

A two-dimensional copper(II) molybdate, $[\text{Cu}_2(\text{tpyprz})\text{Mo}_8\text{O}_{26}]$ (tpyprz is 2,3,5,6-tetra-2-pyridyl-1,4-dihydropyrazine)

Jon Zubieta* and N. Gabriel Armatas

111 College Place, Syracuse University, Syracuse, NY 13244, USA

Correspondence e-mail: jazubiet@syr.edu

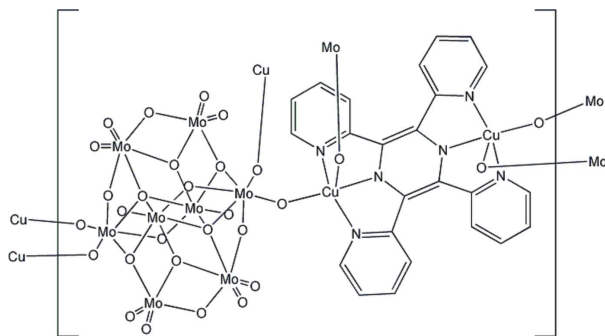
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 Key indicators: single-crystal X-ray study; $T = 90\text{ K}$; mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$; R factor = 0.027; wR factor = 0.062; data-to-parameter ratio = 16.4.

In the title compound, poly $[\mu_2$ -2,3,5,6-tetra-2-pyridyl-1,4-dihydropyrazine- μ -hexacosaoxidooctamolybdato-dicopper(II)], $[\text{Cu}_2\text{Mo}_8\text{O}_{26}(\text{C}_{24}\text{H}_{16}\text{N}_6)]$, the organic linker 2,3,5,6-tetra-2-pyridyl-1,4-dihydropyrazine (tpyprz) brings together four $[\text{Mo}_8\text{O}_{26}]^{4-}$ clusters through the cationic bridge $[\text{Cu}_2(\text{tpyprz})]^{4+}$ to form a two-dimensional layer. The copper(II) cation is five-coordinate in a distorted square-pyramidal configuration, bonding to three N atoms from the tpyprz ligand and two terminal O atoms from the molybdenum cluster. The $[\text{Mo}_8\text{O}_{26}]^{4-}$ cluster shows bonding only through the terminal O atoms attached to the octahedrally coordinated Mo atom along the central axis of the cluster.

Related literature

More information relating to the theory behind the building block approach can be found in an article published by Ferey (2000). Additional information related to the synthesis and structural details can be found in Zubieta & Rarig (2002). For related literature, see: Cockayne & Jones (1972); Greenwood & Earnshaw (1984).



Experimental

Crystal data

$[\text{Cu}_2\text{Mo}_8\text{O}_{26}(\text{C}_{24}\text{H}_{16}\text{N}_6)]$
 $M_r = 849.51$
 Triclinic, $P\bar{1}$
 $a = 9.9920(7)\text{ \AA}$
 $b = 10.0882(7)\text{ \AA}$
 $c = 11.1708(8)\text{ \AA}$
 $\alpha = 78.380(8)^\circ$
 $\beta = 76.815(9)^\circ$

$\gamma = 65.419(5)^\circ$
 $V = 989.75(12)\text{ \AA}^3$
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 3.60\text{ mm}^{-1}$
 $T = 90(2)\text{ K}$
 $0.24 \times 0.16 \times 0.14\text{ mm}$

Data collection

Bruker APEX CCD detector
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.479$, $T_{\max} = 0.633$

10578 measured reflections
 4896 independent reflections
 4307 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.062$
 $S = 0.94$
 4896 reflections

299 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.80\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.89\text{ e \AA}^{-3}$

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b) and CrystalMaker (CrystalMaker Software, 2007); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2040).

