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Crystal structure of an organic–inorganic supramolecular salt based on a 4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium) cation and a β -octamolybdate anion

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Keywords: crystal structure; 4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium) cation; β -octamolybdate anion; hydrogen-bonding network

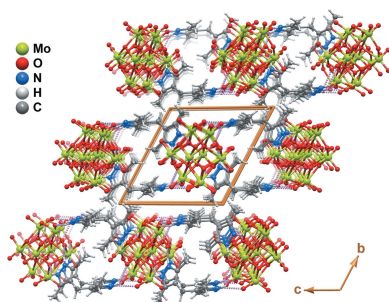
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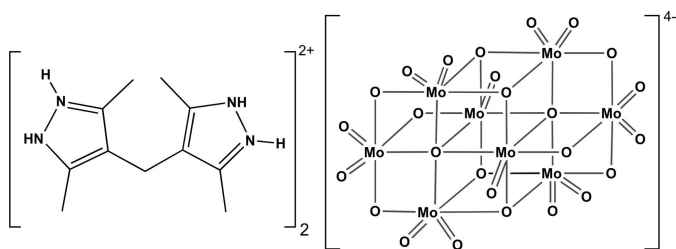
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The asymmetric unit of the title compound, bis[4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium)] β -octamolybdate, $(C_{11}H_{18}N_4)_2[Mo_8O_{26}]$ or $(H_4mbdpz)_2[Mo_8O_{26}]$, is composed of an H_4mbdpz^{2+} cation and half of the β -octamolybdate anion which is completed by inversion symmetry. The organic molecular units are engaged in a series of $N-H\cdots O$ hydrogen bonds with neighbouring anions, with $N\cdots O$ distances and $N-H\cdots O$ angles in the ranges 2.730 (2)–2.941 (2) Å and 122–166°, respectively. These interactions lead to the formation of a supramolecular two-dimensional network parallel to the (010) plane.

1. Chemical context

4,4'-Methylenebis(3,5-dimethylpyrazole) (H_2mbdpz) is a flexible organic molecule which has been extensively used in the last few years by various research groups to design coordination-based and organic solids. While, on the one hand, the central methylene moiety confers some conformational flexibility to the entire molecular unit, on the other the two peripheral pyrazole rings permit not only the coordination to various types of metal atoms but also the involvement of these moieties in complex networks based on hydrogen bonds. It is, thus, not surprising to encounter a rich chemistry and structural diversity associated with this molecule. A search in the literature and in the Cambridge Structural Database (CSD; Allen, 2002; Groom & Allen, 2014) reveals, for example, that H_2mbdpz has been used as an effective bending spacer to construct a large number of metal-organic frameworks (MOFs) or coordination polymers with various remarkable topologies based on a rather diverse range of *d*-block metals (Goswami *et al.*, 2013; Mondal *et al.*, 2008; Timokhin *et al.*, 2015). H_2mbdpz and its derivatives have also been used to prepare a range of supramolecular networks based on either neutral organic molecules or in the formation of salts with a wide range of anions (since, typically, the two pyrazole moieties appear protonated) (Basu *et al.*, 2009; Basu & Mondal, 2010; Hazra *et al.*, 2010). Most of these structural reports available in the literature either use H_2mbdpz purchased from commercial sources or the authors prepare the molecule using published procedures. For the latter case, the standard method dates back to that reported by Trofimenko (1970), but more recent and alternative approaches are also employed to prepare the intended molecule (Kruger *et al.*, 2000).

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In this communication, we report the unexpected isolation of a new supramolecular salt in which 4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium) ($\text{H}_4\text{mbdpz}^{2+}$) is prepared *in situ*, inside the autoclave reaction vessel, starting from 3,5-dimethylpyrazole in a reaction catalysed by Mo^{VI} ions in the presence of hydrogen peroxide. To balance the cationic charge of the protonated $\text{H}_4\text{mbdpz}^{2+}$ moiety, the crystal contains the well-known β -octamolybdate anion. It is remarkable to note that, despite the intensive research on supramolecular structures based on H_2mbdpz , only a couple of very recent reports contain polyoxidometalate-type anions. Indeed, Tian *et al.* (2014, 2015) described various Ag^+ -based MOFs (or coordination polymers) in which Mo^{VI} or W^{VI} Keggin and/or Wells–Dawson polyoxidometalates balance the positive charge of the cationic architectures.

2. Structural commentary

The asymmetric unit of the title compound is composed of a 4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium) cation ($\text{H}_4\text{mbdpz}^{2+}$), and one half of the β -octamolybdate anion, $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ (Fig. 1).

The $\text{H}_4\text{mbdpz}^{2+}$ cation exhibits the typical structural features found in related compounds. The considerable steric

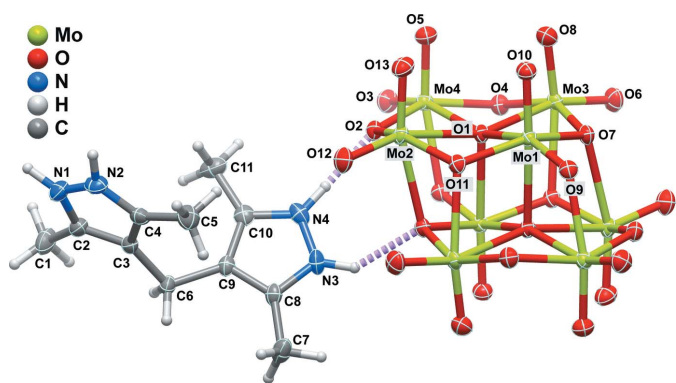


Figure 1

Schematic representation of the molecular entities composing the asymmetric unit of the title compound. The β -octamolybdate anion has been completed by inversion symmetry for the sake of chemical accuracy. All non-hydrogen atoms are represented as displacement ellipsoids drawn at the 60% probability level and hydrogen atoms as small spheres with arbitrary radii. Non-hydrogen atoms belonging to the asymmetric unit have been labelled for clarity. Dashed violet lines indicate $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions (see Table 1 for geometrical details).

