

Bis[μ -bis(imidazol-1-yl)methane]-bis[aqua(oxalato)copper(II)] dihydrate

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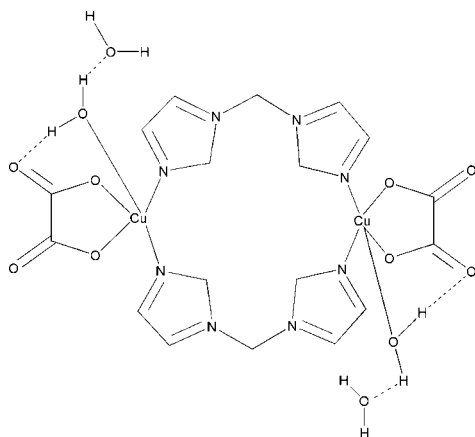
Received 7 October 2007; accepted 15 October 2007

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.027; wR factor = 0.072; data-to-parameter ratio = 12.4.

The title compound, $[\text{Cu}_2(\text{C}_2\text{O}_4)_2(\text{C}_7\text{H}_8\text{N}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, features a centrosymmetric dinuclear complex. The Cu^{II} ion adopts a square-pyramidal geometry. It is coordinated by two N atoms from two bis(*N*-imidazolyl)methane molecules as bridging ligands, two O atoms from one oxalate anion in chelating mode and one water molecule. There are several O—H...O hydrogen bonds in the crystal structure.

Related literature

For related literature, see: Jin & Chen (2007*a,b*); Jin *et al.* (2007); Lehn (1995); Levstein & Calvo (1990); Li *et al.* (1997, 2000); Lightfoot & Snedden (1999); Liu *et al.* (2003); Ma *et al.* (2003, 2004); Maji *et al.* (2003); Nardelli (1999); Oschio & Nagashima (1990); Policar *et al.* (1999); Rather & Zaworotko (2003); Rodriguez-Martin *et al.* (2002, 2001); Rueff *et al.* (2001); Sheldrick (1996); Siemens (1996); Wen *et al.* (2005, 2006, 2007); Yang *et al.* (2005); Zhang *et al.* (2003); Zhu *et al.* (2005).



Experimental

Crystal data

$[\text{Cu}_2(\text{C}_2\text{O}_4)_2(\text{C}_7\text{H}_8\text{N}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	$\beta = 104.582$ (5)°
$M_r = 671.53$	$\gamma = 91.773$ (5)°
Triclinic, $P\bar{1}$	$V = 649.7$ (5) Å ³
$a = 7.970$ (4) Å	$Z = 1$
$b = 9.770$ (4) Å	Mo $K\alpha$ radiation
$c = 9.913$ (4) Å	$\mu = 1.71$ mm ⁻¹
$\alpha = 117.964$ (4)°	$T = 298$ (2) K
	$0.55 \times 0.53 \times 0.49$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	3367 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2248 independent reflections
$T_{\text{min}} = 0.453$, $T_{\text{max}} = 0.487$ (expected range = 0.401–0.432)	1997 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	181 parameters
$wR(F^2) = 0.072$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.37$ e Å ⁻³
2248 reflections	$\Delta\rho_{\text{min}} = -0.36$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O6—H14...O4 ⁱ	0.85	1.98	2.804 (3)	164
O6—H13...O2 ⁱⁱ	0.85	1.97	2.797 (3)	165
O5—H12...O6 ⁱⁱⁱ	0.85	1.98	2.823 (3)	169
O5—H11...O1 ^{iv}	0.85	2.05	2.895 (3)	170

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Siemens, 1996); software used to prepare material for publication: SHELXTL.

The authors thank the Zhejiang Forestry University Science Foundation for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2533).

