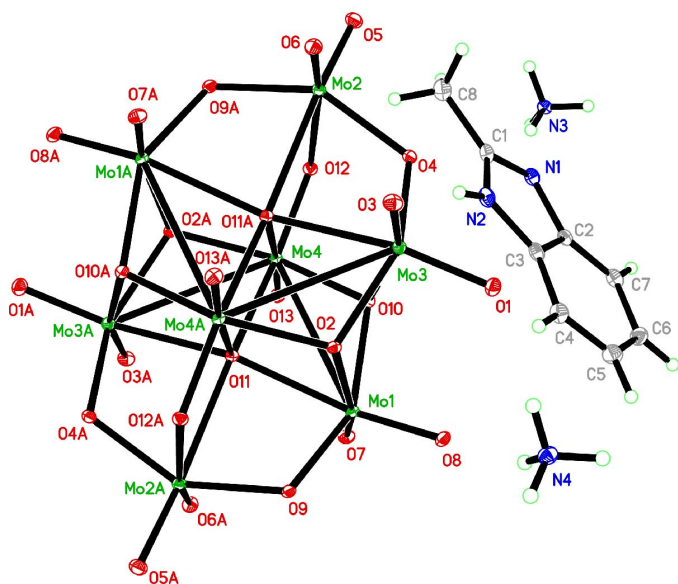


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms shown as arbitrary spheres. Atoms with the suffix A are generated by the symmetry code (1 - x, 1 - y, 2 - z).

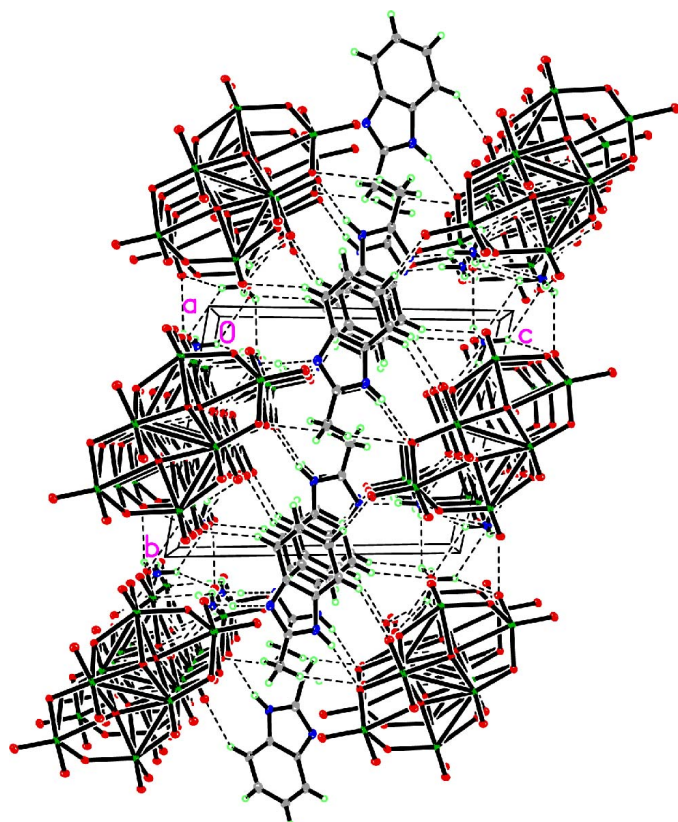


Figure 2
A packing diagram for (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds. Key: gray carbon, jade-green hydrogen, bottle-green molybdenum, red oxygen, and blue nitrogen.

(Table 2 and Fig. 2). In the crystal packing, there is also π - π stacking of 2-methylbenzimidazole molecules, with a contact distance of 3.46 (1) Å.

Experimental

Chemicals of reagent grade were used without further purification. The synthesis was performed under hydrothermal conditions. A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.0863 g), 2-methylbenzimidazole (1 mmol, 0.1321 g), MoO_3 (0.25 mmol, 0.0364 g), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (1.25 mmol, 1.5448 g) and H_2O (15 ml) in a 25 ml stainless steel reactor with a Teflon liner was heated from 293 to 443 K in 2 h and a constant temperature was maintained at 443 K for 72 h, after which the mixture was cooled to 298 K. Yellow crystals of (I) were recovered from the reaction.