Table 1

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O10}^{\text{i}}$	0.94	2.34	2.941 (2)	122
$\text{N2}-\text{H2}\cdots\text{O5}^{\text{i}}$	0.94	2.05	2.852 (2)	143
$\text{N2}-\text{H2}\cdots\text{O8}^{\text{i}}$	0.94	2.31	2.977 (2)	127
$\text{N3}-\text{H3}\cdots\text{O7}^{\text{ii}}$	0.94	1.97	2.759 (2)	141
$\text{N4}-\text{H4}\cdots\text{O2}$	0.94	1.81	2.730 (2)	166

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

hindrance imposed by the two peripheral 3,5-dimethyl-1*H*-pyrazol-2-ium moieties induces a tetrahedral angle of the bridging methylene group of $113.56 (17)^\circ$, which is very close to the median value found in similar structures (from the CSD: median of 114.7° from 109 hits with range of $111.0\text{--}120.0^\circ$). Conversely, the dihedral angle subtended by these two peripheral moieties is significantly more dependent on the crystal structure itself, with the literature values (from 109 hits in the CSD) ranging from as low as 55.1° (a chiral coordination polymer with Cu^{2+} described by Lin *et al.*, 2014) to 90.0° (an Ni^{2+} layered network described by Goswami *et al.*, 2013). Nevertheless, the interplanar angle registered for the title compound, $77.85 (15)^\circ$, agrees well with the median value of all structures deposited in the CSD (81.1°).

The molecular geometrical parameters for the β -octamolybdate anion are typical, exhibiting the usual four families of $\text{Mo}-\text{O}$ bonds: $\text{Mo}-\text{Ot}$ to terminal oxido groups [bond lengths in the $1.6883 (14)\text{--}1.7077 (15) \text{\AA}$ range]; $\text{Mo}-\text{Ob}$ to μ_2 -bridging oxido groups [bond lengths in the $1.7506 (15)\text{--}2.2304 (15) \text{\AA}$ range]; $\text{Mo}-\text{Oc}$ to μ_3 -bridging oxido groups [bond lengths in the $1.9431 (14)\text{--}2.4033 (14) \text{\AA}$ range]; $\text{Mo}-\text{Oc}$ to μ_5 -bridging oxido groups [bond lengths in the $2.1441 (14)\text{--}2.3577 (14) \text{\AA}$ range]. The four crystallographically independent Mo^{VI} metal atoms are hexacoordinated in a typical $\{\text{MoO}_6\}$ fashion resembling highly distorted octahedra: while the *trans* internal $\text{O}-\text{Mo}-\text{O}$ octahedral angles are found in the $142.75 (6)\text{--}174.00 (6)^\circ$ range, the *cis* angles refine instead in the $71.04 (5)\text{--}105.61 (8)^\circ$ interval. This wide dispersion for the internal octahedral angles is a notable and well-known consequence of the marked *trans* effect created by the terminal oxido groups, which displace the metal atoms from the center of the octahedra. The intermetallic Mo^{VI} distances within the β -octamolybdate anion range from $3.1875 (5) \text{\AA}$ (for the $\text{Mo1}\cdots\text{Mo2}$ distance) to $3.5810 (5) \text{\AA}$ [for the $\text{Mo1}\cdots\text{Mo1}^{\text{i}}$ distance across the inversion center of the anion; symmetry operation: (i) $-x, 1 - y, 1 - z$].

3. Supramolecular features

The crystal packing of the title compound is essentially mediated by the presence of various $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions between the $\text{H}_4\text{mbdpz}^{2+}$ cation (which acts as the donor – *D*) and the β -octamolybdate anion (the acceptor – *A*) (Fig. 2*a*). As depicted in Table 1, the $D\cdots A$