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Acta Cryst. (2007). E63, m2755-m2756 [doi:10.1107/S1600536807050465]

Bis[μ -bis(imidazol-1-yl)methane]bis[aqua(oxalato)copper(II)] dihydrate

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Comment

The design and synthesis of metal–organic framework structures have received enormous attention (Lehn, 1995) in recent years. It is well known that carboxylate ligands play an important role in coordination chemistry and can adopt various binding modes such as terminal monodentate, chelating to one metal center, bridging bidentate in a *syn*–*syn*, *syn*–*anti*, and *anti*–*anti* configuration to two metal centers, and bridging tridentate to two metal centers (Polcar *et al.*, 1999; Levstein & Calvo, 1990; Rueff *et al.*, 2001). The use of organic spacers, particularly the flexible dicarboxylates bridging ligands and rigid planar bidentate diimines (bipy or pyz) as building blocks to construct various metal assemblage is of growing interest in the field of molecular materials (Oschio & Nagashima, 1990). Recently great success has been achieved by combination of the flexible aliphatic dicarboxylates and bipy as chelating bridging ligands, which resulted in compounds having 1–three-dimensional frameworks and unique physicochemical properties (Li *et al.*, 1997, 2000; Rodriguez-Martin *et al.*, 2001, 2002; Lightfoot & Snedden, 1999; Maji *et al.*, 2003; Rather & Zaworotko, 2003; Zhang *et al.*, 2003; Liu *et al.*, 2003). In contrast to rigid spacers, the flexible ligands, which can adopt various conformations, may induce coordination polymers with novel topologies. However, the flexible ligands containing imidazolyl groups and polycarboxylate ligands have not been well studied to date (Yang *et al.*, 2005; Ma *et al.*, 2003, 2004; Wen *et al.*, 2005, 2006, 2007). Bis(*N*-imidazolyl)methane (L1) can be used as flexible divergent ligands to construct coordination polymer materials. As an extension of our work (Jin & Chen, 2007*a,b*; Jin *et al.*, 2007), the title complex is reported here.

The compound was obtained by reacting copper chloride dihydrate, oxalic acid, and bis(*N*-imidazolyl)methane (L1) in basic aqueous solution and it was isolated as blue crystals. (I) is a discrete dinuclear complex, and the asymmetric unit consists of one Cu ion, one oxalate, and one bis(*N*-imidazolyl)methane molecule. As shown in Fig. 1, Cu ion adopts square pyramidal geometry, and each copper atom is coordinated by two nitrogen atoms from two bis(*N*-imidazolyl)methane as bridging ligands, two oxygen atoms from one oxalate anion in chelating mode, one water molecule, completing its tetragonal pyramidal geometry in a N₂O₃ donor set. The Cu—N distances of 1.991 (2) and 1.977 (2) Å are normal and well consistent with those of known Cu–imidazole complexes ranging from 1.876 (13) to 2.049 (8) Å (Zhu *et al.*, 2005). The Cu—O(water) bond distance, being 2.229 (2) Å is much longer than those of the Cu—O(carboxylate) bond distance [1.954 (2) Å]. The oxalate anion acts as a bis-unidentate ligand and forms a five-membered ring with the copper ion, while two L1 and two Cu atoms form a sixteen-membered ring. The dimeric units are connected through strong hydrogen bonds with water molecules, yielding three dimensional network structure, which is illustrated in Fig. 2.

Experimental

All reagents and solvents were used as obtained without further purification. The CHN elemental analyses were performed on a Perkin–Elmer elemental analyzer.

A mixture of copper chloride dihydrate (17.1 mg, 0.1 mmol), NaOH (8 mg, 0.2 mmol), and oxalic acid (12.7 mg, 0.1 mmol) in water (5 ml) was stirred for 15 min at 60 degree, then L1 (15 mg, 0.1 mmol) was added to the mixture. After stirring for 50 min, the blue precipitate was collected and dissolved in a minimum amount of ammonia. Blue single crystals of 1

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were obtained by slow evaporation of the ammonia solution at ambient temperature. Yield: 30 mg, 44.7%. Anal. Calculated for $C_{18}H_{24}Cu_2N_8O_{12}$: C, 32.16; H, 3.57; N 16.68. Found: C, 31.96; H, 3.49; N 16.61.

Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.96 Å and O—H = 0.85 Å and U_{iso} set to 1.2 U_{eq} (parent atom). The coordinates of the water H atoms were calculated by the HYDROGEN program (Nardelli, 1999).

Figures



Fig. 1. The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

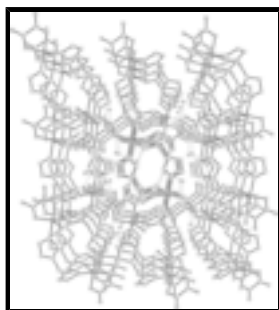


Fig. 2. Three dimensional network structure connected *via* hydrogen bonds.

bis[μ -bis(imidazol-1-yl)methane]bis[aqua(oxalato)copper(II)] dihydrate

Crystal data

$[Cu_2(C_2O_4)_2(C_7H_8N_4)_2(H_2O)_2] \cdot 2H_2O$

$M_r = 671.53$

Triclinic, $P\bar{1}$

$a = 7.970$ (4) Å

$b = 9.770$ (4) Å

$c = 9.913$ (4) Å

$\alpha = 117.964$ (4)°

$\beta = 104.582$ (5)°

$\gamma = 91.773$ (5)°

$V = 649.7$ (5) Å³

$Z = 1$

$F_{000} = 342$

$D_x = 1.716$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2374 reflections

$\theta = 2.4$ – 28.0°

$\mu = 1.71$ mm⁻¹

$T = 298$ (2) K

Block, blue

$0.55 \times 0.53 \times 0.49$ mm

Data collection

Siemens SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

2248 independent reflections

1997 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$

$T = 298(2)$ K $\theta_{\max} = 25.0^\circ$
 φ and ω scans $\theta_{\min} = 2.4^\circ$
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996) $h = -9 \rightarrow 9$
 $T_{\min} = 0.453$, $T_{\max} = 0.487$ $k = -11 \rightarrow 11$
 3367 measured reflections $l = -11 \rightarrow 11$

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
 $wR(F^2) = 0.072$ $w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.2553P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.08$ $(\Delta/\sigma)_{\max} = 0.001$
 2248 reflections $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 181 parameters $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods 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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.86641 (4)	0.71911 (3)	0.95989 (3)	0.02912 (12)
N1	0.7745 (3)	0.3018 (2)	0.5408 (2)	0.0287 (5)
N2	0.8596 (3)	0.5362 (2)	0.7528 (2)	0.0285 (5)
N3	0.5694 (3)	0.1755 (2)	0.2769 (2)	0.0276 (5)
N4	0.3642 (3)	0.2364 (2)	0.1309 (2)	0.0296 (5)
O1	1.1180 (2)	0.7196 (2)	1.0468 (2)	0.0360 (4)
O2	1.3453 (2)	0.8662 (2)	1.2644 (2)	0.0414 (5)
O3	0.9116 (2)	0.9180 (2)	1.1597 (2)	0.0450 (5)
O4	1.1263 (3)	1.0719 (3)	1.3829 (3)	0.0731 (8)
O5	0.7390 (3)	0.5676 (2)	1.0311 (2)	0.0476 (5)
H11	0.7729	0.4808	1.0134	0.071*
H12	0.7205	0.6120	1.1217	0.071*

