

[N-(2-Hydroxyethyl)ethylenediamine]-oxalatocopper(II)

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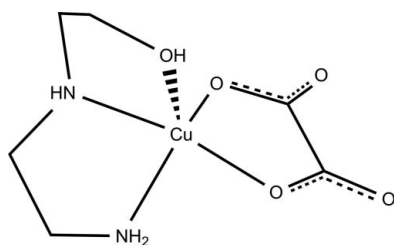
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.029; wR factor = 0.065; data-to-parameter ratio = 13.1.

In the title mononuclear copper(II) compound, $[\text{Cu}(\text{C}_2\text{O}_4)(\text{C}_4\text{H}_{12}\text{N}_2\text{O})]$, the Cu^{II} ion has a slightly distorted square-pyramidal geometry, with a tridentate *N*-(2-hydroxyethyl)ethylenediamine (HydEt-en) and a bidentate oxalate (ox) ligand. The N atoms of the HydEt-en ligand and the O atoms of ox ligand form the basal plane, while the O atom of the ethanol group of the HydEt-en ligand is located in the axial position. The complex molecules participate in a supramolecular assembly through $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between HydEt-en and ox ligands.

Related literature

For general background to the HydEt-en ligand, see: Karadağ *et al.* (2004, 2005); Paşaođlu *et al.* (2005). For transition metal complexes of oxalate, see: Scott *et al.* (1973); Xia *et al.* (2004); Yılmaz *et al.* (2003); Youngme *et al.* (2003). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$[\text{Cu}(\text{C}_2\text{O}_4)(\text{C}_4\text{H}_{12}\text{N}_2\text{O})]$	$V = 906.21(9)$ Å ³
$M_r = 255.72$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.9766(5)$ Å	$\mu = 2.41$ mm ⁻¹
$b = 8.7263(4)$ Å	$T = 296$ K
$c = 13.0191(7)$ Å	$0.52 \times 0.42 \times 0.23$ mm

Data collection

Stoe IPDS-II diffractometer	10045 measured reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	1868 independent reflections
$T_{\text{min}} = 0.570$, $T_{\text{max}} = 0.781$	1780 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.063$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	$\Delta\rho_{\text{max}} = 0.22$ e Å ⁻³
$wR(F^2) = 0.065$	$\Delta\rho_{\text{min}} = -1.30$ e Å ⁻³
$S = 1.08$	Absolute structure: Flack (1983), 797 Friedel pairs
1868 reflections	Flack parameter: 0.017 (17)
143 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected bond lengths (Å).

Cu1—O1	1.9505 (13)	Cu1—N1	2.0066 (18)
Cu1—O4	1.9625 (14)	Cu1—O5	2.4174 (16)
Cu1—N2	1.9717 (18)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O4 ⁱ	0.85 (3)	2.17 (3)	3.015 (2)	173 (2)
N2—H2A \cdots O1 ⁱⁱ	0.94 (3)	2.02 (3)	2.936 (2)	165 (2)
N2—H2B \cdots O2 ⁱⁱⁱ	0.91 (3)	2.02 (3)	2.909 (2)	168 (3)
O5—H5 \cdots O3 ^{iv}	0.72 (3)	2.06 (3)	2.774 (3)	171 (3)

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2929).

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supplementary materials

Acta Cryst. (2009). E65, m1337-m1338 [doi:10.1107/S1600536809040264]

[*N*-(2-Hydroxyethyl)ethylenediamine]oxalatocopper(II)

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Comment

As part of our ongoing research on the preparation and characterization of mixed ligand metal complexes of HydEt-en we report here the synthesis and X-ray analysis of a mononuclear copper(II) complex, [Cu(HydEt-en)(ox)]. This study is an example of the construction of a supramolecular assembly based on hydrogen bonds in mixed-ligand metal complexes.