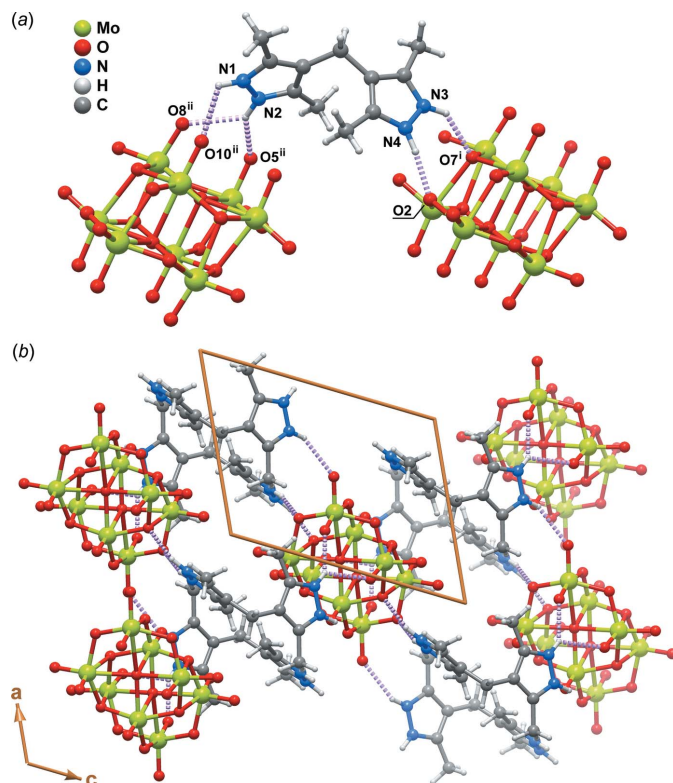


Figure 2

Schematic representation of the type and role of N—H...O hydrogen bond interactions present in the crystal structure of the title compound: (a) description of all interactions which connect the crystallographically independent 4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium) cation to two neighbouring β -octamolybdate anions; (b) portion of the two-dimensional supramolecular layer placed in the *ac* plane of the unit cell formed by the connection between the molecular units present in the title compound. For geometrical details of the represented hydrogen bonds (as violet dashed lines) see Table 1. Symmetry operations used to generate equivalent atoms: (i) $-x, 1 - y, 1 - z$; (ii) $-x, 1 - y, -z$.

distances are relatively short, ranging between 2.730 (2) and 2.977 (2) Å. It is noteworthy that the latter is associated with the N2—H2 group which is engaged in a bifurcated interaction with the neighbouring β -octamolybdate anion (as depicted in Fig. 2*a*), hence leading to an average increase of the inter-atomic distances.

Besides these interactions, the crystal structure is also rich in weak hydrogen bonds of the C—H...O type (not shown) involving mainly the terminal methyl groups of the organic molecule. The various C—H...O interactions present in the crystal structure are rather weak, with C...O distances ranging from 3.203 (3) to 3.457 (3) Å, with $\angle(\text{CHO})$ interaction angles in the 123–168° interval.

The aforementioned hydrogen bonds between cations and anions lead to the formation of a two-dimensional supramolecular network parallel to the (010) plane (Fig. 2*b*). Individual supramolecular entities close-pack perpendicular to (010) to produce the crystal structure of the title compound (Fig. 3).

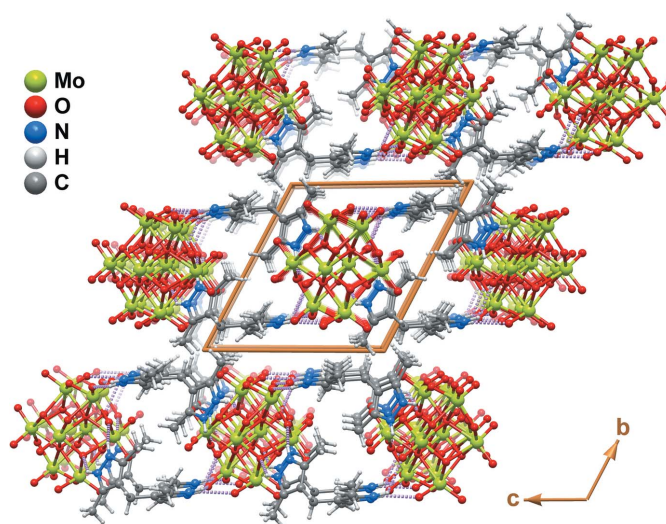


Figure 3

Ball-and-stick schematic representation of the crystal packing of the title compound viewed in perspective along the [100] direction. The figure emphasizes, on the one hand, how the inorganic component of the crystal structure is fully embedded into an organic matrix based on the 4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium) cation. On the other it shows how supramolecular hydrogen-bonded layers pack closely perpendicular to (010).

4. Synthesis and crystallization

MoO₃ (Analar, BDH Chemicals, 99.5%), 3,5-dimethylpyrazole (Aldrich, 99%) and H₂O₂ (50% in water, Sigma-Aldrich) were obtained from commercial sources and used as received. FT-IR spectra were collected using KBr pellets (Sigma-Aldrich, 99%, FT-IR grade) on a Mattson-7000 infrared spectrophotometer.

A mixture of MoO₃ (0.349 g, 2.42 mmol), 3,5-dimethylpyrazole (0.116 g, 1.21 mmol), water (23 mL) and H₂O₂ (2 mL) was heated in a Teflon-lined stainless steel digestion bomb at 433 K for 26 h, at 373 K for 25 h, and finally slowly cooled down to ambient temperature over a period of 13 h. Single crystals of the title compound were obtained inside the Teflon vessel along with a yellow aqueous mother liquor (pH = 6) and a blueish solid, which was confirmed by powder X-ray diffraction studies to be residues of unreacted MoO₃.

FT-IR (cm⁻¹): $\tilde{\nu}$ = 3218 (vs); 3127 (s); 3008 (s); 2859 (s); 2719 (s); 1606 (m); 1579 (s); 1535 (m); 1517 (m); 1438 (s); 1394 (m); 1365 (m); 1253 (m); 1184 (m); 1153 (w); 1070 (w); 1047 (w); 948 (vs); 925 (s); 908 (vs); 844 (s); 721 (s); 705 (s); 671 (s); 655 (s); 543 (s); 522 (m); 480 (w); 458 (w); 445 (w); 414 (m); 401 (m); 360 (m).