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O6	0.6384 (3)	0.7255 (3)	0.3125 (3)	0.0540 (6)
H13	0.5560	0.7690	0.2849	0.081*
H14	0.7054	0.8012	0.3997	0.081*
C1	0.6634 (4)	0.1548 (3)	0.4106 (3)	0.0338 (6)
H1A	0.7356	0.0746	0.3750	0.041*
H1B	0.5795	0.1197	0.4486	0.041*
C2	0.7277 (3)	0.4185 (3)	0.6587 (3)	0.0305 (6)
H2	0.6164	0.4162	0.6720	0.037*
C3	0.9981 (3)	0.4921 (3)	0.6917 (3)	0.0363 (6)
H3	1.1099	0.5524	0.7345	0.044*
C4	0.9473 (3)	0.3485 (3)	0.5607 (3)	0.0388 (7)
H4	1.0155	0.2923	0.4966	0.047*
C5	0.4070 (3)	0.2121 (3)	0.2547 (3)	0.0304 (6)
H5A	0.3350	0.2192	0.3176	0.036*
C6	0.5059 (3)	0.2145 (3)	0.0727 (3)	0.0337 (6)
H6	0.5134	0.2241	-0.0147	0.040*
C7	0.6329 (3)	0.1769 (3)	0.1621 (3)	0.0329 (6)
H7	0.7422	0.1561	0.1481	0.040*
C8	1.1908 (3)	0.8376 (3)	1.1850 (3)	0.0282 (5)
C9	1.0674 (3)	0.9537 (3)	1.2509 (3)	0.0376 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02589 (18)	0.02280 (18)	0.02358 (18)	0.00912 (12)	0.00161 (12)	0.00222 (13)
N1	0.0313 (11)	0.0211 (10)	0.0221 (11)	0.0085 (9)	0.0015 (9)	0.0044 (9)
N2	0.0268 (10)	0.0248 (11)	0.0233 (11)	0.0069 (9)	0.0035 (9)	0.0053 (9)
N3	0.0298 (11)	0.0194 (10)	0.0231 (11)	0.0072 (8)	0.0017 (9)	0.0052 (8)
N4	0.0274 (10)	0.0269 (11)	0.0254 (11)	0.0068 (9)	0.0029 (9)	0.0083 (9)
O1	0.0299 (9)	0.0274 (10)	0.0279 (10)	0.0134 (8)	0.0017 (8)	-0.0011 (8)
O2	0.0283 (10)	0.0393 (11)	0.0388 (11)	0.0068 (8)	-0.0026 (8)	0.0115 (9)
O3	0.0334 (10)	0.0353 (11)	0.0360 (11)	0.0169 (8)	0.0021 (9)	-0.0027 (9)
O4	0.0508 (13)	0.0559 (14)	0.0430 (13)	0.0166 (11)	0.0006 (11)	-0.0239 (11)
O5	0.0670 (13)	0.0411 (11)	0.0494 (12)	0.0287 (10)	0.0295 (11)	0.0269 (10)
O6	0.0396 (11)	0.0561 (14)	0.0495 (13)	0.0163 (10)	0.0099 (10)	0.0142 (11)
C1	0.0451 (15)	0.0194 (12)	0.0249 (13)	0.0063 (11)	0.0005 (11)	0.0065 (11)
C2	0.0291 (13)	0.0274 (13)	0.0257 (13)	0.0063 (11)	0.0065 (11)	0.0067 (11)
C3	0.0276 (13)	0.0396 (16)	0.0280 (14)	0.0039 (11)	0.0053 (11)	0.0076 (12)
C4	0.0318 (14)	0.0427 (16)	0.0285 (14)	0.0147 (12)	0.0102 (11)	0.0061 (12)
C5	0.0283 (13)	0.0287 (14)	0.0271 (13)	0.0072 (11)	0.0075 (11)	0.0086 (11)
C6	0.0337 (14)	0.0369 (15)	0.0280 (14)	0.0102 (11)	0.0086 (11)	0.0141 (12)
C7	0.0283 (13)	0.0317 (14)	0.0298 (14)	0.0099 (11)	0.0073 (11)	0.0085 (11)
C8	0.0266 (13)	0.0239 (13)	0.0273 (13)	0.0052 (10)	0.0043 (11)	0.0092 (11)
C9	0.0362 (15)	0.0269 (14)	0.0312 (15)	0.0074 (11)	0.0068 (12)	0.0014 (12)

Geometric parameters (\AA , $^\circ$)

Cu1—O3	1.9537 (19)	O3—C9	1.262 (3)
Cu1—O1	1.9717 (19)	O4—C9	1.227 (3)