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supplementary materials

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A two-dimensional copper(II) molybdate, [$\{\text{Cu}_2(\text{tpyprz})\}\text{Mo}_8\text{O}_{26}$] (tpyprz is 2,3,5,6-tetra-2-pyridyl-1,4-dihydropyrazine)

J. Zubieta and N. G. Armatas

Comment

Organic–inorganic hybrid materials represent an expanding class of materials characterized by broad compositional range and structural versatility (Greenwood & Earnshaw, 1984). Inorganic oxides possess properties that are useful in the design of materials including but not limited to optical, electronic, magnetic, and mechanical. However, rational synthesis of these materials still remains an elusive goal (Cockayne & Jones, 1972). The molecular building block approach is an established method for synthesis of these materials (Ferey, 2000).

In an ongoing research investigation of such hybrid materials compound **1**, [$\{\text{Cu}_2(\text{tpyprz})\}\text{Mo}_8\text{O}_{26}$] was synthesized under mild hydrothermal conditions. This synthetic approach favors the formation of the $\{\text{Mo}_5\text{O}_{15}(\text{RPO}_3)_2\}^{4-}$ clusters; however, in this reaction the phosphonate does not incorporate, leaving only a molybdenum oxide cluster to act as the oxide building block. The ligand of choice, tetra-2-pyridylpyrazine (tpyprz), along with the appropriate transition metal, act as a bridge between two or more of these molybdenum clusters.

Compound **1** is a two-dimensional layer formed from $\{\text{Mo}_8\text{O}_{26}\}^{4-}$ clusters and $\{\text{Cu}_2(\text{tpyprz})\}^{4+}$ bridging cationic units. The copper-tpyprz moiety is attached to four different molybdenum clusters creating stacked sheets of this continuous layer. Copper is five coordinate in a distorted square pyramidal configuration, bonding to three N atoms from one side of the tpyprz ligand and two terminal O atoms from the molybdenum cluster. A weak bond exists between copper and the axial oxygen, Cu—O9 at 2.37 Å, provides a good valence bond sum for the copper cation. The terminal O atoms on the molybdenum cluster, O9 and O10, are responsible for the expansion of the structure. The equatorial oxygen, O10, extends the structure into a one-dimensional chain. The axial oxygen, O9, lies perpendicular to the chain, connecting adjacent chains. It is interesting to note that O9 aligns above the tpyprz plane on one side and below on the other side; this alternating up-down positioning allows the expansion of the structure into a layer.

Experimental

Synthesis of [$\{\text{Cu}_2(\text{tpyprz})\}\text{Mo}_8\text{O}_{26}$] (**1**). A mixture of MoO_3 (0.160 g, 1.11 mmol), $\text{Co}(\text{OCOCH}_3)_2$ (0.088 g, 0.441 mmol), tpyprz (0.086 g, 0.221 mmol), and H_2O (10 g, 555 mmol) in the mole ratio 5.02:2.00:1.00:2511 was stirred briefly before heating to 453 K for 120 h. Light green plate like crystals of **1** were isolated in 45% yield: initial pH, 6; final pH, 3. IR (KBr pellet, cm^{-1}): 3072(m, br), 2999(s), 1593(w), 1479(w), 1401(m), 1168(m), 1090(m), 1062(s), 952(s), 907(s), 739(s), 658(m).

Refinement

H atoms were implemented geometrically using a riding constraint with a C—H fixed distance of 0.93 Å and a U_{iso} of $1.2U_{\text{eq}}(\text{C})$.

Figures



Fig. 1. - ORTEP drawing of anionic molybdenum cluster $[\text{Mo}_8\text{O}_{26}]^{4-}$ and the cationic $[\text{Cu}_2(\text{tpyprz})]^{4+}$ unit of the title compound (**1**), showing 50% probability displacement ellipsoids. H atoms omitted for clarity.

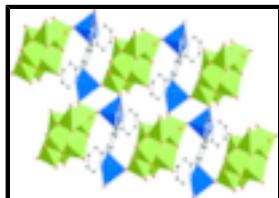


Fig. 2. - Polyhedral representation of a single layer for compound **1**. Cu atoms represented by dark blue polyhedra, Mo by green polyhedra, N by light blue, and C by black. H atoms omitted for clarity.