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bound to carbon were placed at idealized positions with C—H = 0.99 and 0.98 Å for the —CH₂— and methyl groups, respectively, and included in the final structural model in the riding-motion

approximation with isotropic displacement parameters fixed at 1.2 or $1.5U_{\text{eq}}$, respectively, of the carbon atom to which they are attached.

Hydrogen atoms associated with nitrogen atoms were directly located from difference Fourier maps and included in the model with the N—H distances restrained to 0.95 (1) Å in order to ensure a chemically reasonable environment for these moieties. These hydrogen atoms were modelled with isotropic thermal displacement parameters fixed at $1.5U_{\text{eq}}(\text{N})$.

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References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Basu, T. & Mondal, R. (2010). *CrystEngComm*, **12**, 366–369.
 Basu, T., Sparkes, H. A. & Mondal, R. (2009). *Cryst. Growth Des.* **9**, 5164–5175.
 Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2012). *SAINT* and *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Goswami, A., Bala, S., Pachfule, P. & Mondal, R. (2013). *Cryst. Growth Des.* **13**, 5487–5498.
 Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
 Hazra, D. K., Chatterjee, R., Ali, M. & Mukherjee, M. (2010). *Acta Cryst.* **C66**, o190–o193.
 Kruger, P. E., Moubaraki, B., Fallon, G. D. & Murray, K. S. (2000). *J. Chem. Soc. Dalton Trans.* pp. 713–718.

Table 2

Experimental details.

Crystal data	
Chemical formula	(C ₁₁ H ₁₈ N ₄)[Mo ₈ O ₂₆]
<i>M_r</i>	1596.11
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	180
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.6394 (10), 12.0694 (13), 12.2249 (14)
α , β , γ (°)	113.343 (3), 110.629 (4), 96.540 (4)
<i>V</i> (Å ³)	1046.6 (2)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	2.42
Crystal size (mm)	0.28 × 0.18 × 0.15
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2001)
<i>T</i> _{min} , <i>T</i> _{max}	0.595, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	58761, 5605, 4669
<i>R</i> _{int}	0.032
(sin θ/λ) _{max} (Å ^{−1})	0.685
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.021, 0.045, 1.05
No. of reflections	5605
No. of parameters	305
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.45, −0.38

Computer programs: *APEX2* (Bruker, 2012) and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 1999).

- Lin, L., Yu, R., Wu, X.-Y., Yang, W.-B., Zhang, J., Guo, X.-G., Lin, Z.-J. & Lu, C.-Z. (2014). *Inorg. Chem.* **53**, 4794–4796.
 Mondal, R., Bhunia, M. K. & Dhara, K. (2008). *CrystEngComm*, **10**, 1167–1174.
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
 Tian, A., Ning, Y., Yang, Y., Hou, X., Ying, J., Liu, G., Zhang, J. & Wang, X. (2015). *Dalton Trans.* **44**, 16486–16493.
 Tian, A., Yang, Y., Ying, J., Li, N., Lin, X.-L., Zhang, J.-W. & Wang, X.-L. (2014). *Dalton Trans.* **43**, 8405–8413.
 Timokhin, I., Pettinari, C., Marchetti, F., Pettinari, R., Condello, F., Galli, S., Alegria, E. C. B. A., Martins, L. M. D. R. S. & Pombeiro, A. J. L. (2015). *Cryst. Growth Des.* **15**, 2303–2317.
 Trofimenko, S. (1970). *J. Am. Chem. Soc.* **92**, 5118–5126.

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Crystal structure of an organic–inorganic supramolecular salt based on a 4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium) cation and a β -octamolybdate anion

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

Bis[4,4'-methylenebis(3,5-dimethyl-1*H*-pyrazol-2-ium)] β -octamolybdate

Crystal data

(C₁₁H₁₈N₄)[Mo₈O₂₆]

$M_r = 1596.11$

Triclinic, $P\bar{1}$

$a = 8.6394$ (10) Å

$b = 12.0694$ (13) Å

$c = 12.2249$ (14) Å

$\alpha = 113.343$ (3)°

$\beta = 110.629$ (4)°

$\gamma = 96.540$ (4)°

$V = 1046.6$ (2) Å³

$Z = 1$

$F(000) = 768$

$D_x = 2.532$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9149 reflections

$\theta = 2.5$ – 29.0°

$\mu = 2.42$ mm⁻¹

$T = 180$ K

Plate, colourless

$0.28 \times 0.18 \times 0.15$ mm

Data collection

Bruker D8 QUEST

diffractometer

Radiation source: Sealed tube

Multi-layer X-ray mirror monochromator

Detector resolution: 10.4167 pixels mm⁻¹

ω / φ scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\min} = 0.595$, $T_{\max} = 0.746$

58761 measured reflections

5605 independent reflections

4669 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 3.6^\circ$

$h = -11 \rightarrow 11$

$k = -16 \rightarrow 15$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.045$