Cu1—N2	1.977 (2)	O5—H11	0.8499
Cu1—N4 ⁱ	1.991 (2)	O5—H12	0.8499
Cu1—O5	2.229 (2)	O6—H13	0.8500
N1—C2	1.342 (3)	O6—H14	0.8500
N1—C4	1.373 (3)	C1—H1A	0.9700
N1—C1	1.456 (3)	C1—H1B	0.9700
N2—C2	1.313 (3)	C2—H2	0.9300
N2—C3	1.376 (3)	C3—C4	1.345 (4)
N3—C5	1.345 (3)	C3—H3	0.9300
N3—C7	1.362 (3)	C4—H4	0.9300
N3—C1	1.456 (3)	C5—H5A	0.9300
N4—C5	1.322 (3)	C6—C7	1.350 (4)
N4—C6	1.372 (3)	C6—H6	0.9300
N4—Cu1 ⁱ	1.991 (2)	C7—H7	0.9300
O1—C8	1.273 (3)	C8—C9	1.542 (4)
O2—C8	1.224 (3)		
O3—Cu1—O1	83.29 (7)	N3—C1—H1A	109.5
O3—Cu1—N2	169.00 (9)	N1—C1—H1A	109.5
O1—Cu1—N2	90.02 (8)	N3—C1—H1B	109.5
O3—Cu1—N4 ⁱ	91.17 (8)	N1—C1—H1B	109.5
O1—Cu1—N4 ⁱ	165.88 (8)	H1A—C1—H1B	108.1
N2—Cu1—N4 ⁱ	93.33 (8)	N2—C2—N1	111.1 (2)
O3—Cu1—O5	97.83 (9)	N2—C2—H2	124.4
O1—Cu1—O5	101.59 (8)	N1—C2—H2	124.4
N2—Cu1—O5	92.04 (9)	C4—C3—N2	109.8 (2)
N4 ⁱ —Cu1—O5	92.01 (9)	C4—C3—H3	125.1
C2—N1—C4	107.3 (2)	N2—C3—H3	125.1
C2—N1—C1	127.3 (2)	C3—C4—N1	106.0 (2)
C4—N1—C1	125.3 (2)	C3—C4—H4	127.0
C2—N2—C3	105.8 (2)	N1—C4—H4	127.0
C2—N2—Cu1	125.91 (17)	N4—C5—N3	110.4 (2)
C3—N2—Cu1	127.46 (17)	N4—C5—H5A	124.8
C5—N3—C7	107.7 (2)	N3—C5—H5A	124.8
C5—N3—C1	124.9 (2)	C7—C6—N4	109.4 (2)
C7—N3—C1	127.2 (2)	C7—C6—H6	125.3
C5—N4—C6	106.1 (2)	N4—C6—H6	125.3
C5—N4—Cu1 ⁱ	126.32 (17)	C6—C7—N3	106.4 (2)
C6—N4—Cu1 ⁱ	127.45 (18)	C6—C7—H7	126.8
C8—O1—Cu1	113.30 (15)	N3—C7—H7	126.8
C9—O3—Cu1	113.63 (16)	O2—C8—O1	126.3 (2)
Cu1—O5—H11	118.7	O2—C8—C9	119.4 (2)
Cu1—O5—H12	117.8	O1—C8—C9	114.3 (2)
H11—O5—H12	110.1	O4—C9—O3	125.5 (3)
H13—O6—H14	103.0	O4—C9—C8	119.0 (2)
N3—C1—N1	110.6 (2)	O3—C9—C8	115.4 (2)
O3—Cu1—N2—C2	-164.4 (4)	C1—N1—C2—N2	-177.8 (2)
O1—Cu1—N2—C2	143.2 (2)	C2—N2—C3—C4	0.4 (3)

