

(1,4,7,10-Tetraazacyclododecane- $\kappa^4N^1,N^4,N^7,N^{10}$)(tetraoxido-molybdate- κO)copper(II) monohydrate

Dorothea Rohde and Kurt Merzweiler*

 Institut für Chemie, Naturwissenschaftliche Fakultät II, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Strasse 2, 06120 Halle, Germany
 Correspondence e-mail: kurt.merzweiler@chemie.uni-halle.de

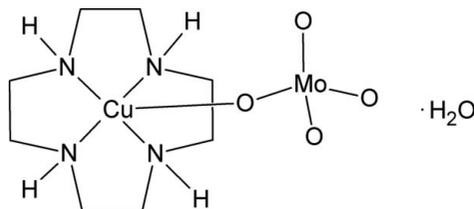
Received 11 June 2010; accepted 1 July 2010

 Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.024; wR factor = 0.063; data-to-parameter ratio = 15.4.

In the title compound, $[CuMoO_4(C_8H_{20}N_4)] \cdot H_2O$, the Cu^{II} atom is coordinated by four N atoms of the 1,4,7,10-tetraazacyclododecane (cyclen) ligand and one O atom of the molybdate unit in a distorted square-pyramidal environment. The water molecules are linked to the complex unit to form centrosymmetric dimers $[R_4^4(12)$ and $R_4^4(16)]$ and discrete $D_3^2(9)$, $D_3^3(11)$ and $D_3^3(13)$ chains by $O-H \cdots O$ and $N-H \cdots O$ interactions. Additionally, the complex molecules are linked into $C_4^4(18)$ chain motifs by $N-H \cdots O$ interactions. As a result [(cyclen) $CuMoO_4$] units and water molecules are linked to layers that are oriented parallel to the ac plane. The stacking of the layers in the b -axis direction is supported by weak $C-H \cdots O$ hydrogen bridges.

Related literature

For inorganic-organic hybrid materials based on copper complexes with bridging molybdate ligands, see, for example: Rarig *et al.* (2002); Hagrman *et al.* (1998). For copper complexes with the cyclen ligand, see: Clay *et al.* (1979); Lu *et al.* (1997); Yeung *et al.* (2000); Guo *et al.* (2008). For related literature, see: Bernstein *et al.* (1995); Choi *et al.* (2004).



Experimental

Crystal data

 $[CuMoO_4(C_8H_{20}N_4)] \cdot H_2O$
 $M_r = 413.78$

 Triclinic, $P\bar{1}$
 $a = 8.6985$ (6) Å

 $b = 8.9784$ (6) Å
 $c = 9.0055$ (6) Å
 $\alpha = 90.358$ (6)°
 $\beta = 91.949$ (6)°
 $\gamma = 100.742$ (5)°
 $V = 690.54$ (8) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 2.47$ mm⁻¹
 $T = 200$ K
 $0.22 \times 0.21 \times 0.13$ mm

Data collection

 Stoe IPDS 2T diffractometer
 Absorption correction: numerical
 ($X-RED$; Stoe & Cie, 2009)
 $T_{min} = 0.612$, $T_{max} = 0.737$

 9700 measured reflections
 3017 independent reflections
 2788 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.037$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.063$
 $S = 1.04$
 3017 reflections
 196 parameters
 6 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.48$ e Å⁻³
 $\Delta\rho_{min} = -1.05$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O5-H5 \cdots O4^i$	0.83 (2)	1.95 (2)	2.770 (2)	169 (3)
$N1-H1 \cdots O5^{ii}$	0.86 (2)	2.35 (2)	3.156 (3)	156 (3)
$N2-H2 \cdots O1^{ii}$	0.89 (2)	2.19 (2)	2.949 (2)	143 (3)
$N3-H3 \cdots O4^i$	0.88 (2)	2.28 (3)	2.955 (3)	133 (3)
$N4-H4 \cdots O5^{iii}$	0.88 (2)	2.10 (2)	2.928 (3)	157 (3)
$O5-H6 \cdots O2^{iv}$	0.84 (2)	1.85 (2)	2.666 (3)	163 (4)
$C3-H3B \cdots O3^v$	0.99	2.36	3.345 (3)	175

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

Data collection: $X-AREA$ (Stoe & Cie, 2009); cell refinement: $X-AREA$; data reduction: $X-RED$ (Stoe & Cie, 2009); program(s) used to solve structure: $SHELXS97$ (Sheldrick, 2008); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 2008); molecular graphics: $DIAMOND$ (Brandenburg, 2009); software used to prepare material for publication: $SHELXL97$ and $PLATON$ (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2287).

