Redetermination of the crystal structure of 3,5-dimethylpyrazolium β-octamolybdate tetrahydrate

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The title compound, (C5H9N2)4[Mo8O26]·4H2O, was reported previously from a room-temperature data collection from which only the metal atoms could be refined anisotropically [FitzRoy et al. (1989). Inorg. Chim. Acta, 157, 187-194]. The current redetermination at 180(2) K models all the non-H atoms with anisotropic displacement parameters and fully describes the supramolecular H⋯O and O⋯O hydrogen-bonded network connecting the 3,5-dimethylpyrazolium cations, the water molecules of crystallization and the β-octamolybdate anion. All H atoms involved in the three-dimensional hydrogen-bonding network could be located from difference Fourier maps, with the exception of those of one disordered water molecule, firstly seen in this structural report [refined over two distinct locations with site-occupancy factors of 0.65 (2) and 0.35 (2)]. The complete β-octamolybdate anion is generated by a crystallographic inversion centre.

Keywords: crystal structure; 3,5 dimethylpyrazolium cations; octamolybdate(VI) anion; structure redetermination; hydrogen bonding network.

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1. Related literature

For the previous determination of the title compound at room temperature (Cambridge Structural Database refcode: JAMFEI), see: FitzRoy et al. (1989). For a description of the Cambridge Structural Database, see: Groom & Allen (2014). For previous studies investigating recovered molybdenum(VI) catalysts, see: Amarante et al. (2015); Lysenko et al. (2015).

2. Experimental

2.1. Crystal data

(C5H9N2)4[Mo8O26]·4H2O

M_r = 1644.15

Triclinic, P1

a = 10.1105 (9) Å  

b = 10.7469 (9) Å  

c = 11.9839 (10) Å  

α = 64.103 (3)°  

β = 84.272 (3)°  

γ = 75.826 (3)°  

V = 1135.67 (17) Å³

Z = 1

Mo Kα radiation

μ = 2.24 mm⁻¹

T = 180 K

0.20 × 0.14 × 0.01 mm

2.2. Data collection

Bruker D8 QUEST diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2001)

Tmin = 0.663, Tmax = 0.745

25625 measured reflections

3175 independent reflections

320 parameters

7 restraints

2.3. Refinement

R[F² > 2σ(F²)] = 0.026

wR(F²) = 0.056

S = 1.06

4141 reflections

71 restraints

Hydrogen bond geometry (Å, °).

Table 1

Hydrogen bond geometry (Å, °).

D−H⋯A  D−H  H⋯A  D⋯A  D−H⋯A

N1−H1···O2W⁴  0.94  1.77  2.689 (7)  164

N2−H2···O1W  0.95  1.84  2.776 (5)  171

N3−H3···O13⁴  0.95  2.28  2.869 (5)  120

N4−H4···O19  0.95  1.93  2.801 (4)  152

O1W−H1X···O5W⁴  0.95  1.88  2.785 (4)  160

O1W−H1Y···O3  0.94  1.91  2.848 (4)  172

Symmetry codes: (i) x, y, z + 1; (ii) x, y + 1, z + 1; (iii) x + 1, y + 1, z + 2.

Data collection: APEX2 (Bruker, 2012); cell refinement: SAINT (Bruker, 2012); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXL2014.

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Redetermination of the crystal structure of 3,5-dimethylpyrazolium $\beta$-octamolybdate tetrahydrate

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S1. Context and introduction

Research efforts in the development and application of new hybrid molybdenum(vi) heterogeneous catalysts require on a daily basis the recovery of used materials and their characterisation in the solid state to check for structural modifications of the employed compound (Amarante et al., 2015; Lysenko et al., 2015). Often, the use of drastic experimental conditions leads to the formation of secondary products, which crystallise in the medium as trace amounts of impurity compounds. It is, thus, imperative that most of these possible products are fully described in the solid state in the most accurate fashion.