In title compound, the HydEt-en ligand chelates through its two N atoms and the O atom of the hydroxyl group. The square-pyramidal coordination shell consists of three five-membered chelate rings (Fig. 1) *viz.* A (Cu1/O1/C1/C2/O4), B (Cu1/N1/C5/C6/N2) and C (Cu1/O5/C3/C4/N1). The mean plane through ring C is perpendicular to that through the ring A, with a dihedral angle of 89.27 (5)°. The bite angles of rings B and C are 86.36 (7)° and 78.65 (7)°, respectively.

The complex participates in a supramolecular assembly through N—H···O and O—H···O hydrogen bonds between HydEt-en and oxalate ligands. The HydEt-en ligand is involved in hydrogen bonds through its amino, imino and hydroxyl groups. In the crystal structure (Fig. 2), N1—H1···O4ⁱ and N2—H2A···O1ⁱⁱ (Table 2) hydrogen bonds constitute a polymeric chain parallel to the [010], giving rise to C(4) chain and $R_2^2(8)$ (Bernstein *et al.*, 1995) rings. These polymeric chains are inter-connected to each other by N2—H2B···O2ⁱⁱⁱ and O5—H5···O3^{iv} hydrogen bonds extending through the *ac* plane, resulting in a three-dimensional supramolecular network as illustrated in Fig. 3.

Experimental

The HydEt-en ligand (0.12 g, 2 mmol) was added dropwise to a solution of Cu(ox).0.5H₂O (0.48 g, 3.0 mmol) in pyridine-water (1:2, 30 ml) at 50° C. The resulting solution was stirred for 1 h at 50° C and then filtered. The reaction mixture was then slowly cooled to room temperature. Violet crystals suitable for X-ray diffraction analysis were obtained after a few days and were washed with 5 ml of ethanol and dried in air.

Refinement

All H atoms involved in hydrogen bondings were located in a difference Fourier map and their positional and U_{iso} parameters were refined. The remaining H atoms were placed in calculated positions and constrained to ride on their parents atoms, with C-H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

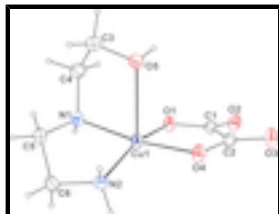


Fig. 1. The molecular structure of [Cu(HydEt-en)(ox)] with atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level for the non hydrogen atoms.

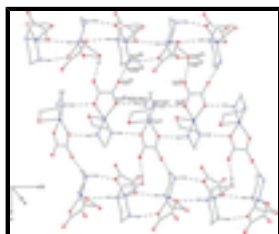


Fig. 2. The assembly of polymeric chains of [Cu(HydEt-en)(ox)] into a two-dimensional layer by N—H...O and O—H...O hydrogen bonds. H atoms not involved in hydrogen bondings have been omitted for clarity. Symmetry codes are as given in Table 2

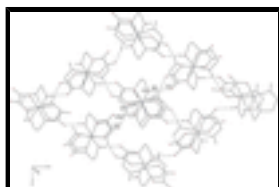


Fig. 3. The supramolecular network of [Cu(HydEt-en)(ox)] projected onto (010). All H atoms except H2b and H5 have been omitted for clarity. Symmetry codes are as given in Table 2.

[N-(2-Hydroxyethyl)ethylenediamine]oxalatocopper(II)

Crystal data

[Cu(C₂O₄)(C₄H₁₂N₂O)]

M_r = 255.72

Orthorhombic, *P*2₁2₁2₁

Hall symbol: P 2ac 2ab

a = 7.9766 (5) Å

b = 8.7263 (4) Å

c = 13.0191 (7) Å

V = 906.21 (9) Å³

Z = 4

*F*₀₀₀ = 524

D_x = 1.874 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 10045 reflections

θ = 1.6–28.0°

μ = 2.41 mm⁻¹

T = 296 K

Prism, violet

0.52 × 0.42 × 0.23 mm

Data collection

Stoe IPDS-II
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: plane graphite

Detector resolution: 6.67 pixels mm⁻¹

T = 296 K

ω scans

Absorption correction: Integration
(X-RED32; Stoe & Cie, 2002)