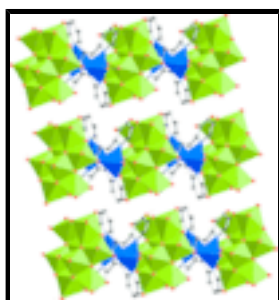


Fig. 3. - Polyhedral representation of three stacking layers of **1**, forming a two-dimensional layer structure.

poly[μ -2,2,3,5,6-tetra-2-pyridyl-1,4-dihydropyrazine- μ - hexacosaoxidooctamolybdato-dicopper(II)]

Crystal data

$[\text{Cu}_2\text{Mo}_8\text{O}_{26}(\text{C}_{24}\text{H}_{16}\text{N}_6)]$

$M_r = 849.51$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 9.9920$ (7) Å

$b = 10.0882$ (7) Å

$c = 11.1708$ (8) Å

$\alpha = 78.380$ (8)°

$\beta = 76.815$ (9)°

$\gamma = 65.419$ (5)°

$V = 989.75$ (12) Å³

$Z = 2$

$F_{000} = 804$

$D_x = 2.851$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 4896 reflections

$\theta = 1.9\text{--}28.3^\circ$

$\mu = 3.60$ mm⁻¹

$T = 90$ (2) K

Plate, green

$0.24 \times 0.16 \times 0.14$ mm

Data collection

Bruker APEX CCD detector
diffractometer

Monochromator: graphite

Detector resolution: 512 pixels mm⁻¹

$T = 90$ (2) K

4896 independent reflections

4307 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 28.3^\circ$

φ and ω scans	$\theta_{\min} = 1.9^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13 \rightarrow 13$
$T_{\min} = 0.479$, $T_{\max} = 0.633$	$k = -13 \rightarrow 13$
10578 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.062$	$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 2.178P]$
$S = 0.94$	where $P = (F_o^2 + 2F_c^2)/3$
4896 reflections	$(\Delta/\sigma)_{\max} = 0.001$
299 parameters	$\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.89 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mo1	0.77935 (3)	0.61288 (3)	0.79284 (3)	0.01016 (7)
Mo2	0.88214 (3)	0.41297 (3)	0.55817 (3)	0.00797 (7)
Mo3	0.73644 (3)	0.77007 (3)	0.46269 (3)	0.00746 (7)
Mo4	0.92292 (3)	0.68237 (3)	0.17919 (3)	0.01363 (8)
Cu1	0.36121 (4)	0.82861 (5)	0.45710 (4)	0.00889 (9)
O1	0.6347 (3)	0.5844 (3)	0.8909 (2)	0.0187 (6)
O2	0.7496 (4)	0.7901 (3)	0.7984 (3)	0.0280 (7)
O3	0.9513 (3)	0.5148 (3)	0.8652 (2)	0.0153 (5)
O4	0.8896 (3)	0.3842 (3)	0.7297 (2)	0.0101 (5)
O5	0.7276 (3)	0.3837 (3)	0.5533 (2)	0.0126 (5)
O6	0.7559 (3)	0.6323 (2)	0.6213 (2)	0.0094 (5)
O7	1.0337 (3)	0.2564 (3)	0.5070 (2)	0.0104 (5)
O8	0.8961 (3)	0.5515 (3)	0.4189 (2)	0.0104 (5)