The title compound, $(\text{C}_5\text{H}_9\text{N}_2)_4[\text{Mo}_8\text{O}_{26}]\cdot 4(\text{H}_2\text{O})$, was previously reported by FitzRoy et al. (1989). Besides the fact that the authors did not fully elucidate the hydrogen bonding network of this material (hydrogen atoms were placed geometrically) and that only the metallic centers could be refined anisotropically (from a room-temperature determination), the unit cell parameters reported in the main text and in the abstract do not match (viz. the $c$ axis length). A search and match at the Cambridge Structural Database (Groom et al., 2014) also seems to ignore the presence of Mo(VI) metal centers. In this context, we decided to recollect the crystal structure of the title compound at low temperature to fully elucidate its finer structural details.

S2. Structure description

The asymmetric unit of the title compound is composed of two 3,5-dimethylpyrazolium cations, $(\text{C}_5\text{H}_9\text{N}_2)^+$, one half of the $\beta$-octamolybdate anion, $\beta$-$[\text{Mo}_8\text{O}_{26}]^{4-}$, and two water molecules of crystallisation. Noteworthy, while one water molecule was fully located in its crystallographic position and even the associated hydrogen atoms found from difference Fourier maps, the other was found to be disordered over two distinct locations, O2W and O3W (Fig. 1). This feature was not disclosed in the previous structural determination by FitzRoy et al. (1989).

The molecular geometrical parameters for the $\beta$-octamolybdate anion are typical, exhibiting the usual four families of Mo—O bonds: Mo—Ot to terminal oxido groups [bond distances in the 1.691 (3)-1.715 (3) Å range]; Mo—Ob to $\mu_2$-bridging oxido groups [bond distances in the 1.754 (3)-2.268 (3) Å range]; Mo—Oc to $\mu_1$-bridging oxido groups [bond distances in the 1.953 (3)-2.351 (3) Å range]; Mo—Oc to $\mu_5$-bridging oxido groups [bond distances in the 2.146 (3)-2.435 (3) Å range]. The four crystallographically independent Mo(VI) metal centers are thus hexacoordinated in a typical $\{\text{MoO}_6\}$ fashion resembling highly distorted octahedra: while this trans internal O—Mo—O octahedral angles were found in the 145.29 (11)-173.17 (12)° range, the cis angles refined instead in the 70.01 (9)-105.85 (14)° interval. We note that 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 centers from the center of the octahedra.
The β-octamolybdate anion, located in the center of the unit cell, interacts with the remaining chemical species through a series of both electrostatic interactions and hydrogen bonds (Fig. 2). One crystallographically independent 3,5-dimethylpyrazolium cation donates both the hydrogen atoms bound to nitrogen to form two strong [D···A distances of 2.801 (4) and 2.869 (5) Å] and relatively directional [<(DHA) angles of 120 and 152°] charged N—H···O interactions with the polyoxoanion. The other cation has, however, a completely distinct behaviour: the same hydrogen atoms are instead donated in similar (strong and highly directional) interactions with neighbouring water molecules: while the D···A distances are 2.689 (7) and 2.776 (5) Å, the <(DHA) interaction angles are close to linearity, being 171 and 164°. The water molecules are instead interacting with the β-octamolybdate anion as depicted in both Figs. 1 and 2. Indeed, as depicted in Fig. 3 the water molecules play a decisive role in the overall crystal packing, acting as molecular fillers to effectively occupy the available space left from the arrangement of inorganic anions and organic cations.

S3. Synthesis and crystallization

All chemicals were purchased from commercial sources and used as received without additional purification steps.

A Teflon-lined stainless steel vessel was charged with a reaction mixture composed of MoO3 (0.34 g, 2.43 mmol), 3,5-dimethylpyrazole (0.11 g, 1.21 mmol) and water (ca. 25 mL) and heated in an oven at 160 °C for 26 h. The resultant blueish solid was filtered from the aqueous mother liquor and washed with an excess of water and (4×10 mL) diethyl ether, dried at ambient temperature and characterized in the solid state. Colourless plates of the title compound were directly harvested from the walls of the Teflon vessel.

Selected FT—IR (KBr, cm⁻¹): ų = 948 (vs), 910 (vs), 843 (s), 733 (s), 714 (s), 663 (s).

S4. Refinement details

Hydrogen atoms bound to carbon atoms were placed at idealized positions with C—H = 0.95 or 0.98 Å (for the aromatic and methyl groups, respectively), and included in the final structural model in riding-motion approximation with the isotropic thermal displacement parameters fixed at 1.2 or 1.5×\(U_{eq}\), respectively, of the carbon atom to which they are attached.