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brandenburg, K. (2009). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Choi, K.-Y., Whang, M.-A., Lee, H.-H., Lee, K.-C. & Kim, M.-J. (2004). *Transition Met. Chem.* **29**, 792–796.
- Clay, R., Murray-Rust, P. & Murray-Rust, J. (1979). *Acta Cryst.* **B35**, 1894–1895.
- Guo, J.-F., Yeung, W.-F., Gao, S., Lee, G.-H., Peng, S.-M., Lam, M. H.-W. & Lau, T.-C. (2008). *Eur. J. Inorg. Chem.* pp. 158–163.
- Hagrman, D., Warren, C. J., Haushalter, R. C., Seip, C., O'Connor, C. J., Rarig, R. S., Johnson, K. M., LaDuca, R. L. & Zubietta, J. (1998). *Chem. Mater.* **10**, 3294–3297.
- Lu, T.-H., Lin, J.-L., Lan, W.-J. & Chung, C.-S. (1997). *Acta Cryst.* **C53**, 1598–1600.
- Rarig, R. S., Lam, R., Zavalij, P. Y., Ngala, J. K., LaDuca, R. L., Greedan, J. E. & Zubietta, J. (2002). *Inorg. Chem.* **41**, 2124–2133.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (2009). $X-AREA$ and $X-RED$. Stoe & Cie, Darmstadt, Germany.
- Yeung, W.-F., Wong, W.-T., Zuo, J.-L. & Lau, T.-C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 629–631.

supplementary materials

Acta Cryst. (2010). E66, m894 [doi:10.1107/S1600536810026000]

(1,4,7,10-Tetraazacyclododecane- $\kappa^4N^1,N^4,N^7,N^{10}$)(tetraoxido-molybdate- κO)copper(II) mono-hydrate

D. Rohde and K. Merzweiler

Comment

In the title compound (I) the central copper atom is coordinated by four nitrogen atoms of the cyclen ligand and one oxygen atom of the molybdate group. This leads to a distorted square pyramidal coordination environment with the four N atoms in the basal positions and the molybdate oxygen atom at the apex. The arrangement of the four nitrogen atoms is nearly co-planar within a maximum deviation of 0.015 Å and the copper atom lies 0.569 Å above this plane. The Cu—N distances ranging from 2.033 (2) to 2.049 (2) Å which is comparable to the Cu—N bond lengths observed in other cyclen copper complexes, like [(cyclen)Cu(NO₃)]NO₃ (Clay *et al.*, 1979), [(cyclen)Cu(SCN)]₂[Ca(NCS)₆] H₂O (Lu *et al.*, 1997), [(cyclen)Cu(Ag(CN)₂)] [Ag(CN)₂] (Yeung *et al.*, 2000) and [(cyclen)Cu(MnN(CN)₅)] (Guo *et al.*, 2008). The molybdate unit coordinates as a monodentate ligand with a Cu—O distance of 2.104 (2) Å. The Mo—O distances ranging from 1.749 to 1.765 Å for the terminal oxygen atoms. In the case of the μ -bridging O atom O1 the Mo—O distance is slightly enlarged to 1.796 (2) Å. A similar monodentate coordination of molybdate has been observed in the copper complex [LCuMoO₄]₂ 5H₂O ($L = 1,3,10, 12,16,19$ -hexaazatetracyclo[17,3,1,1^{12,16},0^{4,9}]tetracosane with Cu—O distances of 2.320 (12) and 2.418 (11) Å and Mo—O distances ranging from 1.621 to 1.849 Å (Choi *et al.*, 2004).

