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**A new inorganic–organic hybrid: tetraimidazolium octamolybdate(VI) containing the  $\beta$ -form of the  $[\text{Mo}_8\text{O}_{26}]^{4-}$  anion**

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# A new inorganic–organic hybrid: tetraimidazolium octamolybdate(VI) containing the $\beta$ -form of the [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anion

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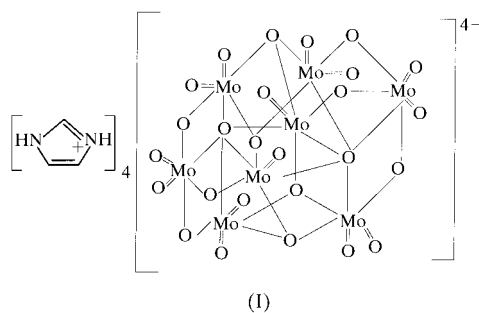
Data validation number: IUC0000252

The title compound, (C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>4</sub>[ $\beta$ -Mo<sub>8</sub>O<sub>26</sub>], has been prepared from imidazole octamolybdate, (C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>4</sub>[(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>( $\gamma$ -Mo<sub>8</sub>O<sub>26</sub>)], which was described previously. The  $\gamma \rightarrow \beta$  conversion is produced in the presence of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and is reported for the first time in this work. The X-ray structure analysis confirmed the presence of the [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anion. The structure consists of  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> polyanions and imidazolium cations. These cations are linked to the terminal and bridging O atoms of the anion by hydrogen bonds.

## Comment

Polyoxometalates of organic cations present considerable interest as a consequence of their photochemical and photochromic properties in solution as well as in the solid state (Yamase, 1998).

In our investigation of octamolybdates, we have tried to prepare a molybdenum oxide cluster in which the octamolybdate ions are linked to the transition metal atoms. Instead of this, we obtained the  $\beta$ -octamolybdate. An



imidazole octamolybdate, (C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>4</sub>[(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>( $\gamma$ -Mo<sub>8</sub>O<sub>26</sub>)], containing imidazole coordinatively bound to the Mo atom in [ $\gamma$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> has been described previously (Martín-Zarza *et al.*, 1993). When an aqueous solution of this compound is

treated with an aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in a molar ratio Mo:Cu of 1:1, the  $\beta$ -form, (C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>4</sub>[ $\beta$ -Mo<sub>8</sub>O<sub>26</sub>], (I), is obtained. The  $\beta$ -form does not contain N–Mo bonds and the organic cations are linked to terminal and bridging O atoms of the anion through hydrogen bonds.

Mechanisms of interconversion of polyoxometalates have been described (Masters *et al.*, 1980; Kemplerer & Shum, 1976) but the  $\gamma \rightarrow \beta$  conversion in the presence of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O to our knowledge has not been described previously. The structure of the title compound consists of  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> polyanions and organic cations. These anions are constituted by eight MoO<sub>6</sub> octahedra sharing edges and corners. The octahedra have different Mo–O bonds, which can be classified as short terminal [1.690 (3)–1.715 (3) Å], intermediate length [1.761 (2)–1.959 (2) Å] and long bonds [1.992 (3)–2.537 (2) Å]. In the idealized octamolybdate anion, there are three different types of MoO<sub>6</sub> octahedra: (i) octahedra formed by atoms Mo1 and Mo1a, which, being closest to the centroid of the polyanion, are the least distorted; (ii) octahedra formed by atoms Mo3 and Mo3a, which are the most distorted since they are furthest from the centroid; and (iii) octahedra formed by atoms Mo2, Mo2a, Mo4 and Mo4a, which have an intermediate degree of distortion. Comparing the title compound with (C<sub>6</sub>H<sub>16</sub>N)<sub>4</sub>[ $\beta$ -Mo<sub>8</sub>O<sub>26</sub>]·2H<sub>2</sub>O (Fun *et al.*, 1996), it can be seen that there are only slight differences in the Mo–O bond distances. These differences are due to the cation–polyanion interactions.

Finally, hydrogen bonds are observed between terminal and bridging O atoms of the polyanion and the imidazolium cations: N1–H···O5 2.864 (4) Å, 171.36°; N2–H···O10 2.827 (5) Å, 167.48°; N3–H···O7 2.819 (5) Å, 152.72°; N4–H···O11 2.884 (5) Å, 168.93°.