1868 independent reflections

1780 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.063

θ_{max} = 26.5°

θ_{min} = 2.8°

h = -10→10

k = -10→10

$T_{\min} = 0.570$, $T_{\max} = 0.781$
10045 measured reflections

$l = -15 \rightarrow 16$

Refinement

Refinement on F^2

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

H atoms treated by a mixture of independent and constrained refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$

$$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.065$

$(\Delta/\sigma)_{\max} = 0.001$

$S = 1.08$

$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$

1868 reflections

$\Delta\rho_{\min} = -1.30 \text{ e } \text{\AA}^{-3}$

143 parameters

Extinction correction: none

Primary atom site location: structure-invariant direct methods

Absolute structure: Flack (1983), 797 Friedel pairs

Secondary atom site location: difference Fourier map Flack parameter: 0.017 (17)

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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6054 (2)	0.4652 (2)	0.44437 (15)	0.0242 (4)
C2	0.7217 (3)	0.3322 (2)	0.41059 (16)	0.0274 (4)
C3	0.1649 (3)	0.2157 (3)	0.28011 (18)	0.0389 (5)
H3A	0.0821	0.1836	0.3302	0.047*
H3B	0.1451	0.1589	0.2172	0.047*
C4	0.1448 (3)	0.3853 (2)	0.25922 (18)	0.0374 (5)
H4A	0.0389	0.4029	0.2244	0.045*
H4B	0.1422	0.4404	0.3239	0.045*
C5	0.2752 (3)	0.3933 (3)	0.08732 (16)	0.0334 (4)
H5A	0.1974	0.4569	0.0492	0.040*
H5B	0.2357	0.2883	0.0845	0.040*
C6	0.4476 (3)	0.4039 (3)	0.04004 (16)	0.0339 (4)
H6A	0.4487	0.3530	-0.0262	0.041*
H6B	0.4780	0.5105	0.0299	0.041*

supplementary materials

Cu1	0.50643 (3)	0.38250 (2)	0.252350 (16)	0.02606 (11)
N1	0.2830 (2)	0.44501 (19)	0.19527 (13)	0.0271 (4)
N2	0.5680 (2)	0.3297 (2)	0.11000 (14)	0.0282 (4)
O1	0.48949 (18)	0.49776 (14)	0.38029 (11)	0.0288 (3)
O2	0.6303 (2)	0.53159 (18)	0.52577 (12)	0.0364 (4)
O3	0.8216 (2)	0.27578 (18)	0.47136 (13)	0.0408 (4)
O4	0.70385 (19)	0.28980 (16)	0.31740 (11)	0.0328 (3)
O5	0.3275 (2)	0.18117 (19)	0.31756 (14)	0.0351 (3)
H1	0.280 (3)	0.542 (3)	0.1959 (18)	0.028 (6)*
H2A	0.559 (3)	0.223 (3)	0.102 (2)	0.038 (7)*
H2B	0.668 (4)	0.371 (4)	0.093 (2)	0.052 (8)*
H5	0.319 (3)	0.186 (3)	0.373 (2)	0.030 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0248 (9)	0.0247 (8)	0.0231 (9)	-0.0019 (7)	-0.0017 (8)	-0.0006 (7)
C2	0.0259 (9)	0.0240 (8)	0.0323 (10)	0.0001 (8)	-0.0045 (8)	0.0010 (8)
C3	0.0350 (12)	0.0418 (11)	0.0400 (11)	-0.0101 (10)	-0.0008 (10)	0.0076 (9)
C4	0.0307 (10)	0.0416 (11)	0.0399 (13)	0.0025 (8)	0.0031 (9)	0.0028 (11)
C5	0.0340 (10)	0.0397 (10)	0.0266 (10)	-0.0020 (10)	-0.0076 (8)	0.0005 (9)
C6	0.0419 (11)	0.0360 (9)	0.0238 (10)	-0.0051 (9)	-0.0019 (9)	0.0035 (8)
Cu1	0.02695 (16)	0.02892 (15)	0.02230 (18)	0.00454 (9)	-0.00390 (9)	-0.00309 (8)
N1	0.0286 (8)	0.0228 (8)	0.0299 (9)	0.0020 (6)	-0.0050 (7)	-0.0012 (6)
N2	0.0280 (9)	0.0289 (8)	0.0276 (9)	-0.0039 (7)	0.0030 (7)	-0.0019 (7)
O1	0.0315 (7)	0.0291 (6)	0.0258 (6)	0.0055 (6)	-0.0055 (6)	-0.0039 (5)
O2	0.0366 (9)	0.0409 (7)	0.0316 (8)	0.0008 (7)	-0.0068 (7)	-0.0103 (7)
O3	0.0415 (9)	0.0449 (8)	0.0359 (8)	0.0151 (7)	-0.0119 (7)	-0.0018 (7)
O4	0.0321 (7)	0.0363 (8)	0.0299 (7)	0.0109 (6)	-0.0046 (7)	-0.0068 (6)
O5	0.0370 (8)	0.0366 (8)	0.0318 (8)	-0.0002 (7)	0.0049 (7)	0.0061 (7)