Hydrogen atoms associated with nitrogen atoms have been directly located from difference Fourier maps and were 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 the isotropic thermal displacement parameters fixed at 1.5×\(U_{eq}(N)\).

A total of two water molecules of crystallisation were directly located from difference Fourier maps. Though O1W was included in the final structural model by assuming full site occupancy and a typical anisotropic displacement behaviour, the second molecule was found to be disordered over two close crystallographic positions: O2W and O3W. These species were included in the structural model with linked site occupancy [which ultimately refined to 0.65 (2) and 0.35 (2), respectively] and by assuming an independent isotropic displacement behaviour. For O1W the two hydrogen atoms were markedly visible in difference Fourier maps and were included in the final model with the O—H and H···H distances restrained to 0.95 (1) and 1.55 (1) Å, respectively, in order to ensure a chemically reasonable geometry for this molecule. These hydrogen atoms were modelled with the isotropic thermal displacement parameters fixed at 1.5×\(U_{eq}(O1W)\).
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 green broken lines indicate N—H···O and O—H···O hydrogen-bonding interactions (see Table for geometrical details).
Figure 2
Crystal packing of the title compound viewed in perspective along the (a) [100] (b) [010] directions of the unit cell emphasising the supramolecular N—H···O and O—H···O hydrogen-bonding interactions (dashed green lines) interconnecting the three types of chemical species present in the crystal structure of the title compound.
Figure 3
Mixed polyhedral (for the $\beta$-octamolybdate anion), ball-and-stick (for the 3,5-dimethylpyrazolium cations) and space filling (for the water molecules of crystallisation) schematic representation of the crystal packing of the title compound viewed in perspective along the [100] direction of the unit cell. The Figure illustrates well how the inorganic component of the crystal structure is embedded into an organic matrix, with the entrapped water molecules of crystallization acting as molecular fillers interacting with the hybrid network through hydrogen bonds.

Tetrakis(3,5-dimethylpyrazolium) $\beta$-octamolybdate tetrahydrate

Crystal data

\[
\begin{align*}
(C_5H_9N_2)_4[Mo_8O_{26}] \cdot 4H_2O \\
M_r & = 1644.15 \\
\text{Triclinic, }P & \text{I} \\
a & = 10.1105 (9) \text{ Å} \\
b & = 10.7469 (9) \text{ Å} \\
c & = 11.9839 (10) \text{ Å} \\
\alpha & = 64.103 (3)^\circ \\
\beta & = 84.272 (3)^\circ \\
\gamma & = 75.826 (3)^\circ \\
V & = 1135.67 (17) \text{ Å}^3 \\
Z & = 1 \\
F(000) & = 796 \\
D_c & = 2.404 \text{ Mg m}^{-3} \\
\text{Mo }K\alpha \text{ radiation, } \lambda & = 0.71073 \text{ Å} \\
\text{Cell parameters from 9938 reflections} \\
\theta & = 2.6–25.4^\circ \\
\mu & = 2.24 \text{ mm}^{-1} \\
T & = 180 \text{ K} \\
\text{Plate, colourless} \\
\end{align*}
\]

Data collection

\[
\begin{align*}
\text{Bruker D8 QUEST diffractometer} \\
\text{Sealed tube} \\
\text{Multi-layer X-ray mirror monochromator} \\
\text{Detector resolution: 10.4167 pixels mm}^{-1} \\
\omega / \phi \text{ scans} \\
\text{Absorption correction: multi-scan} \\
\text{SADABS; Bruker, 2001} \\
T_{\text{min}} = 0.663, T_{\text{max}} = 0.745 \\
25625 \text{ measured reflections} \\
4141 \text{ independent reflections} \\
3175 \text{ reflections with } I > 2\sigma(I) \\
R_{\text{int}} = 0.042 \\
\theta_{\text{min}} = 25.4^\circ, \theta_{\text{max}} = 3.7^\circ \\
h = -12 \rightarrow 12 \\
k = -12 \rightarrow 12 \\
l = -14 \rightarrow 14
\end{align*}
\]
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.056$
$S = 1.06$