$S = 1.05$

5605 reflections

305 parameters

4 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0188P)^2 + 0.8837P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$

$$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mo1	−0.21482 (2)	0.51375 (2)	0.44384 (2)	0.01325 (5)
Mo2	−0.03289 (2)	0.47766 (2)	0.25116 (2)	0.01588 (5)
Mo3	0.09806 (2)	0.76466 (2)	0.66882 (2)	0.01539 (5)
Mo4	0.29881 (2)	0.72827 (2)	0.48193 (2)	0.01568 (5)
O1	0.03817 (17)	0.59486 (13)	0.47061 (13)	0.0144 (3)
O2	0.20451 (18)	0.57180 (14)	0.31700 (14)	0.0173 (3)
O3	0.5019 (2)	0.78869 (15)	0.50477 (16)	0.0241 (3)
O4	0.30714 (18)	0.80224 (14)	0.65515 (14)	0.0181 (3)
O5	0.1782 (2)	0.81272 (15)	0.42422 (15)	0.0231 (3)
O6	0.1581 (2)	0.85684 (15)	0.83252 (15)	0.0250 (4)
O7	−0.10203 (18)	0.63200 (13)	0.63336 (13)	0.0154 (3)
O8	−0.0215 (2)	0.83770 (14)	0.59176 (15)	0.0221 (3)
O9	−0.37025 (18)	0.41295 (14)	0.45016 (14)	0.0171 (3)
O10	−0.32215 (19)	0.60161 (14)	0.38551 (14)	0.0194 (3)
O11	−0.20542 (18)	0.39078 (13)	0.28676 (13)	0.0158 (3)
O12	−0.0557 (2)	0.35530 (15)	0.10928 (15)	0.0250 (4)
O13	−0.1414 (2)	0.57098 (15)	0.20309 (16)	0.0240 (3)
N1	0.3125 (3)	0.17745 (19)	−0.33840 (19)	0.0245 (4)
H1	0.327 (3)	0.200 (2)	−0.400 (2)	0.037*
N2	0.1581 (3)	0.15545 (18)	−0.33513 (19)	0.0236 (4)
H2	0.065 (2)	0.170 (3)	−0.391 (2)	0.035*
N3	0.2863 (2)	0.27594 (18)	0.22445 (18)	0.0216 (4)
H3	0.242 (3)	0.280 (2)	0.285 (2)	0.032*
N4	0.3249 (2)	0.37686 (18)	0.20751 (19)	0.0222 (4)
H4	0.302 (3)	0.4503 (16)	0.255 (2)	0.033*
C1	0.6179 (3)	0.2024 (3)	−0.2101 (3)	0.0315 (6)
H1A	0.6526	0.2767	−0.2201	0.047*
H1B	0.6313	0.1287	−0.2749	0.047*
H1C	0.6910	0.2175	−0.1205	0.047*
C2	0.4340 (3)	0.1784 (2)	−0.2327 (2)	0.0208 (5)
C3	0.3525 (3)	0.1549 (2)	−0.1608 (2)	0.0167 (4)
C4	0.1777 (3)	0.1416 (2)	−0.2286 (2)	0.0190 (4)
C5	0.0296 (3)	0.1179 (2)	−0.1979 (2)	0.0279 (5)
H5A	−0.0785	0.0794	−0.2794	0.042*
H5B	0.0260	0.1980	−0.1351	0.042*
H5C	0.0434	0.0607	−0.1587	0.042*