## Experimental

(C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>4</sub>[(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>( $\gamma$ -Mo<sub>8</sub>O<sub>26</sub>)] containing the  $\gamma$ -form of the [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anion was prepared as described previously (Martín-Zarza *et al.*, 1993). An aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.1141 g, 0.47 mmol) was added to an aqueous solution of (C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>4</sub>[(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>( $\gamma$ -Mo<sub>8</sub>O<sub>26</sub>)] (0.750 g, 0.47 mmol) in 600 ml of distilled water. The mixture was heated under reflux with stirring for 1 h. When the volume of this solution was reduced to 100 ml, the solution was allowed to stand at room temperature for few days. Colourless crystals of suitable size for X-ray diffraction analysis were obtained of (I). An uncharacterized pale-green precipitate was also obtained.

### Crystal data

(C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]  
*M<sub>r</sub>* = 1459.88  
 Triclinic, *P* $\bar{1}$   
*a* = 9.3491 (15) Å  
*b* = 9.7506 (12) Å  
*c* = 10.3634 (16) Å  
 $\alpha$  = 83.938 (11)°  
 $\beta$  = 75.667 (12)°  
 $\gamma$  = 64.891 (10)°  
*V* = 828.8 (2) Å<sup>3</sup>

*Z* = 1  
*D<sub>x</sub>* = 2.925 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 2.80–30.44°  
 $\mu$  = 3.035 mm<sup>-1</sup>  
*T* = 293 K  
 Prism, colourless  
 0.3 × 0.25 × 0.20 mm

Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.402$ ,  $T_{\max} = 0.569$   
 5293 measured reflections  
 5012 independent reflections  
 4355 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$   
 $\theta_{\text{max}} = 30.40^\circ$   
 $h = 0 \rightarrow 13$   
 $k = -12 \rightarrow 13$   
 $l = -14 \rightarrow 14$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

Refinement

Refinement on  $F^2$   
 $R(F) = 0.024$   
 $wR(F^2) = 0.076$   
 $S = 0.927$   
 5012 reflections  
 246 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.54 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.98 \text{ e } \text{Å}^{-3}$

**Table 1**  
 Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ ).

Mo1—O1	2.386 (2)	Mo3—O11	1.715 (3)
Mo1—O2	1.9282 (19)	Mo3—O3 <sup>i</sup>	1.917 (2)
Mo1—O7	1.761 (2)	Mo4—O1	2.2936 (19)
Mo1—O12	1.690 (3)	Mo4—O2	2.3645 (19)
Mo1—O1 <sup>i</sup>	2.130 (2)	Mo4—O4	1.893 (3)
Mo1—O5 <sup>i</sup>	1.9588 (19)	Mo4—O5	2.031 (2)
Mo2—O2	1.992 (2)	Mo4—O6	1.697 (2)
Mo2—O3	1.902 (3)	Mo4—O13	1.701 (3)
Mo2—O5	2.353 (2)	N1—C1	1.312 (5)
Mo2—O8	1.695 (2)	N1—C3	1.370 (5)
Mo2—O10	1.703 (3)	N2—C1	1.321 (6)
Mo2—O1 <sup>i</sup>	2.313 (2)	N2—C2	1.364 (6)
Mo3—O1	2.537 (2)	N3—C6	1.359 (6)
Mo3—O4	1.913 (2)	N3—C4	1.302 (6)
Mo3—O7	2.2857 (19)	N4—C4	1.305 (6)
Mo3—O9	1.695 (3)	N4—C5	1.343 (6)
O1—Mo1—O2	77.34 (8)	O4—Mo3—O11	98.75 (10)
O1—Mo1—O7	80.99 (8)	O3 <sup>i</sup> —Mo3—O4	141.93 (9)
O1—Mo1—O12	175.13 (11)	O7—Mo3—O9	88.94 (11)
O1—Mo1—O1 <sup>i</sup>	75.26 (7)	O7—Mo3—O11	164.77 (11)
O1—Mo1—O5 <sup>i</sup>	77.84 (7)	O3 <sup>i</sup> —Mo3—O7	77.29 (8)
O2—Mo1—O7	97.00 (9)	O9—Mo3—O11	106.28 (14)
O2—Mo1—O12	102.49 (10)	O3 <sup>i</sup> —Mo3—O9	101.53 (13)
O1 <sup>i</sup> —Mo1—O2	78.68 (8)	O3 <sup>i</sup> —Mo3—O11	98.65 (11)
O2—Mo1—O5 <sup>i</sup>	149.71 (9)	O1—Mo4—O2	71.41 (7)
O7—Mo1—O12	103.84 (12)	O1—Mo4—O4	78.66 (8)
O1 <sup>i</sup> —Mo1—O7	156.24 (9)	O1—Mo4—O5	73.25 (7)
O5 <sup>i</sup> —Mo1—O7	95.98 (9)	O1—Mo4—O6	157.61 (10)
O1 <sup>i</sup> —Mo1—O12	99.90 (11)	O1—Mo4—O13	96.03 (11)
O5 <sup>i</sup> —Mo1—O12	100.77 (10)	O2—Mo4—O4	83.84 (8)
O1 <sup>i</sup> —Mo1—O5 <sup>i</sup>	78.44 (8)	O2—Mo4—O5	70.91 (8)
O2—Mo2—O3	146.53 (9)	O2—Mo4—O6	86.46 (10)
O2—Mo2—O5	71.79 (8)	O2—Mo4—O13	164.30 (11)
O2—Mo2—O8	101.19 (11)	O4—Mo4—O5	146.86 (8)
O2—Mo2—O10	97.47 (11)	O4—Mo4—O6	102.90 (12)
O1 <sup>i</sup> —Mo2—O2	73.12 (7)	O4—Mo4—O13	103.32 (12)
O3—Mo2—O5	83.27 (8)	O5—Mo4—O6	96.75 (11)
O3—Mo2—O8	99.70 (12)	O5—Mo4—O13	96.83 (12)
O3—Mo2—O10	101.67 (12)	O6—Mo4—O13	105.17 (14)
O1 <sup>i</sup> —Mo2—O3	78.29 (8)	Mo1—O1—Mo3	90.72 (7)
O5—Mo2—O8	87.68 (10)	Mo1—O1—Mo4	97.80 (8)
O5—Mo2—O10	164.47 (9)	Mo1—O1—Mo1 <sup>i</sup>	104.74 (8)
O1 <sup>i</sup> —Mo2—O5	72.20 (7)	Mo1—O1—Mo2 <sup>i</sup>	97.49 (7)
O8—Mo2—O10	105.74 (12)	Mo3—O1—Mo4	85.06 (6)
O1 <sup>i</sup> —Mo2—O8	159.89 (10)	Mo1 <sup>i</sup> —O1—Mo3	164.52 (10)
O1 <sup>i</sup> —Mo2—O10	94.21 (9)	Mo2 <sup>i</sup> —O1—Mo3	85.16 (7)
O1—Mo3—O4	72.25 (9)	Mo1 <sup>i</sup> —O1—Mo4	93.51 (8)
O1—Mo3—O7	68.85 (7)	Mo2 <sup>i</sup> —O1—Mo4	161.93 (9)
O1—Mo3—O9	157.70 (11)	Mo1 <sup>i</sup> —O1—Mo2 <sup>i</sup>	91.87 (8)
O1—Mo3—O11	95.92 (11)	Mo1—O2—Mo2	109.17 (9)
O1—Mo3—O3 <sup>i</sup>	72.47 (9)	Mo1—O2—Mo4	110.07 (9)
O4—Mo3—O7	77.07 (8)	Mo2—O2—Mo4	105.09 (9)
O4—Mo3—O9	105.64 (13)	Mo2—O3—Mo3 <sup>i</sup>	118.72 (13)