4141 reflections
320 parameters
7 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0188P)^2 + 2.2481P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.70$ e Å$^{-3}$
$\Delta\rho_{\text{min}} = -0.54$ e Å$^{-3}$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| Atom | x     | y     | z     | $U_{eq}$ | Occ. (<1) |
|------|-------|-------|-------|----------|-----------|
| Mo1  | 0.44983 (3) | 0.44979 (4) | 0.75253 (3) | 0.01430 (9) |          |
| Mo2  | 0.45658 (3) | 0.68126 (4) | 0.47103 (3) | 0.01229 (9) |          |
| Mo3  | 0.23903 (3) | 0.56541 (4) | 0.38528 (3) | 0.01415 (9) |          |
| Mo4  | 0.23047 (3) | 0.32798 (4) | 0.67012 (3) | 0.01511 (9) |          |
| O1   | 0.3753 (3) | 0.4944 (3) | 0.5589 (2) | 0.0142 (6) |          |
| O2   | 0.3635 (3) | 0.3005 (3) | 0.7899 (2) | 0.0177 (6) |          |
| O3   | 0.5489 (3) | 0.3881 (3) | 0.8808 (3) | 0.0235 (7) |          |
| O4   | 0.5539 (3) | 0.5839 (3) | 0.6298 (2) | 0.0145 (6) |          |
| O5   | 0.3166 (3) | 0.5748 (3) | 0.7683 (3) | 0.0208 (7) |          |
| O6   | 0.5740 (3) | 0.7845 (3) | 0.3880 (2) | 0.0168 (6) |          |
| O7   | 0.3838 (3) | 0.6770 (3) | 0.3281 (2) | 0.0153 (6) |          |
| O8   | 0.3261 (3) | 0.7924 (3) | 0.5040 (3) | 0.0190 (6) |          |
| O9   | 0.1894 (3) | 0.5797 (3) | 0.2484 (3) | 0.0232 (7) |          |
| O10  | 0.1936 (3) | 0.3896 (3) | 0.4970 (2) | 0.0160 (6) |          |
| O11  | 0.1191 (3) | 0.6842 (3) | 0.4197 (3) | 0.0220 (7) |          |
| O12  | 0.1720 (3) | 0.1773 (3) | 0.7422 (3) | 0.0255 (7) |          |
| O13  | 0.1090 (3) | 0.4568 (3) | 0.6928 (3) | 0.0213 (7) |          |
| N1   | 0.7819 (4) | 0.8121 (5) | 0.9458 (3) | 0.0294 (9) |          |
| H1   | 0.865 (3) | 0.747 (4) | 0.979 (4) | 0.044* |          |
| N2   | 0.6839 (4) | 0.7657 (4) | 0.9163 (4) | 0.0281 (9) |          |
| H2   | 0.692 (5) | 0.6692 (19) | 0.934 (5) | 0.042* |          |
| N3   | -0.0378 (4) | 0.2498 (4) | 0.3524 (4) | 0.0295 (9) |          |
| H3   | -0.116 (3) | 0.314 (4) | 0.362 (5) | 0.044* |          |
| N4   | 0.0827 (4) | 0.2507 (4) | 0.3913 (4) | 0.0289 (9) |          |
| H4   | 0.090 (5) | 0.314 (4) | 0.425 (4) | 0.043* |          |
| C1   | 0.8229 (6) | 1.0327 (6) | 0.9381 (5) | 0.0491 (15) |          |
| H1A  | 0.8535 | 0.9870 | 1.0247 | 0.074* |          |
| H1B  | 0.7696 | 1.1293 | 0.9183 | 0.074* |          |
| H1C  | 0.9023 | 1.0365 | 0.8837 | 0.074* |          |
| C2   | 0.7364 (5) | 0.9494 (5) | 0.9191 (4) | 0.0319 (11) |          |
| Atom | Coordinates (Å) | Atomic displacement parameters (Å²) |
|------|-----------------|-----------------------------------|
| C3   | 0.6048 (5)      | 0.9913 (5) 0.8718 (4) 0.0316 (11) |
| H3A  | 0.5471          | 1.0837 0.8443 0.038*               |
| C4   | 0.5743 (5)      | 0.8733 (5) 0.8726 (4) 0.0312 (11) |
| C5   | 0.4486 (5)      | 0.8533 (6) 0.8341 (5) 0.0420 (14) |
| H5A  | 0.4728          | 0.7778 0.8058 0.063*               |
| H5B  | 0.4035          | 0.9420 0.7663 0.063*               |
| H5C  | 0.3866          | 0.8271 0.9047 0.063*               |
| C6   | −0.1363 (5)     | 0.1101 (5) 0.2791 (5) 0.0329 (12) |
| H6A  | −0.2222         | 0.1413 0.3150 0.049*               |
| H6B  | −0.1209         | 0.0082 0.3021 0.049*               |
| H6C  | −0.1412         | 0.1624 0.1885 0.049*               |
| C7   | −0.0218 (4)     | 0.1381 (5) 0.3270 (4) 0.0208 (10) |
| C8   | 0.1130 (4)      | 0.0663 (5) 0.3502 (4) 0.0225 (10) |
| H8   | 0.1545          | −0.0174 0.3399 0.027*              |
| C9   | 0.1768 (4)      | 0.1398 (5) 0.3917 (4) 0.0208 (10) |
| C10  | 0.3202 (4)      | 0.1135 (5) 0.4290 (5) 0.0303 (11) |
| H10A | 0.3497          | 0.2034 0.3936 0.045*               |
| H10B | 0.3787          | 0.0479 0.3983 0.045*               |
| H10C | 0.3268          | 0.0717 0.5196 0.045*               |
| O1W  | 0.7299 (3)      | 0.4764 (4) 0.9840 (3) 0.0276 (7)  |
| H1X  | 0.711 (5)       | 0.439 (5) 1.0698 (12) 0.041*      |
| H1Y  | 0.676 (4)       | 0.449 (5) 0.943 (3) 0.041*        |
| O2W  | 0.9897 (6)      | 0.5952 (10) 0.0682 (5) 0.031 (2)* |
| O3W  | 1.0101 (11)     | 0.6562 (19) 0.0507 (10) 0.033 (4)* |