C6	0.4344 (3)	0.1463 (2)	−0.0344 (2)	0.0188 (4)
H6A	0.5618	0.1776	0.0017	0.023*
H6B	0.4039	0.0565	−0.0549	0.023*
C7	0.2913 (3)	0.0554 (2)	0.1437 (2)	0.0265 (5)
H7A	0.2436	0.0594	0.2065	0.040*
H7B	0.4020	0.0367	0.1703	0.040*
H7C	0.2101	−0.0113	0.0548	0.040*
C8	0.3187 (3)	0.1786 (2)	0.1426 (2)	0.0181 (4)
C9	0.3792 (3)	0.2204 (2)	0.0700 (2)	0.0167 (4)
C10	0.3814 (3)	0.3458 (2)	0.1134 (2)	0.0194 (4)
C11	0.4314 (3)	0.4388 (2)	0.0725 (2)	0.0280 (5)
H11A	0.4545	0.5243	0.1415	0.042*
H11B	0.3371	0.4233	−0.0105	0.042*
H11C	0.5359	0.4305	0.0594	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01265 (9)	0.01485 (9)	0.01065 (9)	0.00461 (7)	0.00402 (7)	0.00530 (7)
Mo2	0.01593 (9)	0.01973 (10)	0.01075 (9)	0.00480 (7)	0.00481 (7)	0.00702 (7)
Mo3	0.01680 (9)	0.01357 (9)	0.01255 (9)	0.00375 (7)	0.00645 (7)	0.00330 (7)
Mo4	0.01521 (9)	0.01665 (10)	0.01562 (9)	0.00504 (7)	0.00687 (7)	0.00775 (7)
O1	0.0138 (7)	0.0161 (7)	0.0114 (7)	0.0040 (6)	0.0047 (6)	0.0055 (6)
O2	0.0176 (7)	0.0210 (8)	0.0145 (7)	0.0060 (6)	0.0081 (6)	0.0083 (6)
O3	0.0201 (8)	0.0265 (9)	0.0267 (9)	0.0054 (7)	0.0115 (7)	0.0127 (7)
O4	0.0158 (7)	0.0176 (8)	0.0151 (7)	0.0020 (6)	0.0045 (6)	0.0050 (6)
O5	0.0253 (8)	0.0244 (9)	0.0235 (8)	0.0106 (7)	0.0105 (7)	0.0139 (7)
O6	0.0301 (9)	0.0218 (8)	0.0158 (8)	0.0046 (7)	0.0092 (7)	0.0036 (7)
O7	0.0154 (7)	0.0162 (7)	0.0121 (7)	0.0039 (6)	0.0061 (6)	0.0044 (6)
O8	0.0229 (8)	0.0200 (8)	0.0229 (8)	0.0075 (7)	0.0098 (7)	0.0094 (7)
O9	0.0145 (7)	0.0192 (8)	0.0156 (7)	0.0049 (6)	0.0051 (6)	0.0075 (6)
O10	0.0193 (8)	0.0207 (8)	0.0182 (8)	0.0082 (6)	0.0067 (6)	0.0098 (6)
O11	0.0147 (7)	0.0175 (8)	0.0112 (7)	0.0039 (6)	0.0038 (6)	0.0049 (6)
O12	0.0259 (9)	0.0284 (9)	0.0159 (8)	0.0052 (7)	0.0085 (7)	0.0072 (7)
O13	0.0219 (8)	0.0309 (9)	0.0236 (8)	0.0101 (7)	0.0081 (7)	0.0177 (7)
N1	0.0309 (11)	0.0266 (11)	0.0215 (10)	0.0096 (9)	0.0126 (9)	0.0151 (9)
N2	0.0243 (10)	0.0250 (11)	0.0203 (10)	0.0107 (8)	0.0055 (8)	0.0123 (8)
N3	0.0214 (10)	0.0241 (10)	0.0181 (9)	0.0042 (8)	0.0127 (8)	0.0059 (8)
N4	0.0198 (10)	0.0206 (10)	0.0201 (10)	0.0071 (8)	0.0083 (8)	0.0042 (8)
C1	0.0293 (13)	0.0458 (16)	0.0349 (14)	0.0136 (12)	0.0208 (12)	0.0265 (13)
C2	0.0255 (12)	0.0210 (12)	0.0194 (11)	0.0087 (9)	0.0107 (9)	0.0115 (9)
C3	0.0201 (11)	0.0164 (11)	0.0150 (10)	0.0071 (8)	0.0089 (9)	0.0069 (8)
C4	0.0215 (11)	0.0148 (11)	0.0199 (11)	0.0074 (9)	0.0084 (9)	0.0074 (9)
C5	0.0215 (12)	0.0335 (14)	0.0304 (13)	0.0101 (10)	0.0128 (10)	0.0148 (11)
C6	0.0214 (11)	0.0247 (12)	0.0178 (11)	0.0103 (9)	0.0121 (9)	0.0127 (9)
C7	0.0346 (14)	0.0221 (12)	0.0201 (12)	0.0007 (10)	0.0132 (10)	0.0084 (10)
C8	0.0157 (10)	0.0216 (11)	0.0131 (10)	0.0028 (8)	0.0058 (8)	0.0057 (9)
C9	0.0132 (10)	0.0215 (11)	0.0136 (10)	0.0041 (8)	0.0049 (8)	0.0078 (9)

C10	0.0143 (10)	0.0237 (12)	0.0156 (10)	0.0051 (8)	0.0029 (8)	0.0083 (9)
C11	0.0323 (13)	0.0220 (12)	0.0236 (12)	0.0038 (10)	0.0048 (10)	0.0125 (10)

Geometric parameters (Å, °)

Mo1—O10	1.6883 (14)	N2—C4	1.332 (3)
Mo1—O9	1.7506 (15)	N2—H2	0.935 (10)
Mo1—O11	1.9431 (14)	N3—N4	1.339 (3)
Mo1—O7	1.9561 (14)	N3—C8	1.342 (3)
Mo1—O1	2.1441 (14)	N3—H3	0.937 (10)
Mo1—O1 ⁱ	2.3577 (14)	N4—C10	1.341 (3)
Mo1—Mo2	3.1874 (4)	N4—H4	0.937 (10)
Mo1—Mo3	3.2153 (4)	C1—C2	1.485 (3)
Mo2—O13	1.6939 (15)	C1—H1A	0.9800
Mo2—O12	1.7005 (16)	C1—H1B	0.9800
Mo2—O2	1.9304 (15)	C1—H1C	0.9800
Mo2—O11	1.9933 (15)	C2—C3	1.391 (3)
Mo2—O1	2.2824 (14)	C3—C4	1.397 (3)
Mo2—O7 ⁱ	2.4033 (14)	C3—C6	1.508 (3)
Mo3—O6	1.6984 (15)	C4—C5	1.484 (3)
Mo3—O8	1.7063 (15)	C5—H5A	0.9800
Mo3—O4	1.8928 (15)	C5—H5B	0.9800
Mo3—O7	2.0078 (15)	C5—H5C	0.9800
Mo3—O1	2.2975 (14)	C6—C9	1.509 (3)
Mo3—O11 ⁱ	2.3502 (14)	C6—H6A	0.9900
Mo4—O3	1.6999 (15)	C6—H6B	0.9900
Mo4—O5	1.7077 (15)	C7—C8	1.485 (3)
Mo4—O4	1.9147 (15)	C7—H7A	0.9800
Mo4—O2	1.9416 (15)	C7—H7B	0.9800
Mo4—O9 ⁱ	2.2304 (15)	C7—H7C	0.9800
O1—Mo1 ⁱ	2.3577 (14)	C8—C9	1.393 (3)
O7—Mo2 ⁱ	2.4033 (14)	C9—C10	1.386 (3)
O9—Mo4 ⁱ	2.2304 (15)	C10—C11	1.477 (3)
O11—Mo3 ⁱ	2.3502 (14)	C11—H11A	0.9800
N1—C2	1.342 (3)	C11—H11B	0.9800
N1—N2	1.347 (3)	C11—H11C	0.9800
N1—H1	0.935 (10)		
O10—Mo1—O9	104.79 (7)	O4—Mo4—O9 ⁱ	78.01 (6)
O10—Mo1—O11	101.71 (7)	O2—Mo4—O9 ⁱ	77.29 (6)
O9—Mo1—O11	97.75 (6)	Mo1—O1—Mo2	92.07 (5)
O10—Mo1—O7	100.07 (7)	Mo1—O1—Mo3	92.69 (5)
O9—Mo1—O7	96.20 (6)	Mo2—O1—Mo3	160.42 (7)
O11—Mo1—O7	150.11 (6)	Mo1—O1—Mo1 ⁱ	105.30 (6)
O10—Mo1—O1	99.34 (7)	Mo2—O1—Mo1 ⁱ	99.34 (5)
O9—Mo1—O1	155.85 (6)	Mo3—O1—Mo1 ⁱ	97.70 (5)
O11—Mo1—O1	78.04 (6)	Mo2—O2—Mo4	116.88 (7)
O7—Mo1—O1	78.43 (6)	Mo3—O4—Mo4	117.46 (7)