Compound (I) contains a water molecule which is involved into two strong hydrogen bonds to the molybdate O2 and O4 oxygen atoms. This leads to [(cyclen)CuMoO₄]₂(H₂O)₂ dimers containing a centrosymmetric Mo₂O₆H₄ ring of the type $R_4^4(12)$ (Fig. 2) (Bernstein *et al.*, 1995). Additionally the NH groups of the cyclen ligand are also involved in hydrogen bonds either to water molecules (N1H1 and N4H4) or to molybdate groups (N2H2 and N3H3). As a result of these hydrogen bonds [(cyclen)CuMoO₄] units and water are interlinked to layers which are oriented parallel to the crystallographic *a*-*c* plane. The stacking of the layers in direction of the crystallographic *b* axis is supported by weak C—H \cdots O hydrogen bonds (C \cdots O 3.35 Å) between cyclen ligands and molybdate units.

Experimental

To a stirred suspension of 0.440 mg (2.0 mmol) CuMoO₄ in 70 ml of aqueous methanol (90%) 0.350 mg (2.0 mmol) cyclen was added. After four hours the blue suspension was filtered and the filtrate evaporated to dryness. Yield. 420 mg (50%). The residue was dissolved in 3 ml of methanol and then the solution was layered with 2-propanol. After one week single crystals of (I) were formed at the methanol/2-propanol interface. IR (cm⁻¹): 3172(s), 2960(w), 2937(w), 2920(w), 2869(w), 1631(w), 1592(w), 824(s); Elemental Analysis [Cu(cyclen)MoO₄] H₂O (413.78), C 23.0 (calc. 23.2), H 5.4 (5.4), N 13.1 (13.5) %.

Refinement

C-bound H atoms of the cyclen ligand were positioned geometrically and refined using a riding model with $U_{iso}(H) = 1.2 U_{eq}(C)$ [(C-H) = 0.99 Å]. H atoms attached to N and O were located from difference fourier maps and refined with N-H

supplementary materials

distances fixed in a range of 0.87 (2) to 0.89 (2) Å and O-H distances fixed at 0.83 (2) and 0.84 (2) Å. The corresponding $U_{\text{iso}}(\text{H})$ were refined freely.

Figures

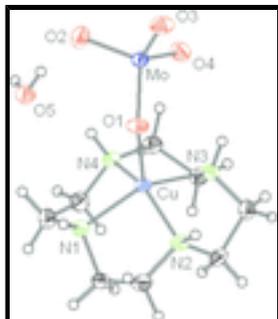


Fig. 1. Molecular structure of the [(cyclen)CuMoO₄] unit. Thermal ellipsoids are drawn at the 50% probability level.

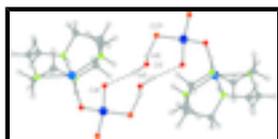


Fig. 2. [(cyclen)CuMoO₄]₂(H₂O)₂ dimers formed by hydrogen bonds. Symmetry codes: (i) 1 - x, 1 - y, 1 - z; (iv) x, y, -1 + z

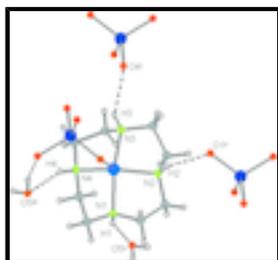


Fig. 3. N—H...O hydrogen bonds around the [(cyclen)CuMoO₄] unit. Symmetry codes (i) 1 - x, 1 - y, 1 - z; (ii) 2 - x, 1 - y, 1 - z; (iii) x, y, 1 + z

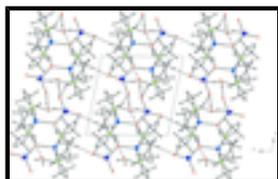


Fig. 4. Stacking of the [(cyclen)CuMoO₄]H₂O layers along the crystallographic *b* axis.