Atomic displacement parameters (Å²)

|        | U¹¹   | U²²   | U³³   | U¹²   | U¹³   | U²³   |
|--------|-------|-------|-------|-------|-------|-------|
| Mo1    | 0.01445 (18) | 0.0179 (2) | 0.01272 (18) | −0.00473 (15) | 0.00061 (14) | −0.00798 (16) |
| Mo2    | 0.01153 (18) | 0.01158 (19) | 0.01458 (18) | −0.00190 (14) | −0.00116 (14) | −0.00643 (15) |
| Mo3    | 0.01088 (18) | 0.0166 (2) | 0.01578 (19) | −0.00309 (15) | −0.00217 (14) | −0.00718 (16) |
| Mo4    | 0.01333 (18) | 0.0163 (2) | 0.01719 (19) | −0.00532 (15) | 0.00086 (14) | −0.00759 (16) |
| O1     | 0.0124 (14) | 0.0157 (15) | 0.0150 (14) | −0.0038 (12) | 0.0002 (11) | −0.0069 (12) |
| O2     | 0.0179 (15) | 0.0185 (16) | 0.0157 (14) | −0.0065 (12) | 0.0021 (12) | −0.0055 (13) |
| O3     | 0.0232 (16) | 0.0307 (19) | 0.0185 (16) | −0.0101 (14) | −0.0013 (13) | −0.0100 (14) |
| O4     | 0.0142 (14) | 0.0157 (15) | 0.0179 (15) | −0.0041 (12) | −0.0013 (11) | −0.0104 (13) |
| O5     | 0.0194 (15) | 0.0228 (17) | 0.0223 (16) | −0.0053 (13) | 0.0038 (13) | −0.0122 (14) |
| O6     | 0.0184 (15) | 0.0146 (15) | 0.0171 (15) | −0.0040 (12) | −0.0022 (12) | −0.0058 (13) |
| O7     | 0.0128 (14) | 0.0170 (16) | 0.0150 (14) | −0.0024 (12) | −0.0010 (11) | −0.0060 (12) |
| O8     | 0.0186 (15) | 0.0155 (16) | 0.0227 (16) | −0.0007 (12) | −0.0028 (12) | −0.0091 (13) |
| O9     | 0.0201 (16) | 0.0316 (19) | 0.0194 (16) | −0.0067 (14) | −0.0042 (13) | −0.0110 (14) |
| O10    | 0.0146 (14) | 0.0169 (16) | 0.0199 (15) | −0.0045 (12) | −0.0005 (12) | −0.0010 (13) |
| O11    | 0.0159 (15) | 0.0214 (17) | 0.0273 (17) | −0.0002 (13) | −0.0014 (13) | −0.0110 (14) |
| O12    | 0.0243 (16) | 0.0219 (17) | 0.0313 (18) | −0.0108 (14) | 0.0025 (14) | −0.0099 (15) |
| O13    | 0.0171 (15) | 0.0227 (17) | 0.0232 (16) | −0.0038 (13) | 0.0018 (13) | −0.0098 (14) |
| N1     | 0.023 (2) | 0.038 (3) | 0.022 (2) | −0.0038 (19) | −0.0028 (17) | −0.0087 (19) |
| N2     | 0.027 (2) | 0.029 (2) | 0.024 (2) | −0.0071 (19) | −0.0013 (17) | −0.0067 (19) |
| N3     | 0.020 (2) | 0.029 (2) | 0.046 (3) | 0.0003 (17) | 0.0004 (18) | −0.026 (2) |
### Geometric parameters (Å, °)