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O9	0.6673 (3)	0.9306 (3)	0.5254 (2)	0.0121 (5)
O10	0.5772 (3)	0.7536 (3)	0.4371 (2)	0.0103 (5)
O11	0.8197 (3)	0.8207 (3)	0.3041 (2)	0.0103 (5)
O13	0.9652 (3)	0.7952 (3)	0.0572 (3)	0.0260 (7)
N1	0.3303 (3)	0.8814 (3)	0.2808 (3)	0.0100 (6)
N2	0.1442 (3)	0.9181 (3)	0.4810 (3)	0.0076 (5)
N3	0.3167 (3)	0.7618 (3)	0.6371 (3)	0.0097 (6)
C1	0.4353 (4)	0.8375 (4)	0.1833 (3)	0.0169 (8)
H1	0.5349	0.7982	0.1935	0.020*
C2	0.4015 (5)	0.8481 (5)	0.0670 (4)	0.0230 (9)
H2	0.4770	0.8196	-0.0004	0.028*
C3	0.2537 (5)	0.9018 (4)	0.0535 (4)	0.0203 (8)
H3	0.2283	0.9048	-0.0224	0.024*
C4	0.1424 (4)	0.9517 (4)	0.1543 (3)	0.0133 (7)
H4	0.0421	0.9893	0.1466	0.016*
C5	0.1848 (4)	0.9439 (3)	0.2650 (3)	0.0095 (6)
C6	0.0799 (4)	0.9875 (4)	0.3812 (3)	0.0086 (6)
C7	0.0729 (4)	0.9208 (4)	0.5985 (3)	0.0086 (6)
C8	0.1688 (4)	0.8103 (4)	0.6846 (3)	0.0094 (6)
C9	0.1152 (4)	0.7432 (4)	0.7943 (3)	0.0109 (7)
H9	0.0135	0.7757	0.8244	0.013*
C10	0.2172 (4)	0.6257 (4)	0.8587 (3)	0.0130 (7)
H10	0.1839	0.5787	0.9325	0.016*
C11	0.3657 (4)	0.5803 (4)	0.8129 (3)	0.0151 (7)
H11	0.4349	0.5037	0.8560	0.018*
C12	0.4123 (4)	0.6499 (4)	0.7008 (3)	0.0139 (7)
H12	0.5136	0.6175	0.6690	0.017*
O12	0.7658 (3)	0.6700 (4)	0.1582 (3)	0.0368 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01090 (15)	0.01001 (14)	0.00936 (14)	-0.00350 (11)	-0.00285 (11)	-0.00054 (11)
Mo2	0.00654 (14)	0.00650 (13)	0.01088 (14)	-0.00218 (11)	-0.00178 (11)	-0.00146 (10)
Mo3	0.00551 (13)	0.00683 (13)	0.00904 (14)	-0.00141 (11)	-0.00132 (10)	-0.00081 (10)
Mo4	0.00738 (14)	0.01504 (16)	0.01633 (16)	-0.00004 (12)	-0.00278 (12)	-0.00587 (12)
Cu1	0.00514 (19)	0.0108 (2)	0.0090 (2)	-0.00178 (16)	-0.00113 (16)	-0.00028 (15)
O1	0.0112 (13)	0.0305 (16)	0.0132 (13)	-0.0066 (11)	-0.0002 (10)	-0.0051 (11)
O2	0.048 (2)	0.0129 (14)	0.0300 (17)	-0.0112 (13)	-0.0254 (15)	0.0020 (12)
O3	0.0087 (12)	0.0176 (13)	0.0192 (14)	-0.0011 (10)	-0.0030 (10)	-0.0093 (11)
O4	0.0099 (12)	0.0106 (12)	0.0093 (12)	-0.0034 (9)	-0.0017 (9)	-0.0006 (9)
O5	0.0097 (12)	0.0122 (12)	0.0155 (13)	-0.0035 (10)	-0.0032 (10)	-0.0016 (10)
O6	0.0093 (12)	0.0081 (11)	0.0089 (11)	-0.0020 (9)	-0.0020 (9)	0.0005 (9)
O7	0.0079 (11)	0.0087 (11)	0.0148 (12)	-0.0033 (9)	-0.0012 (10)	-0.0024 (9)
O8	0.0079 (11)	0.0094 (11)	0.0132 (12)	-0.0023 (9)	-0.0023 (10)	-0.0013 (9)
O9	0.0107 (12)	0.0090 (12)	0.0158 (13)	-0.0024 (10)	-0.0026 (10)	-0.0020 (10)
O10	0.0079 (11)	0.0113 (12)	0.0113 (12)	-0.0035 (9)	-0.0029 (9)	0.0007 (9)
O11	0.0088 (12)	0.0073 (11)	0.0115 (12)	-0.0014 (9)	-0.0004 (10)	0.0008 (9)