(1,4,7,10-Tetraazacyclododecane- $\kappa^4 N^1, N^4, N^7, N^{10}$)(tetraoxidomolybdate- κO)copper(II) monohydrate

Crystal data

[CuMoO₄(C₈H₂₀N₄)]·H₂O

$M_r = 413.78$

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

$a = 8.6985$ (6) Å

$b = 8.9784$ (6) Å

$c = 9.0055$ (6) Å

$\alpha = 90.358$ (6)°

$\beta = 91.949$ (6)°

$\gamma = 100.742$ (5)°

$Z = 2$

$F(000) = 418$

$D_x = 1.990$ Mg m⁻³

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

Cell parameters from 16326 reflections

$\theta = 3.0$ – 29.6 °

$\mu = 2.47$ mm⁻¹

$T = 200$ K

Plate, blue

$0.22 \times 0.21 \times 0.13$ mm

$$V = 690.54 (8) \text{ \AA}^3$$

Data collection

Stoe IPDS 2T diffractometer	3017 independent reflections
Radiation source: fine-focus sealed tube graphite	2788 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{\text{int}} = 0.037$
rotation method scans	$\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 2009)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.612$, $T_{\text{max}} = 0.737$	$k = -11 \rightarrow 11$
9700 measured reflections	$l = -11 \rightarrow 10$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.063$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.2037P]$
3017 reflections	where $P = (F_o^2 + 2F_c^2)/3$
196 parameters	$(\Delta/\sigma)_{\text{max}} = 0.002$
6 restraints	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
0 constraints	$\Delta\rho_{\text{min}} = -1.05 \text{ e \AA}^{-3}$

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.0572 (3)	0.1738 (3)	0.7826 (3)	0.0250 (4)
H1B	0.9796	0.0794	0.7636	0.030*

supplementary materials

H1A	1.1463	0.1485	0.8422	0.030*
C2	1.1135 (3)	0.2435 (3)	0.6371 (3)	0.0262 (5)
H2B	1.2008	0.3300	0.6565	0.031*
H2A	1.1523	0.1675	0.5757	0.031*
C3	0.8796 (3)	0.1769 (2)	0.4653 (2)	0.0226 (4)
H3B	0.8488	0.0845	0.5248	0.027*
H3A	0.9349	0.1504	0.3775	0.027*
C4	0.7365 (3)	0.2401 (3)	0.4169 (3)	0.0264 (5)
H4B	0.7672	0.3273	0.3506	0.032*
H4A	0.6610	0.1614	0.3615	0.032*
C5	0.5518 (3)	0.1652 (2)	0.6197 (3)	0.0227 (4)
H5B	0.5989	0.0732	0.6275	0.027*
H5A	0.4539	0.1403	0.5579	0.027*
C6	0.5167 (3)	0.2183 (3)	0.7734 (3)	0.0246 (5)
H6B	0.4571	0.3019	0.7645	0.030*
H6A	0.4521	0.1338	0.8261	0.030*
C7	0.7290 (3)	0.1527 (3)	0.9414 (3)	0.0272 (5)
H7B	0.7284	0.0635	0.8761	0.033*
H7A	0.6640	0.1198	1.0277	0.033*
C8	0.8955 (3)	0.2202 (3)	0.9938 (3)	0.0289 (5)
H8B	0.8945	0.3004	1.0695	0.035*
H8A	0.9460	0.1405	1.0393	0.035*
N1	0.9846 (2)	0.2852 (2)	0.8642 (2)	0.0224 (4)
H1	1.060 (3)	0.356 (3)	0.895 (3)	0.027 (7)*
N2	0.9827 (2)	0.2966 (2)	0.5561 (2)	0.0214 (4)
H2	1.023 (3)	0.370 (3)	0.494 (3)	0.028 (7)*
N3	0.6625 (2)	0.2895 (2)	0.5510 (2)	0.0216 (4)
H3	0.616 (3)	0.365 (3)	0.526 (4)	0.036 (8)*
N4	0.6657 (2)	0.2715 (2)	0.8587 (2)	0.0218 (4)
H4	0.650 (4)	0.339 (3)	0.924 (3)	0.032 (8)*
O1	0.86208 (19)	0.58802 (17)	0.7174 (2)	0.0254 (3)
O2	0.6912 (2)	0.7196 (2)	0.9423 (2)	0.0353 (4)
O3	0.7520 (2)	0.87043 (18)	0.6678 (2)	0.0310 (4)
O4	0.5312 (2)	0.58763 (19)	0.6764 (2)	0.0290 (4)
Cu	0.83378 (3)	0.35012 (3)	0.71091 (3)	0.01771 (8)
Mo	0.70937 (2)	0.692556 (18)	0.750742 (19)	0.01796 (7)
O5	0.6967 (2)	0.4797 (2)	0.1142 (2)	0.0292 (4)
H5	0.621 (3)	0.452 (3)	0.168 (3)	0.033 (8)*
H6	0.678 (5)	0.556 (3)	0.069 (4)	0.058 (12)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0261 (11)	0.0227 (10)	0.0282 (11)	0.0109 (9)	-0.0037 (9)	-0.0040 (9)
C2	0.0220 (11)	0.0245 (11)	0.0330 (12)	0.0070 (9)	0.0008 (9)	-0.0045 (9)
C3	0.0269 (11)	0.0193 (10)	0.0219 (10)	0.0044 (8)	0.0027 (8)	-0.0037 (8)
C4	0.0320 (12)	0.0280 (11)	0.0195 (10)	0.0068 (9)	-0.0017 (9)	-0.0009 (8)
C5	0.0204 (10)	0.0188 (10)	0.0281 (11)	0.0021 (8)	-0.0020 (9)	-0.0031 (8)