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| N4 | 0.026 (2) | 0.031 (2) | 0.041 (2) | -0.0094 (18) | 0.0027 (18) | -0.026 (2) |
| C1 | 0.061 (4) | 0.053 (4) | 0.039 (3) | -0.024 (3) | -0.005 (3) | -0.017 (3) |
| C2 | 0.036 (3) | 0.035 (3) | 0.020 (2) | -0.010 (2) | 0.004 (2) | -0.007 (2) |
| C3 | 0.032 (3) | 0.025 (3) | 0.025 (3) | -0.002 (2) | -0.001 (2) | -0.001 (2) |
| C4 | 0.027 (3) | 0.033 (3) | 0.022 (2) | -0.004 (2) | -0.002 (2) | -0.001 (2) |
| C5 | 0.028 (3) | 0.046 (4) | 0.036 (3) | -0.011 (2) | -0.006 (2) | 0.000 (3) |
| C6 | 0.024 (3) | 0.035 (3) | 0.050 (3) | -0.003 (3) | -0.008 (2) | -0.027 (3) |
| C7 | 0.021 (2) | 0.020 (2) | 0.026 (2) | -0.0049 (19) | 0.0010 (18) | -0.014 (2) |
| C8 | 0.023 (2) | 0.024 (3) | 0.026 (2) | -0.0022 (19) | -0.0022 (19) | -0.017 (2) |
| C9 | 0.022 (2) | 0.024 (2) | 0.019 (2) | -0.0054 (19) | 0.0015 (18) | -0.011 (2) |
| C10 | 0.025 (2) | 0.030 (3) | 0.043 (3) | -0.006 (2) | -0.005 (2) | -0.021 (2) |
| O1W | 0.0298 (18) | 0.036 (2) | 0.0240 (17) | -0.0078 (15) | -0.0003 (14) | -0.0192 (16) |