Mo3—O4—Mo4	118.44 (14)	C4—N4—C5	109.9 (4)
Mo2—O5—Mo4	104.19 (9)	N1—C1—N2	107.9 (3)
Mo1 <sup>i</sup> —O5—Mo2	109.68 (8)	N2—C2—C3	106.7 (4)
Mo1 <sup>i</sup> —O5—Mo4	107.78 (9)	N1—C3—C2	106.7 (3)
Mo1—O7—Mo3	119.44 (11)	N3—C4—N4	107.6 (4)
C1—N1—C3	109.3 (3)	N4—C5—C6	106.8 (4)
C1—N2—C2	109.4 (4)	N3—C6—C5	105.8 (4)
C4—N3—C6	109.8 (4)		

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

**Table 2**  
 Hydrogen-bonding geometry ( $\text{Å}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H7 $\cdots$ O5 <sup>i</sup>	0.86	2.01	2.867 (3)	172
N2—H8 $\cdots$ O10 <sup>ii</sup>	0.86	1.98	2.825 (5)	168
N3—H9 $\cdots$ O7 <sup>iii</sup>	0.86	2.02	2.817 (4)	153
N4—H10 $\cdots$ O11 <sup>iv</sup>	0.86	2.03	2.882 (5)	169
C1—H1 $\cdots$ O12 <sup>ii</sup>	0.93	2.33	3.036 (4)	132
C2—H2 $\cdots$ O6 <sup>v</sup>	0.93	2.48	3.355 (5)	158
C3—H3 $\cdots$ O9 <sup>vi</sup>	0.93	2.51	3.158 (5)	127
C4—H4 $\cdots$ O13 <sup>iv</sup>	0.93	2.52	3.162 (5)	127

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

All H atoms were generated geometrically and allowed to ride on their parent C or N atoms. A global  $U_{\text{iso}}$  was refined for H atoms attached to C atoms and another one for those attached to N atoms.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4/PC* (Harms, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990).

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