C6	0.0189 (10)	0.0226 (10)	0.0319 (12)	0.0029 (8)	0.0021 (9)	-0.0027 (9)
C7	0.0331 (13)	0.0239 (11)	0.0247 (11)	0.0047 (9)	0.0038 (9)	0.0039 (9)
C8	0.0357 (13)	0.0306 (12)	0.0215 (11)	0.0099 (10)	-0.0027 (9)	-0.0001 (9)
N1	0.0219 (9)	0.0202 (9)	0.0251 (9)	0.0053 (7)	-0.0039 (7)	-0.0042 (7)
N2	0.0231 (9)	0.0162 (8)	0.0247 (9)	0.0028 (7)	0.0027 (7)	-0.0005 (7)
N3	0.0233 (9)	0.0183 (8)	0.0245 (9)	0.0078 (7)	-0.0026 (7)	0.0005 (7)
N4	0.0255 (9)	0.0164 (8)	0.0238 (9)	0.0048 (7)	0.0005 (7)	-0.0032 (7)
O1	0.0254 (8)	0.0135 (7)	0.0378 (9)	0.0048 (6)	0.0036 (7)	0.0007 (6)
O2	0.0475 (11)	0.0360 (10)	0.0237 (9)	0.0112 (8)	0.0024 (8)	-0.0024 (7)
O3	0.0388 (10)	0.0194 (8)	0.0370 (10)	0.0095 (7)	0.0086 (8)	0.0038 (7)
O4	0.0268 (9)	0.0279 (8)	0.0325 (9)	0.0062 (7)	-0.0039 (7)	-0.0001 (7)
Cu	0.01851 (14)	0.01362 (13)	0.02126 (14)	0.00388 (10)	-0.00018 (10)	-0.00115 (10)
Mo	0.02191 (11)	0.01353 (10)	0.01901 (11)	0.00478 (7)	0.00084 (7)	0.00004 (7)
O5	0.0301 (9)	0.0259 (8)	0.0324 (9)	0.0067 (7)	0.0048 (7)	-0.0017 (7)

Geometric parameters (Å, °)