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**Acta Cryst.** (2015). E71, m244 m245  
**sup-8**
| Bond                  | Angle (°) (RMS) |
|----------------------|----------------|
| O3—Mo1—O5           | 104.71 (14)    |
| O3—Mo1—O2           | 102.12 (13)    |
| O5—Mo1—O2           | 100.72 (13)    |
| O3—Mo1—O4           | 99.75 (12)     |
| O5—Mo1—O4           | 97.01 (13)     |
| O2—Mo1—O4           | 147.18 (11)    |
| O3—Mo1—O7i          | 89.69 (12)     |
| O5—Mo1—O7i          | 163.56 (12)    |
| O2—Mo1—O7i          | 83.57 (11)     |
| O4—Mo1—O7i          | 72.34 (10)     |
| O3—Mo1—O1           | 161.88 (12)    |
| O5—Mo1—O1           | 93.03 (11)     |
| O2—Mo1—O1           | 77.65 (10)     |
| O4—Mo1—O1           | 74.01 (10)     |
| O7i—Mo1—O1          | 72.23 (9)      |
| O3—Mo1—Mo2          | 134.82 (10)    |
| O5—Mo1—Mo2          | 84.85 (10)     |
| O2—Mo1—Mo2          | 119.63 (8)     |
| O4—Mo1—Mo2          | 35.14 (7)      |
| O7i—Mo1—Mo2         | 79.31 (7)      |
| O1—Mo1—Mo2          | 41.99 (7)      |
| O8—Mo2—O6           | 105.54 (13)    |
| O8—Mo2—O7           | 101.63 (12)    |
| O6—Mo2—O7           | 96.27 (12)     |
| O8—Mo2—O4           | 99.93 (12)     |
| O6—Mo2—O4           | 97.02 (11)     |
| O7—Mo2—O4           | 150.55 (11)    |
| O8—Mo2—O1           | 97.27 (12)     |
| O6—Mo2—O1           | 157.19 (11)    |
| O7—Mo2—O1           | 78.87 (10)     |
| O4—Mo2—O1           | 78.71 (10)     |
| O8—Mo2—O1i          | 173.17 (12)    |
| O6—Mo2—O1i          | 81.21 (11)     |
| O7—Mo2—O1i          | 78.31 (10)     |
| O4—Mo2—O1i          | 77.92 (10)     |
| O1—Mo2—O1i          | 75.99 (10)     |
| O8—Mo2—Mo1          | 88.75 (10)     |
| O6—Mo2—Mo1          | 132.75 (9)     |
| O7—Mo2—Mo1          | 125.17 (8)     |
| O4—Mo2—Mo1          | 35.73 (8)      |
| O1—Mo2—Mo1          | 46.33 (7)      |
| O1i—Mo2—Mo1         | 85.79 (7)      |
| O8—Mo2—Mo3          | 89.31 (9)      |
| O6—Mo2—Mo3          | 132.20 (9)     |
| O7—Mo2—Mo3          | 35.93 (8)      |
| O4—Mo2—Mo3          | 125.36 (8)     |
| O1—Mo2—Mo3          | 46.65 (7)      |

*Acta Cryst. (2015). E71, m244 m245*
O1 — Mo2 — Mo3 86.76 (6)  C2 — C3 — H3A 126.7
Mo1 — Mo2 — Mo3 91.724 (14)  N2 — C4 — C3 107.8 (4)
O9 — Mo3 — O11 105.85 (14)  N2 — C4 — C5 121.2 (5)
O9 — Mo3 — O10 100.45 (13)  C3 — C4 — C5 130.9 (5)
O11 — Mo3 — O10 101.76 (13)  C4 — C5 — H5A 109.5
O9 — Mo3 — O7 100.71 (12)  C4 — C5 — H5B 109.5
O11 — Mo3 — O7 97.58 (12)  H5A — C5 — H5B 109.5
O10 — Mo3 — O7 146.06 (11)  C4 — C5 — H5C 109.5
O9 — Mo3 — O1 159.60 (12)  H5A — C5 — H5C 109.5
O11 — Mo3 — O1 94.36 (12)  H5B — C5 — H5C 109.5
O10 — Mo3 — O1 77.54 (10)  H6A — C6 — H6B 109.5
O7 — Mo3 — O1 73.40 (10)  C7 — C6 — H6A 109.5
O9 — Mo3 — O4i 88.84 (12)  C7 — C6 — H6B 109.5
O11 — Mo3 — O4i 163.17 (11)  C7 — C6 — H6C 109.5
O10 — Mo3 — O4i 83.12 (10)  H6A — C6 — H6C 109.5
O7 — Mo3 — O4i 71.11 (10)  C7 — C6 — H6C 109.5
O1 — Mo3 — O4i 70.77 (9)  N3 — C7 — C8 107.4 (4)
O9 — Mo3 — Mo2 135.69 (10)  N3 — C7 — C6 121.8 (4)
O11 — Mo3 — Mo2 85.49 (10)  C8 — C7 — C6 130.8 (4)
O10 — Mo3 — Mo2 119.34 (8)  C7 — C8 — C9 126.5
O7 — Mo3 — Mo2 35.00 (7)  C9 — C8 — H8 126.5
O1 — Mo3 — Mo2 41.81 (7)  C7 — C8 — C9 126.5
O4i — Mo3 — Mo2 78.16 (6)  C9 — C8 — C9 106.9 (4)
O12 — Mo4 — O13 105.75 (14)  N4 — C9 — C10 121.9 (4)
O12 — Mo4 — O10 103.91 (13)  C8 — C9 — C10 131.2 (4)
O13 — Mo4 — O10 97.77 (13)  C9 — C10 — H10A 109.5
O12 — Mo4 — O2 101.63 (13)  C9 — C10 — H10B 109.5
O13 — Mo4 — O2 97.49 (13)  H10A — C10 — H10B 109.5
O10 — Mo4 — O2 145.29 (11)  C9 — C10 — H10C 109.5
O12 — Mo4 — O6i 92.59 (12)  H10A — C10 — H10C 109.5
O13 — Mo4 — O6i 161.61 (12)  H10B — C10 — H10C 109.5
O10 — Mo4 — O6i 78.80 (10)  H1X — O1W — H1Y 109.9 (16)
O2 — Mo4 — O6i 76.95 (11)