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

C1—O2	1.224 (2)	C5—H5A	0.97
C1—O1	1.277 (2)	C5—H5B	0.97
C1—C2	1.549 (3)	C6—N2	1.473 (3)
C2—O3	1.226 (3)	C6—H6A	0.97
C2—O4	1.276 (3)	C6—H6B	0.97
C3—O5	1.418 (3)	Cu1—O1	1.9505 (13)
C3—C4	1.514 (3)	Cu1—O4	1.9625 (14)
C3—H3A	0.97	Cu1—N2	1.9717 (18)
C3—H3B	0.97	Cu1—N1	2.0066 (18)
C4—N1	1.477 (3)	Cu1—O5	2.4174 (16)
C4—H4A	0.97	N1—H1	0.85 (3)
C4—H4B	0.97	N2—H2A	0.94 (3)
C5—N1	1.477 (3)	N2—H2B	0.91 (3)
C5—C6	1.509 (3)	O5—H5	0.72 (3)
O2—C1—O1	125.27 (18)	H6A—C6—H6B	108.4

O2—C1—C2	120.22 (17)	O1—Cu1—O4	84.24 (6)
O1—C1—C2	114.50 (16)	O1—Cu1—N2	160.11 (7)
O3—C2—O4	124.72 (19)	O4—Cu1—N2	96.29 (7)
O3—C2—C1	120.44 (18)	O1—Cu1—N1	96.58 (6)
O4—C2—C1	114.83 (16)	O4—Cu1—N1	169.93 (7)
O5—C3—C4	111.52 (19)	N2—Cu1—N1	86.36 (7)
O5—C3—H3A	109.3	O1—Cu1—O5	91.94 (6)
C4—C3—H3A	109.3	O4—Cu1—O5	91.30 (6)
O5—C3—H3B	109.3	N2—Cu1—O5	107.90 (7)
C4—C3—H3B	109.3	N1—Cu1—O5	78.65 (7)
H3A—C3—H3B	108.0	C4—N1—C5	113.41 (17)
N1—C4—C3	111.52 (19)	C4—N1—Cu1	111.01 (13)
N1—C4—H4A	109.3	C5—N1—Cu1	107.84 (13)
C3—C4—H4A	109.3	C4—N1—H1	109.0 (17)
N1—C4—H4B	109.3	C5—N1—H1	108.3 (16)
C3—C4—H4B	109.3	Cu1—N1—H1	107.1 (16)
H4A—C4—H4B	108.0	C6—N2—Cu1	108.44 (13)
N1—C5—C6	109.33 (17)	C6—N2—H2A	108.3 (16)
N1—C5—H5A	109.8	Cu1—N2—H2A	108.5 (16)
C6—C5—H5A	109.8	C6—N2—H2B	104 (2)
N1—C5—H5B	109.8	Cu1—N2—H2B	111 (2)
C6—C5—H5B	109.8	H2A—N2—H2B	116 (3)
H5A—C5—H5B	108.3	C1—O1—Cu1	113.13 (11)
N2—C6—C5	108.33 (17)	C2—O4—Cu1	112.35 (12)
N2—C6—H6A	110.0	C3—O5—Cu1	105.36 (12)