C1—N1	1.482 (3)	C7—C8	1.520 (4)
C1—C2	1.513 (3)	C7—H7B	0.9900
C1—H1B	0.9900	C7—H7A	0.9900
C1—H1A	0.9900	C8—N1	1.484 (3)
C2—N2	1.484 (3)	C8—H8B	0.9900
C2—H2B	0.9900	C8—H8A	0.9900
C2—H2A	0.9900	N1—Cu	2.034 (2)
C3—N2	1.486 (3)	N1—H1	0.864 (17)
C3—C4	1.513 (3)	N2—Cu	2.0493 (19)
C3—H3B	0.9900	N2—H2	0.890 (17)
C3—H3A	0.9900	N3—Cu	2.033 (2)
C4—N3	1.491 (3)	N3—H3	0.881 (18)
C4—H4B	0.9900	N4—Cu	2.0413 (19)
C4—H4A	0.9900	N4—H4	0.875 (17)
C5—N3	1.485 (3)	O1—Mo	1.7955 (16)
C5—C6	1.520 (3)	O1—Cu	2.1043 (15)
C5—H5B	0.9900	O2—Mo	1.7571 (18)
C5—H5A	0.9900	O3—Mo	1.7490 (16)
C6—N4	1.482 (3)	O4—Mo	1.7652 (17)
C6—H6B	0.9900	O5—H5	0.829 (18)
C6—H6A	0.9900	O5—H6	0.838 (19)
C7—N4	1.482 (3)		
N1—C1—C2	108.15 (18)	N1—C8—H8A	109.9
N1—C1—H1B	110.1	C7—C8—H8A	109.9
C2—C1—H1B	110.1	H8B—C8—H8A	108.3
N1—C1—H1A	110.1	C1—N1—C8	113.52 (18)
C2—C1—H1A	110.1	C1—N1—Cu	103.80 (14)
H1B—C1—H1A	108.4	C8—N1—Cu	109.08 (15)
N2—C2—C1	109.64 (18)	C1—N1—H1	107 (2)
N2—C2—H2B	109.7	C8—N1—H1	109 (2)
C1—C2—H2B	109.7	Cu—N1—H1	115 (2)
N2—C2—H2A	109.7	C2—N2—C3	114.06 (17)

supplementary materials

C1—C2—H2A	109.7	C2—N2—Cu	107.64 (14)
H2B—C2—H2A	108.2	C3—N2—Cu	102.43 (13)
N2—C3—C4	107.08 (18)	C2—N2—H2	108.6 (19)
N2—C3—H3B	110.3	C3—N2—H2	107.2 (19)
C4—C3—H3B	110.3	Cu—N2—H2	117 (2)
N2—C3—H3A	110.3	C5—N3—C4	113.35 (17)
C4—C3—H3A	110.3	C5—N3—Cu	103.78 (14)
H3B—C3—H3A	108.6	C4—N3—Cu	107.78 (14)
N3—C4—C3	109.07 (18)	C5—N3—H3	111 (2)
N3—C4—H4B	109.9	C4—N3—H3	109 (2)
C3—C4—H4B	109.9	Cu—N3—H3	112 (2)
N3—C4—H4A	109.9	C6—N4—C7	115.36 (18)
C3—C4—H4A	109.9	C6—N4—Cu	107.91 (14)
H4B—C4—H4A	108.3	C7—N4—Cu	104.25 (14)
N3—C5—C6	108.09 (17)	C6—N4—H4	108 (2)
N3—C5—H5B	110.1	C7—N4—H4	107 (2)
C6—C5—H5B	110.1	Cu—N4—H4	114.3 (19)
N3—C5—H5A	110.1	Mo—O1—Cu	125.18 (8)
C6—C5—H5A	110.1	N3—Cu—N1	148.36 (7)
H5B—C5—H5A	108.4	N3—Cu—N4	85.93 (8)
N4—C6—C5	109.38 (18)	N1—Cu—N4	84.96 (8)
N4—C6—H6B	109.8	N3—Cu—N2	85.57 (8)
C5—C6—H6B	109.8	N1—Cu—N2	85.70 (8)
N4—C6—H6A	109.8	N4—Cu—N2	146.84 (7)
C5—C6—H6A	109.8	N3—Cu—O1	102.97 (7)
H6B—C6—H6A	108.2	N1—Cu—O1	108.66 (7)
N4—C7—C8	107.65 (18)	N4—Cu—O1	106.23 (7)
N4—C7—H7B	110.2	N2—Cu—O1	106.91 (7)
C8—C7—H7B	110.2	O3—Mo—O2	108.43 (9)
N4—C7—H7A	110.2	O3—Mo—O4	110.51 (9)
C8—C7—H7A	110.2	O2—Mo—O4	108.75 (9)
H7B—C7—H7A	108.5	O3—Mo—O1	110.04 (8)
N1—C8—C7	108.83 (19)	O2—Mo—O1	110.65 (9)
N1—C8—H8B	109.9	O4—Mo—O1	108.45 (8)
C7—C8—H8B	109.9	H5—O5—H6	106 (4)
N1—C1—C2—N2	-53.5 (2)	C1—N1—Cu—N4	121.02 (14)
N2—C3—C4—N3	-55.8 (2)	C8—N1—Cu—N4	-0.30 (15)
N3—C5—C6—N4	-53.4 (2)	C1—N1—Cu—N2	-27.13 (14)
N4—C7—C8—N1	-53.0 (2)	C8—N1—Cu—N2	-148.44 (15)
C2—C1—N1—C8	168.05 (19)	C1—N1—Cu—O1	-133.53 (13)
C2—C1—N1—Cu	49.76 (19)	C8—N1—Cu—O1	105.15 (15)
C7—C8—N1—C1	-87.1 (2)	C6—N4—Cu—N3	-1.03 (14)
C7—C8—N1—Cu	28.1 (2)	C7—N4—Cu—N3	122.10 (15)
C1—C2—N2—C3	-84.7 (2)	C6—N4—Cu—N1	-150.70 (15)
C1—C2—N2—Cu	28.2 (2)	C7—N4—Cu—N1	-27.57 (14)
C4—C3—N2—C2	168.62 (18)	C6—N4—Cu—N2	-76.5 (2)
C4—C3—N2—Cu	52.62 (18)	C7—N4—Cu—N2	46.6 (2)
C6—C5—N3—C4	165.92 (19)	C6—N4—Cu—O1	101.31 (14)
C6—C5—N3—Cu	49.29 (19)	C7—N4—Cu—O1	-135.56 (14)