O3 — Mo1 — O2 — Mo4 177.15 (15)  N2 — N1 — C2 — C1 −178.3 (4)
O5 — Mo1 — O2 — Mo4 69.40 (17)  N1 — C2 — C3 — C4 0.4 (5)
O4 — Mo1 — O2 — Mo4 −52.1 (3)  C1 — C2 — C3 — C4 179.0 (5)
O7i — Mo1 — O2 — Mo4 −94.55 (15)  N1 — N2 — C4 — C3 1.4 (5)
O1 — Mo1 — O2 — Mo4 −21.39 (13)  N1 — N2 — C4 — C5 −179.1 (4)
Mo2 — Mo1 — O2 — Mo4 −20.75 (18)  C2 — C3 — C4 — N2 −1.1 (5)
O8 — Mo2 — O6 — Mo4i 178.38 (13)  C2 — C3 — C4 — C5 179.4 (5)
O7 — Mo2 — O6 — Mo4i −77.67 (14)  N4 — N3 — C7 — C8 −0.1 (5)
O4 — Mo2 — O6 — Mo4i 75.99 (14)  N4 — N3 — C7 — C6 −178.6 (4)
O1 — Mo2 — O6 — Mo4i −1.5 (4)  N3 — C7 — C8 — C9 0.4 (5)
O1i — Mo2 — O6 — Mo4i −0.57 (12)  C6 — C7 — C8 — C9 178.7 (5)
Mo1 — Mo2 — O6 — Mo4i 75.31 (16)  N3 — N4 — C9 — C8 0.5 (5)
Mo3 — Mo2 — O6 — Mo4i −78.01 (15)  N3 — N4 — C9 — C10 179.3 (4)
C2 — N1 — N2 — C4 −1.1 (5)  C7 — C8 — C9 — N4 −0.6 (5)
C7—N3—N4—C9  
C7—C8—C9—C10  
N2—N1—C2—C3

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

Hydrogen bond geometry (Å, °)

| D—H | D—H | H···A | D···A | D—H···A |
|-----|-----|------|------|---------|
| N1—H1···O2\(ii\) | 0.94 | 1.77 | 2.689 (7) | 164 |
| N2—H2···O1\(i\) | 0.95 | 1.84 | 2.776 (5) | 171 |
| N3—H3···O13\(iii\) | 0.95 | 2.28 | 2.869 (5) | 120 |
| N4—H4···O10 | 0.95 | 1.93 | 2.801 (4) | 152 |
| O1\(\bar{W}\)—H1\(X\)···O5\(iv\) | 0.95 | 1.88 | 2.785 (4) | 160 |
| O1\(\bar{W}\)—H1\(Y\)···O3 | 0.94 | 1.91 | 2.848 (4) | 172 |

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