O10—Mo1—O1 ⁱ	174.00 (6)	Mo1—O7—Mo3	108.41 (7)
O9—Mo1—O1 ⁱ	81.15 (6)	Mo1—O7—Mo2 ⁱ	108.04 (6)
O11—Mo1—O1 ⁱ	78.01 (5)	Mo3—O7—Mo2 ⁱ	103.79 (6)
O7—Mo1—O1 ⁱ	78.19 (5)	Mo1—O9—Mo4 ⁱ	120.16 (7)
O1—Mo1—O1 ⁱ	74.70 (6)	Mo1—O11—Mo2	108.13 (7)
O10—Mo1—Mo2	89.83 (5)	Mo1—O11—Mo3 ⁱ	109.11 (6)
O9—Mo1—Mo2	134.21 (5)	Mo2—O11—Mo3 ⁱ	106.18 (6)
O11—Mo1—Mo2	36.46 (4)	C2—N1—N2	109.03 (18)
O7—Mo1—Mo2	124.12 (4)	C2—N1—H1	128.8 (17)
O1—Mo1—Mo2	45.69 (4)	N2—N1—H1	121.5 (17)
O1 ⁱ —Mo1—Mo2	86.48 (3)	C4—N2—N1	109.52 (18)
O10—Mo1—Mo3	89.84 (5)	C4—N2—H2	129.5 (17)
O9—Mo1—Mo3	132.50 (5)	N1—N2—H2	119.3 (17)
O11—Mo1—Mo3	123.58 (4)	N4—N3—C8	109.53 (18)
O7—Mo1—Mo3	36.33 (4)	N4—N3—H3	120.5 (16)
O1—Mo1—Mo3	45.54 (4)	C8—N3—H3	129.9 (16)
O1 ⁱ —Mo1—Mo3	85.40 (4)	N3—N4—C10	109.06 (18)
Mo2—Mo1—Mo3	89.640 (10)	N3—N4—H4	118.4 (16)
O13—Mo2—O12	105.61 (8)	C10—N4—H4	132.4 (16)
O13—Mo2—O2	101.67 (7)	C2—C1—H1A	109.5
O12—Mo2—O2	99.58 (7)	C2—C1—H1B	109.5
O13—Mo2—O11	99.61 (7)	H1A—C1—H1B	109.5
O12—Mo2—O11	99.06 (7)	C2—C1—H1C	109.5
O2—Mo2—O11	146.63 (6)	H1A—C1—H1C	109.5
O13—Mo2—O1	95.07 (7)	H1B—C1—H1C	109.5
O12—Mo2—O1	159.06 (7)	N1—C2—C3	107.6 (2)
O2—Mo2—O1	78.95 (5)	N1—C2—C1	120.7 (2)
O11—Mo2—O1	73.82 (5)	C3—C2—C1	131.8 (2)
O13—Mo2—O7 ⁱ	165.12 (6)	C2—C3—C4	106.25 (19)
O12—Mo2—O7 ⁱ	87.62 (6)	C2—C3—C6	127.50 (19)
O2—Mo2—O7 ⁱ	82.35 (6)	C4—C3—C6	126.25 (19)
O11—Mo2—O7 ⁱ	71.04 (5)	N2—C4—C3	107.61 (19)
O1—Mo2—O7 ⁱ	71.46 (5)	N2—C4—C5	121.7 (2)
O13—Mo2—Mo1	86.49 (5)	C3—C4—C5	130.7 (2)
O12—Mo2—Mo1	134.42 (6)	C4—C5—H5A	109.5
O2—Mo2—Mo1	121.20 (4)	C4—C5—H5B	109.5
O11—Mo2—Mo1	35.40 (4)	H5A—C5—H5B	109.5
O1—Mo2—Mo1	42.24 (4)	C4—C5—H5C	109.5
O7 ⁱ —Mo2—Mo1	79.26 (3)	H5A—C5—H5C	109.5
O6—Mo3—O8	104.89 (8)	H5B—C5—H5C	109.5
O6—Mo3—O4	102.17 (7)	C3—C6—C9	113.56 (17)
O8—Mo3—O4	101.97 (7)	C3—C6—H6A	108.9
O6—Mo3—O7	97.97 (7)	C9—C6—H6A	108.9
O8—Mo3—O7	96.88 (7)	C3—C6—H6B	108.9
O4—Mo3—O7	147.68 (6)	C9—C6—H6B	108.9
O6—Mo3—O1	161.95 (7)	H6A—C6—H6B	107.7
O8—Mo3—O1	92.20 (6)	C8—C7—H7A	109.5
O4—Mo3—O1	79.39 (6)	C8—C7—H7B	109.5