C3—C4—N3—C5	-85.7 (2)	C2—N2—Cu—N3	-150.00 (14)
C3—C4—N3—Cu	28.5 (2)	C3—N2—Cu—N3	-29.46 (13)
C5—C6—N4—C7	-87.4 (2)	C2—N2—Cu—N1	-0.44 (13)
C5—C6—N4—Cu	28.7 (2)	C3—N2—Cu—N1	120.10 (14)
C8—C7—N4—C6	168.22 (19)	C2—N2—Cu—N4	-74.40 (19)
C8—C7—N4—Cu	50.08 (19)	C3—N2—Cu—N4	46.1 (2)
C5—N3—Cu—N1	46.9 (2)	C2—N2—Cu—O1	107.77 (13)
C4—N3—Cu—N1	-73.6 (2)	C3—N2—Cu—O1	-131.69 (13)
C5—N3—Cu—N4	-26.66 (13)	Mo—O1—Cu—N3	56.76 (13)
C4—N3—Cu—N4	-147.15 (14)	Mo—O1—Cu—N1	-122.84 (11)
C5—N3—Cu—N2	121.25 (14)	Mo—O1—Cu—N4	-32.74 (13)
C4—N3—Cu—N2	0.77 (14)	Mo—O1—Cu—N2	146.02 (11)
C5—N3—Cu—O1	-132.40 (13)	Cu—O1—Mo—O3	-153.37 (11)
C4—N3—Cu—O1	107.12 (14)	Cu—O1—Mo—O2	86.82 (12)
C1—N1—Cu—N3	47.2 (2)	Cu—O1—Mo—O4	-32.38 (13)
C8—N1—Cu—N3	-74.1 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5...O4 ⁱ	0.83 (2)	1.95 (2)	2.770 (2)	169 (3)
N1—H1...O5 ⁱⁱ	0.86 (2)	2.35 (2)	3.156 (3)	156 (3)
N2—H2...O1 ⁱⁱ	0.89 (2)	2.19 (2)	2.949 (2)	143 (3)
N3—H3...O4 ⁱ	0.88 (2)	2.28 (3)	2.955 (3)	133 (3)
N4—H4...O5 ⁱⁱⁱ	0.88 (2)	2.10 (2)	2.928 (3)	157 (3)
O5—H6...O2 ^{iv}	0.84 (2)	1.85 (2)	2.666 (3)	163 (4)
C3—H3B...O3 ^v	0.99	2.36	3.345 (3)	175