O13	0.0285 (16)	0.0223 (15)	0.0112 (13)	0.0046 (12)	-0.0027 (12)	-0.0002 (11)
N1	0.0091 (14)	0.0087 (14)	0.0108 (14)	-0.0026 (11)	-0.0004 (11)	-0.0009 (11)
N2	0.0065 (13)	0.0065 (13)	0.0116 (14)	-0.0043 (10)	-0.0011 (11)	-0.0012 (11)
N3	0.0094 (14)	0.0112 (14)	0.0090 (14)	-0.0049 (11)	-0.0017 (11)	-0.0002 (11)
C1	0.0086 (17)	0.0187 (19)	0.0147 (18)	0.0018 (14)	0.0006 (14)	-0.0014 (15)
C2	0.016 (2)	0.026 (2)	0.0154 (19)	0.0017 (16)	0.0005 (16)	-0.0039 (16)
C3	0.024 (2)	0.021 (2)	0.0107 (18)	-0.0005 (16)	-0.0056 (16)	-0.0048 (15)
C4	0.0117 (17)	0.0105 (16)	0.0159 (18)	-0.0015 (13)	-0.0046 (14)	-0.0010 (13)
C5	0.0085 (16)	0.0043 (14)	0.0133 (17)	-0.0010 (12)	-0.0013 (13)	0.0005 (12)
C6	0.0070 (15)	0.0086 (15)	0.0106 (16)	-0.0031 (12)	-0.0019 (13)	-0.0009 (12)
C7	0.0089 (16)	0.0072 (15)	0.0131 (16)	-0.0054 (13)	-0.0039 (13)	-0.0015 (12)
C8	0.0073 (16)	0.0109 (16)	0.0122 (16)	-0.0048 (13)	-0.0026 (13)	-0.0023 (13)
C9	0.0091 (16)	0.0122 (16)	0.0111 (16)	-0.0040 (13)	-0.0014 (13)	-0.0017 (13)
C10	0.0144 (18)	0.0127 (17)	0.0118 (17)	-0.0049 (14)	-0.0032 (14)	-0.0008 (13)
C11	0.0138 (18)	0.0121 (17)	0.0169 (18)	-0.0028 (14)	-0.0069 (15)	0.0040 (14)
C12	0.0061 (16)	0.0132 (17)	0.0211 (19)	-0.0027 (13)	-0.0035 (14)	0.0003 (14)
O12	0.0107 (14)	0.0404 (19)	0.063 (2)	0.0013 (13)	-0.0092 (15)	-0.0364 (18)

Geometric parameters (Å, °)