Crystal data

$(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}] \cdot 2\text{C}_8\text{H}_8\text{N}_2$
 $M_r = 1520.02$
Triclinic, $P\bar{1}$
 $a = 8.7122$ (19) Å
 $b = 10.400$ (2) Å
 $c = 12.007$ (3) Å
 $\alpha = 93.292$ (3)°
 $\beta = 107.373$ (2)°
 $\gamma = 112.457$ (2)°
 $V = 941.2$ (4) Å³

$Z = 1$
 $D_x = 2.682$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2898 reflections
 $\theta = 2.5$ – 27.0 °
 $\mu = 2.68$ mm⁻¹
 $T = 293$ (2) K
Block, yellow
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\text{min}} = 0.475$, $T_{\text{max}} = 0.585$
4606 measured reflections

3247 independent reflections
2812 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 25.0$ °
 $h = -10 \rightarrow 9$
 $k = -12 \rightarrow 10$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.089$
 $S = 1.04$
3247 reflections
263 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 1.1475P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.15$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mo1—O8	1.700 (3)	Mo3—O1	1.695 (3)
Mo1—O7	1.703 (3)	Mo3—O3	1.697 (4)
Mo1—O9	1.906 (3)	Mo3—O4	1.904 (3)
Mo1—O10	1.981 (3)	Mo3—O2	1.983 (3)
Mo1—O11	2.320 (3)	Mo3—O11 ⁱ	2.355 (3)
Mo1—O2	2.338 (3)	Mo3—O10	2.363 (3)
Mo2—O5	1.686 (3)	Mo4—O13	1.688 (3)
Mo2—O6	1.701 (4)	Mo4—O12	1.749 (3)
Mo2—O9 ^j	1.925 (3)	Mo4—O2 ⁱ	1.952 (3)
Mo2—O4	1.936 (3)	Mo4—O10	1.954 (3)
Mo2—O12	2.278 (3)	Mo4—O11	2.141 (3)
Mo2—O11 ⁱ	2.414 (3)	Mo4—O11 ⁱ	2.345 (3)
O8—Mo1—Mo4	135.49 (12)	O10—Mo1—Mo4	35.22 (9)
O7—Mo1—Mo4	85.95 (11)	O11—Mo1—Mo4	41.90 (7)
O9—Mo1—Mo4	118.98 (9)	O2—Mo1—Mo4	79.22 (7)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H44 \cdots O6 ⁱⁱ	0.87	2.38	3.042 (6)	133
N4—H43 \cdots O6 ⁱⁱⁱ	0.87	2.34	3.117 (6)	149
N4—H42 \cdots O13 ^{iv}	0.87	2.26	2.932 (6)	134
N4—H41 \cdots O8	0.87	2.15	2.964 (6)	156
N3—H34 \cdots N4 ^v	0.88	2.40	3.192 (6)	151
N3—H33 \cdots O2 ^v	0.88	2.48	3.128 (5)	131
N3—H32 \cdots O9 ^v	0.87	2.11	2.851 (5)	143
N3—H31 \cdots N1 ^{iv}	0.87	1.93	2.757 (6)	159
N2—H2 \cdots O4	0.86	2.16	2.992 (6)	164
C4—H4 \cdots O1	0.93	2.46	3.299 (7)	150
C8—H8B \cdots O12	0.96	2.56	3.401 (7)	147
C7—H7 \cdots O7 ^{vi}	0.93	2.48	3.369 (6)	159

Symmetry codes: (ii) $x, y - 1, z$; (iii) $2 - x, 1 - y, 2 - z$; (iv) $1 + x, y, z$; (v) $x, y, z - 1$; (vi) $-x, -y, 1 - z$.

H atoms attached to C atoms were placed in geometrically idealized positions ($C-H = 0.930-0.96$ Å) and refined as riding [$U_{iso}(H) = 1.2U_{eq}(\text{carrier})$ or $1.5U_{eq}(\text{methyl carrier})$]. H atoms attached to the N were located in a difference Fourier map, relocated in idealized positions ($N-H = 0.86-0.88$ Å) and refined as riding, with $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(N)$. The deepest hole in the electron-density map is 0.70 Å from atom Mo3.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL/PC (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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