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

Fig. 2

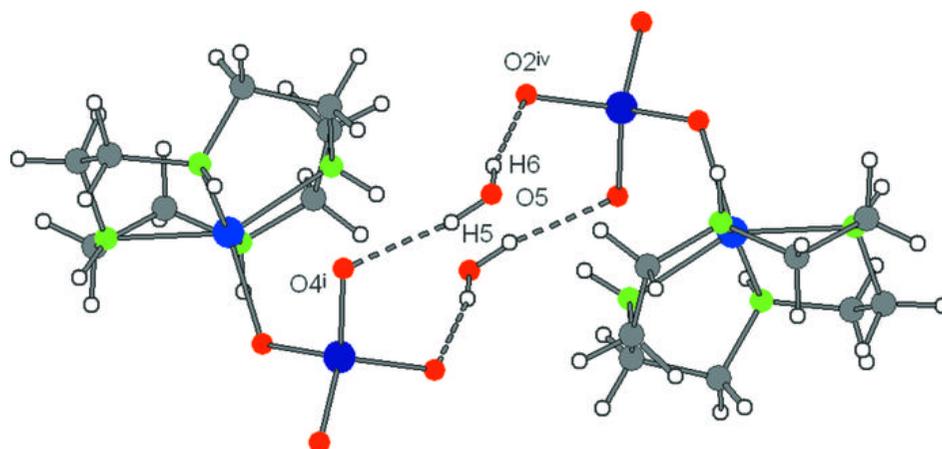


Fig. 3

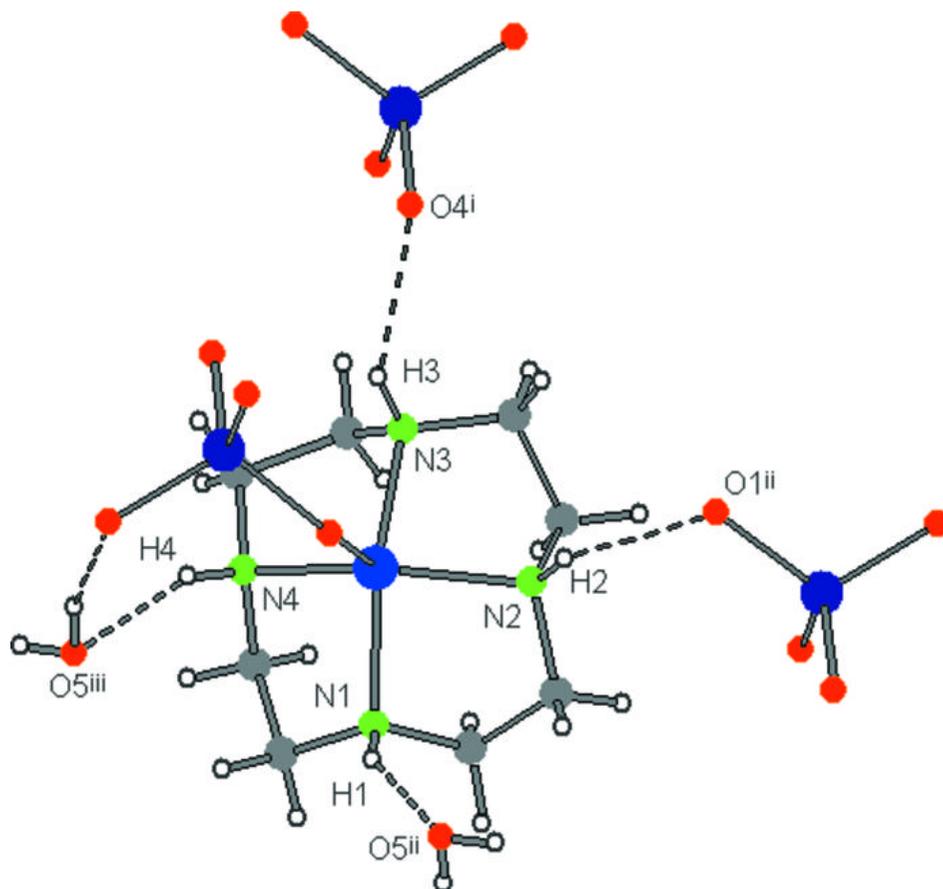


Fig. 4