Mo1—O1	1.694 (3)	Cu1—N3	1.998 (3)
Mo1—O2	1.698 (3)	Cu1—O9 ⁱⁱ	2.368 (2)
Mo1—O3	1.866 (3)	O3—Mo4 ⁱ	1.954 (3)
Mo1—O6	1.944 (2)	O4—Mo4 ⁱ	2.132 (2)
Mo1—O4	2.285 (2)	O7—Mo3 ⁱ	2.296 (2)
Mo2—O5	1.703 (2)	O8—Mo2 ⁱ	2.462 (2)
Mo2—O7	1.759 (2)	O9—Cu1 ⁱⁱ	2.368 (2)
Mo2—O8	1.892 (2)	N1—C1	1.330 (5)
Mo2—O4	1.893 (2)	N1—C5	1.361 (4)
Mo2—O6	2.210 (2)	N2—C6	1.335 (4)
Mo2—O8 ⁱ	2.462 (2)	N2—C7	1.343 (4)
Mo3—O9	1.702 (2)	N3—C12	1.335 (4)
Mo3—O10	1.757 (2)	N3—C8	1.360 (4)
Mo3—O11	1.846 (2)	C1—C2	1.389 (5)
Mo3—O6	2.012 (2)	C2—C3	1.379 (6)
Mo3—O8	2.190 (2)	C3—C4	1.396 (5)
Mo3—O7 ⁱ	2.296 (2)	C4—C5	1.374 (5)
Mo4—O13	1.686 (3)	C5—C6	1.485 (5)
Mo4—O12	1.696 (3)	C6—C7 ⁱⁱⁱ	1.411 (5)
Mo4—O3 ⁱ	1.954 (3)	C7—C6 ⁱⁱⁱ	1.411 (5)
Mo4—O11	1.972 (2)	C7—C8	1.478 (5)
Mo4—O4 ⁱ	2.132 (2)	C8—C9	1.384 (5)
Cu1—O10	1.942 (2)	C9—C10	1.395 (5)
Cu1—N2	1.948 (3)	C10—C11	1.363 (5)
Cu1—N1	1.994 (3)	C11—C12	1.389 (5)
O1—Mo1—O2	105.33 (15)	N2—Cu1—N1	80.29 (12)
O1—Mo1—O3	108.95 (12)	O10—Cu1—N3	99.31 (11)

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O2—Mo1—O3	100.57 (13)	N2—Cu1—N3	80.51 (12)
O1—Mo1—O6	110.97 (11)	N1—Cu1—N3	156.47 (12)
O2—Mo1—O6	97.97 (12)	O10—Cu1—O9 ⁱⁱ	93.15 (9)
O3—Mo1—O6	129.13 (11)	N2—Cu1—O9 ⁱⁱ	82.34 (10)
O1—Mo1—O4	96.02 (11)	N1—Cu1—O9 ⁱⁱ	92.50 (10)
O2—Mo1—O4	158.56 (13)	N3—Cu1—O9 ⁱⁱ	98.29 (10)
O3—Mo1—O4	73.73 (10)	Mo1—O3—Mo4 ⁱ	116.04 (13)
O6—Mo1—O4	71.98 (9)	Mo2—O4—Mo4 ⁱ	129.26 (12)
O5—Mo2—O7	105.04 (11)	Mo2—O4—Mo1	105.88 (10)
O5—Mo2—O8	105.02 (11)	Mo4 ⁱ —O4—Mo1	94.31 (9)