supplementary materials

N4 ⁱ —Cu1—N2—C2	-50.5 (2)	Cu1—N2—C3—C4	170.18 (19)
O5—Cu1—N2—C2	41.6 (2)	N2—C3—C4—N1	-0.6 (3)
O3—Cu1—N2—C3	27.7 (5)	C2—N1—C4—C3	0.5 (3)
O1—Cu1—N2—C3	-24.6 (2)	C1—N1—C4—C3	178.1 (2)
N4 ⁱ —Cu1—N2—C3	141.7 (2)	C6—N4—C5—N3	-0.1 (3)
O5—Cu1—N2—C3	-126.2 (2)	Cu1 ⁱ —N4—C5—N3	176.06 (15)
O3—Cu1—O1—C8	1.64 (18)	C7—N3—C5—N4	0.1 (3)
N2—Cu1—O1—C8	172.90 (18)	C1—N3—C5—N4	174.5 (2)
N4 ⁱ —Cu1—O1—C8	69.1 (4)	C5—N4—C6—C7	0.1 (3)
O5—Cu1—O1—C8	-95.02 (19)	Cu1 ⁱ —N4—C6—C7	-176.04 (17)
O1—Cu1—O3—C9	-2.0 (2)	N4—C6—C7—N3	0.0 (3)
N2—Cu1—O3—C9	-54.8 (5)	C5—N3—C7—C6	0.0 (3)
N4 ⁱ —Cu1—O3—C9	-169.0 (2)	C1—N3—C7—C6	-174.2 (2)
O5—Cu1—O3—C9	98.9 (2)	Cu1—O1—C8—O2	-179.4 (2)
C5—N3—C1—N1	-92.8 (3)	Cu1—O1—C8—C9	-1.1 (3)
C7—N3—C1—N1	80.5 (3)	Cu1—O3—C9—O4	-179.4 (3)
C2—N1—C1—N3	86.0 (3)	Cu1—O3—C9—C8	1.9 (3)
C4—N1—C1—N3	-91.2 (3)	O2—C8—C9—O4	-0.9 (4)
C3—N2—C2—N1	-0.1 (3)	O1—C8—C9—O4	-179.3 (3)
Cu1—N2—C2—N1	-170.06 (16)	O2—C8—C9—O3	177.9 (2)
C4—N1—C2—N2	-0.3 (3)	O1—C8—C9—O3	-0.6 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H14 ⁱⁱ —O4 ⁱⁱ	0.85	1.98	2.804 (3)	164
O6—H13 ⁱⁱⁱ —O2 ⁱⁱⁱ	0.85	1.97	2.797 (3)	165
O5—H12 ^{iv} —O6 ^{iv}	0.85	1.98	2.823 (3)	169
O5—H11 ^v —O1 ^v	0.85	2.05	2.895 (3)	170

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

Fig. 1

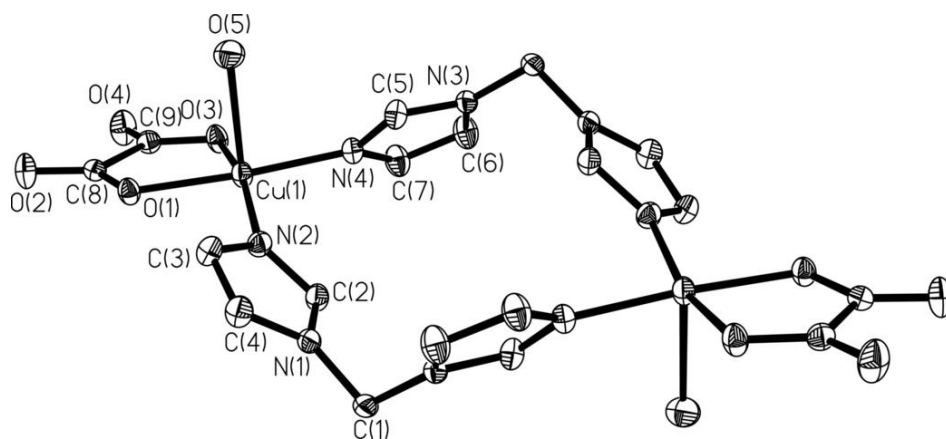


Fig. 2