C5—C6—H6A	110.0	C3—O5—H5	104 (2)
N2—C6—H6B	110.0	Cu1—O5—H5	112 (2)
C5—C6—H6B	110.0		
O2—C1—C2—O3	11.9 (3)	O4—Cu1—N2—C6	-173.13 (13)
O1—C1—C2—O3	-169.41 (19)	N1—Cu1—N2—C6	16.62 (13)
O2—C1—C2—O4	-167.92 (19)	O5—Cu1—N2—C6	93.46 (14)
O1—C1—C2—O4	10.8 (2)	O2—C1—O1—Cu1	173.14 (16)
O5—C3—C4—N1	50.6 (3)	C2—C1—O1—Cu1	-5.5 (2)
N1—C5—C6—N2	49.2 (2)	O4—Cu1—O1—C1	0.32 (13)
C3—C4—N1—C5	71.6 (2)	N2—Cu1—O1—C1	-92.3 (2)
C3—C4—N1—Cu1	-50.0 (2)	N1—Cu1—O1—C1	170.23 (14)
C6—C5—N1—C4	-157.56 (17)	O5—Cu1—O1—C1	91.43 (13)
C6—C5—N1—Cu1	-34.2 (2)	O3—C2—O4—Cu1	170.12 (18)
O1—Cu1—N1—C4	-64.96 (14)	C1—C2—O4—Cu1	-10.1 (2)
O4—Cu1—N1—C4	29.1 (4)	O1—Cu1—O4—C2	5.92 (14)
N2—Cu1—N1—C4	134.79 (14)	N2—Cu1—O4—C2	165.93 (14)
O5—Cu1—N1—C4	25.71 (13)	N1—Cu1—O4—C2	-89.3 (4)
O1—Cu1—N1—C5	170.23 (13)	O5—Cu1—O4—C2	-85.90 (14)
O4—Cu1—N1—C5	-95.7 (4)	C4—C3—O5—Cu1	-25.7 (2)
N2—Cu1—N1—C5	9.98 (14)	O1—Cu1—O5—C3	96.66 (14)
O5—Cu1—N1—C5	-99.10 (14)	O4—Cu1—O5—C3	-179.06 (14)
C5—C6—N2—Cu1	-39.46 (19)	N2—Cu1—O5—C3	-82.02 (15)
O1—Cu1—N2—C6	-82.7 (2)	N1—Cu1—O5—C3	0.34 (14)

supplementary materials

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O4 ⁱ	0.85 (3)	2.17 (3)	3.015 (2)	173 (2)
N2—H2A \cdots O1 ⁱⁱ	0.94 (3)	2.02 (3)	2.936 (2)	165 (2)
N2—H2B \cdots O2 ⁱⁱⁱ	0.91 (3)	2.02 (3)	2.909 (2)	168 (3)
O5—H5 \cdots O3 ^{iv}	0.72 (3)	2.06 (3)	2.774 (3)	171 (3)

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $-x+1, y-1/2, -z+1/2$; (iii) $-x+3/2, -y+1, z-1/2$; (iv) $x-1/2, -y+1/2, -z+1$.