O7—Mo2—O8	99.35 (11)	Mo1—O6—Mo3	143.27 (13)
O5—Mo2—O4	103.33 (11)	Mo1—O6—Mo2	106.96 (10)
O7—Mo2—O4	101.78 (11)	Mo3—O6—Mo2	103.63 (10)
O8—Mo2—O4	138.54 (10)	Mo2—O7—Mo3 ⁱ	115.98 (12)
O5—Mo2—O6	94.74 (10)	Mo2—O8—Mo3	108.69 (11)
O7—Mo2—O6	160.16 (10)	Mo2—O8—Mo2 ⁱ	101.18 (10)
O8—Mo2—O6	73.47 (9)	Mo3—O8—Mo2 ⁱ	95.55 (9)
O4—Mo2—O6	74.62 (9)	Mo3—O9—Cu1 ⁱⁱ	156.88 (14)
O5—Mo2—O8 ⁱ	175.91 (10)	Mo3—O10—Cu1	148.28 (15)
O7—Mo2—O8 ⁱ	75.43 (9)	Mo3—O11—Mo4	123.85 (12)
O8—Mo2—O8 ⁱ	78.82 (10)	C1—N1—C5	118.8 (3)
O4—Mo2—O8 ⁱ	72.65 (9)	C1—N1—Cu1	125.4 (2)
O6—Mo2—O8 ⁱ	84.96 (8)	C5—N1—Cu1	114.5 (2)
O9—Mo3—O10	103.92 (12)	C6—N2—C7	125.2 (3)
O9—Mo3—O11	102.31 (11)	C6—N2—Cu1	117.5 (2)
O10—Mo3—O11	102.10 (11)	C7—N2—Cu1	116.7 (2)
O9—Mo3—O6	98.04 (11)	C12—N3—C8	118.8 (3)
O10—Mo3—O6	95.09 (10)	C12—N3—Cu1	124.7 (2)
O11—Mo3—O6	149.19 (10)	C8—N3—Cu1	114.2 (2)
O9—Mo3—O8	157.58 (11)	N1—C1—C2	122.3 (3)
O10—Mo3—O8	96.96 (10)	C3—C2—C1	118.5 (4)
O11—Mo3—O8	80.86 (10)	C2—C3—C4	119.7 (4)
O6—Mo3—O8	71.74 (9)	C5—C4—C3	118.3 (3)
O9—Mo3—O7 ⁱ	86.65 (10)	N1—C5—C4	122.1 (3)
O10—Mo3—O7 ⁱ	168.87 (10)	N1—C5—C6	113.1 (3)
O11—Mo3—O7 ⁱ	78.61 (10)	C4—C5—C6	124.6 (3)
O6—Mo3—O7 ⁱ	79.76 (9)	N2—C6—C7 ⁱⁱⁱ	117.3 (3)
O8—Mo3—O7 ⁱ	72.10 (9)	N2—C6—C5	111.5 (3)
O13—Mo4—O12	106.36 (17)	C7 ⁱⁱⁱ —C6—C5	131.0 (3)
O13—Mo4—O3 ⁱ	104.35 (13)	N2—C7—C6 ⁱⁱⁱ	117.3 (3)
O12—Mo4—O3 ⁱ	92.74 (13)	N2—C7—C8	111.7 (3)
O13—Mo4—O11	100.43 (12)	C6 ⁱⁱⁱ —C7—C8	130.6 (3)
O12—Mo4—O11	94.88 (12)	N3—C8—C9	121.6 (3)
O3 ⁱ —Mo4—O11	150.80 (10)	N3—C8—C7	113.6 (3)