O7—Mo3—O1	73.84 (5)	H7A—C7—H7B	109.5
O6—Mo3—O11 ⁱ	90.45 (7)	C8—C7—H7C	109.5
O8—Mo3—O11 ⁱ	162.37 (6)	H7A—C7—H7C	109.5
O4—Mo3—O11 ⁱ	82.78 (6)	H7B—C7—H7C	109.5
O7—Mo3—O11 ⁱ	71.98 (5)	N3—C8—C9	107.23 (19)
O1—Mo3—O11 ⁱ	71.81 (5)	N3—C8—C7	120.65 (19)
O6—Mo3—Mo1	133.10 (6)	C9—C8—C7	132.1 (2)
O8—Mo3—Mo1	84.13 (5)	C10—C9—C8	106.44 (19)
O4—Mo3—Mo1	121.16 (4)	C10—C9—C6	126.00 (19)
O7—Mo3—Mo1	35.26 (4)	C8—C9—C6	127.6 (2)
O1—Mo3—Mo1	41.77 (3)	N4—C10—C9	107.7 (2)
O11 ⁱ —Mo3—Mo1	78.97 (4)	N4—C10—C11	121.0 (2)
O3—Mo4—O5	105.36 (8)	C9—C10—C11	131.3 (2)
O3—Mo4—O4	105.00 (7)	C10—C11—H11A	109.5
O5—Mo4—O4	96.53 (7)	C10—C11—H11B	109.5
O3—Mo4—O2	104.14 (7)	H11A—C11—H11B	109.5
O5—Mo4—O2	97.61 (7)	C10—C11—H11C	109.5
O4—Mo4—O2	142.75 (6)	H11A—C11—H11C	109.5
O3—Mo4—O9 ⁱ	94.00 (6)	H11B—C11—H11C	109.5
O5—Mo4—O9 ⁱ	160.64 (7)		
O6—Mo3—O4—Mo4	−175.31 (8)	N1—N2—C4—C5	179.2 (2)
O8—Mo3—O4—Mo4	−66.98 (9)	C2—C3—C4—N2	0.6 (2)
O7—Mo3—O4—Mo4	57.37 (15)	C6—C3—C4—N2	−179.9 (2)
O1—Mo3—O4—Mo4	23.03 (8)	C2—C3—C4—C5	−178.8 (2)
O11 ⁱ —Mo3—O4—Mo4	95.79 (8)	C6—C3—C4—C5	0.7 (4)
Mo1—Mo3—O4—Mo4	23.37 (10)	C2—C3—C6—C9	133.1 (2)
O10—Mo1—O9—Mo4 ⁱ	178.98 (8)	C4—C3—C6—C9	−46.3 (3)
O11—Mo1—O9—Mo4 ⁱ	74.63 (8)	N4—N3—C8—C9	−0.5 (2)
O7—Mo1—O9—Mo4 ⁱ	−78.87 (8)	N4—N3—C8—C7	178.4 (2)
O1—Mo1—O9—Mo4 ⁱ	−3.4 (2)	N3—C8—C9—C10	0.3 (2)
O1 ⁱ —Mo1—O9—Mo4 ⁱ	−1.88 (7)	C7—C8—C9—C10	−178.5 (2)
Mo2—Mo1—O9—Mo4 ⁱ	74.35 (9)	N3—C8—C9—C6	179.6 (2)
Mo3—Mo1—O9—Mo4 ⁱ	−77.24 (9)	C7—C8—C9—C6	0.7 (4)
C2—N1—N2—C4	−0.2 (3)	C3—C6—C9—C10	−50.6 (3)
C8—N3—N4—C10	0.6 (2)	C3—C6—C9—C8	130.3 (2)
N2—N1—C2—C3	0.6 (3)	N3—N4—C10—C9	−0.4 (2)
N2—N1—C2—C1	−179.2 (2)	N3—N4—C10—C11	179.19 (19)
N1—C2—C3—C4	−0.7 (2)	C8—C9—C10—N4	0.0 (2)
C1—C2—C3—C4	179.0 (2)	C6—C9—C10—N4	−179.2 (2)
N1—C2—C3—C6	179.8 (2)	C8—C9—C10—C11	−179.5 (2)
C1—C2—C3—C6	−0.4 (4)	C6—C9—C10—C11	1.3 (4)
N1—N2—C4—C3	−0.2 (2)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O10 ⁱⁱ	0.94	2.34	2.941 (2)	122
N2—H2 $\cdots$ O5 ⁱⁱ	0.94	2.05	2.852 (2)	143
N2—H2 $\cdots$ O8 ⁱⁱ	0.94	2.31	2.977 (2)	127
N3—H3 $\cdots$ O7 ⁱ	0.94	1.97	2.759 (2)	141
N4—H4 $\cdots$ O2	0.94	1.81	2.730 (2)	166

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