Fig. 1

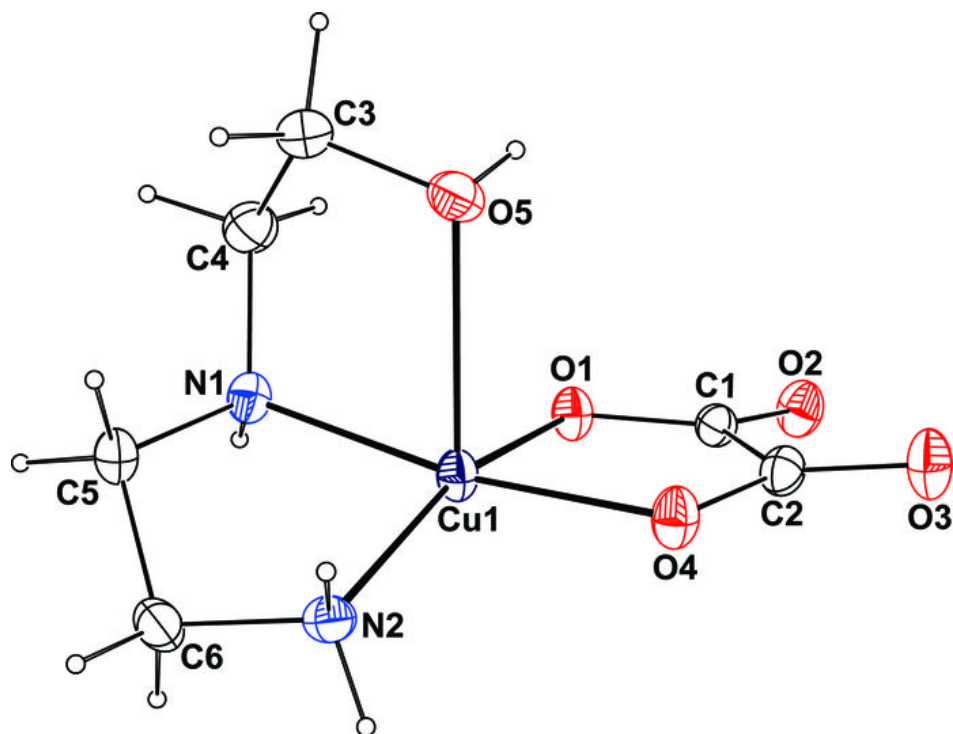


Fig. 2

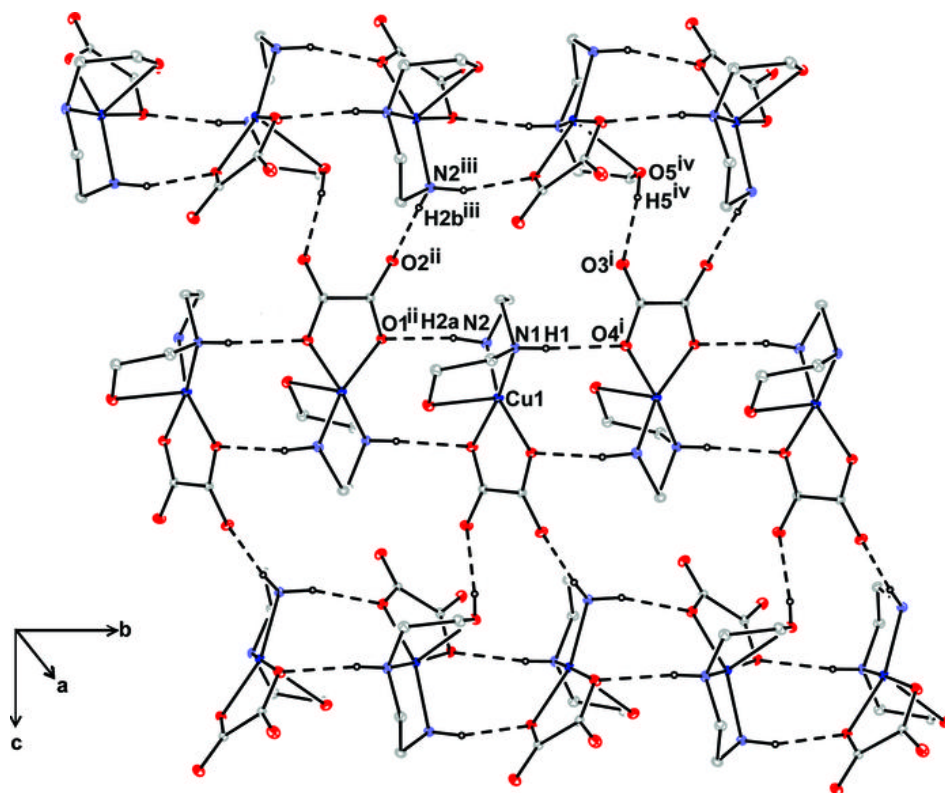


Fig. 3