O13—Mo4—O4 ⁱ	100.53 (13)	C9—C8—C7	124.0 (3)
O12—Mo4—O4 ⁱ	152.68 (15)	C8—C9—C10	118.5 (3)
O3 ⁱ —Mo4—O4 ⁱ	75.76 (10)	C11—C10—C9	119.7 (3)
O11—Mo4—O4 ⁱ	84.80 (10)	C10—C11—C12	119.1 (3)
O10—Cu1—N2	175.40 (11)	N3—C12—C11	122.3 (3)
O10—Cu1—N1	100.91 (11)		

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

Fig. 1

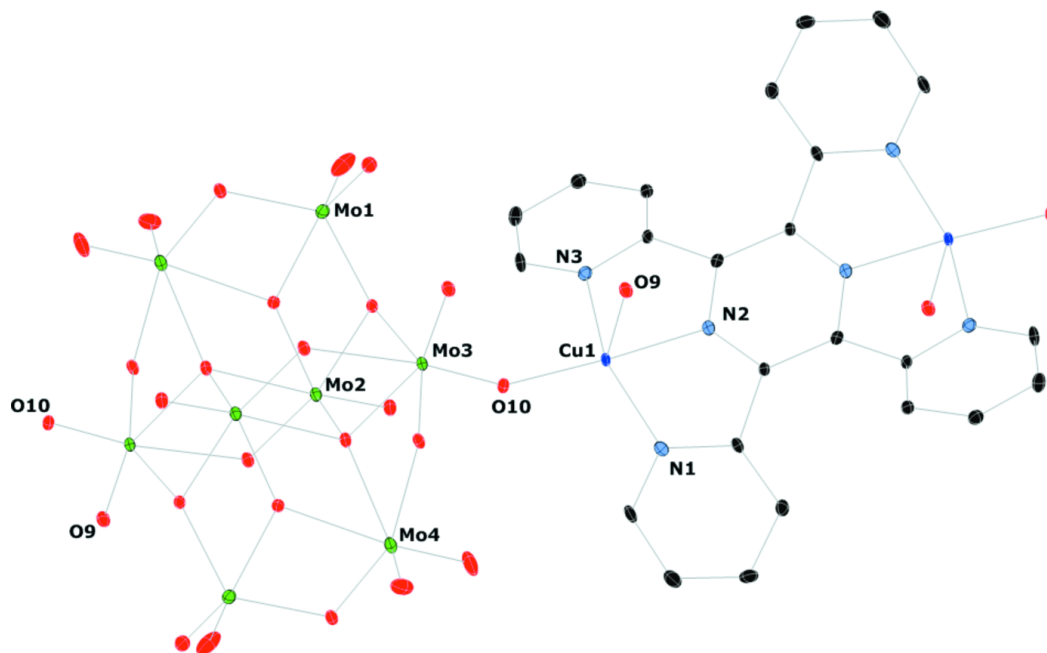


Fig. 2

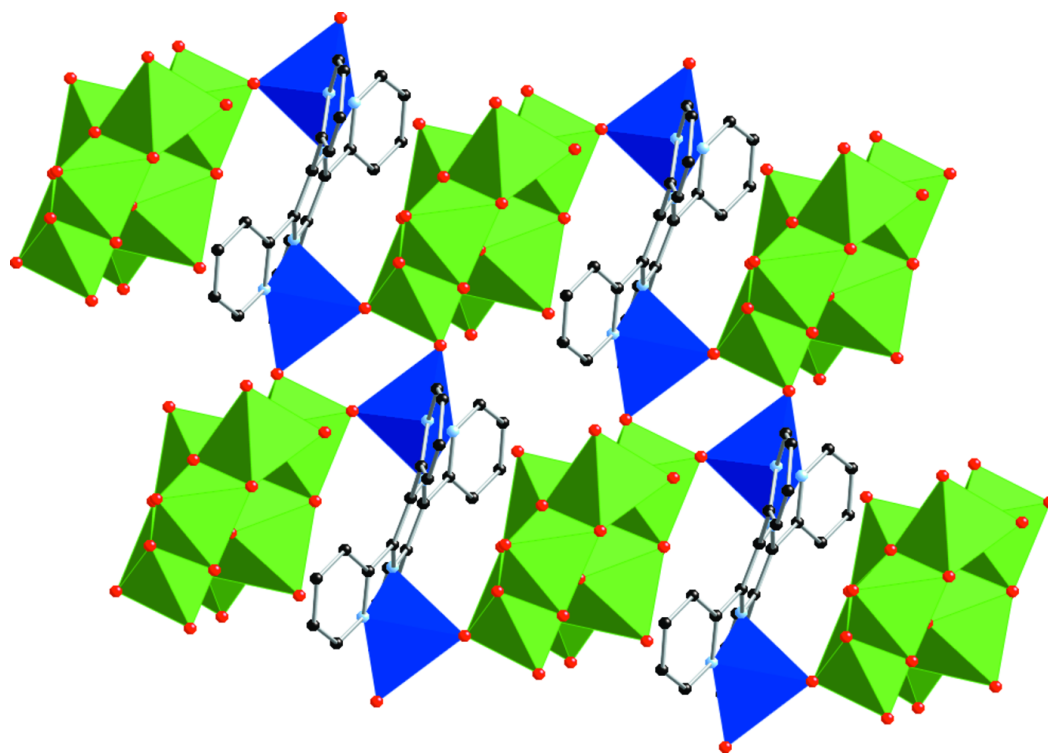


Fig. 3

