

Tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]phenolato)-tetracopper(II)

Jian-Fang Dong, Lian-Zhi Li,* Hong-Yu Xu and Da-Qi Wang

School of Chemistry and Chemical Engineering, Liaocheng University, Shandong 252059, People's Republic of China

Correspondence e-mail: lillianzhi1963@yahoo.com.cn

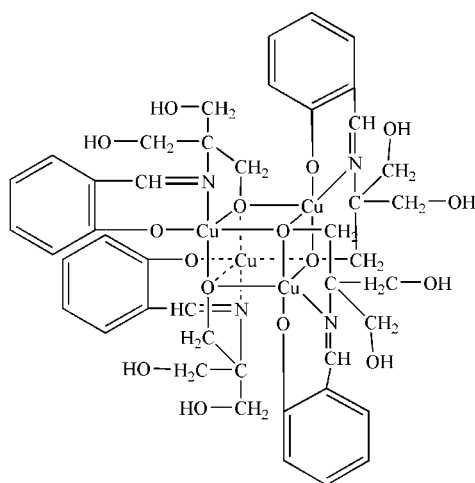
Received 27 June 2007; accepted 1 August 2007

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 = 0.075; data-to-parameter ratio = 14.1.

In the title tetranuclear complex, $[\text{Cu}_4(\text{C}_{11}\text{H}_{13}\text{NO}_4)_4]$, which has crystallographic $\bar{4}$ symmetry, the Cu^{II} ions are coordinated by the tridentate Schiff base ligands, forming a tetranuclear Cu_4O_4 cubane-like configuration. The Cu^{II} ion adopts a CuNO_4 distorted square-pyramidal coordination environment. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{O}$ bonds help to form a three-dimensional structure.

Related literature

For related literature, see: Beinert (1980); Dong *et al.* (2007); Mishtu *et al.* (2002); Si *et al.* (2002).



Experimental

Crystal data

$[\text{Cu}_4(\text{C}_{11}\text{H}_{13}\text{NO}_4)_4]$
 $M_r = 1147.06$
 Tetragonal, $I4_1/a$

$a = 17.209$ (3) Å
 $c = 16.836$ (3) Å
 $V = 4986.0$ (13) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.75$ mm⁻¹

$T = 298$ (2) K
 $0.53 \times 0.49 \times 0.48$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.457$, $T_{\text{max}} = 0.487$
 (expected range = 0.405–0.431)

12748 measured reflections
 2203 independent reflections
 1821 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.075$
 $S = 1.06$
 2203 reflections

156 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—O1	1.9063 (16)	Cu1—O2	1.9451 (16)
Cu1—N1	1.9218 (19)	Cu1—O2 ⁱⁱ	2.5930 (16)
Cu1—O2 ⁱ	1.9438 (15)		

Symmetry codes: (i) $y - \frac{1}{4}, -x + \frac{5}{4}, -z + \frac{9}{4}$; (ii) $-x + 1, -y + \frac{3}{2}, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3}\cdots\text{O4}^{\text{iii}}$	0.82	1.91	2.723 (3)	172
$\text{O4}-\text{H4}\cdots\text{O1}^{\text{iv}}$	0.82	1.85	2.668 (2)	171

Symmetry codes: (iii) $y - \frac{1}{4}, -x + \frac{3}{4}, z - \frac{1}{4}$; (iv) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{9}{4}$.

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

The authors thank the Natural Science Foundation of Shandong Province (grant No. Y2004B02) for a research grant.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2463).

References

- Beinert, H. (1980). *Coord. Chem. Rev.* **33**, 55–85.
 Dong, J.-F., Li, L.-Z., Xu, T., Cui, H. & Wang, D.-Q. (2007). *Acta Cryst.* **E63**, m1501–m1502.
 Mishtu, D., Chebrolu, P. R., Pauli, K. S. & Kari, R. (2002). *Inorg. Chem. Commun.* **5**, 380–383.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997a). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Si, S.-F., Tang, J.-K., Liao, D.-Z., Jiang, Z.-H. & Yan, S.-P. (2002). *Inorg. Chem. Commun.* **5**, 76–77.
 Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supplementary materials

Acta Cryst. (2007). E63, m2300 [doi:10.1107/S1600536807037920]

Tetrakis(μ_3 -2-[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)tetracopper(II)

J.-F. Dong, L.-Z. Li, H.-Y. Xu and D.-Q. Wang

Comment

Considerable efforts have been devoted to the study of polynuclear Cu^{II} complexes due to their importance as models for enzymatic systems (Beinert, 1980) and in studying metal-metal interactions. The chemistry of transition metal complexes of hydroxy(aryl-OH and alkyl-OH) rich molecules containing imine/amine group is important in the biomimetic studies of metalloproteins (Mishtu *et al.*, 2002).

A few structurally characterized multinuclear complexes containing Schiff base ligands has been reported (Mishtu *et al.*, 2002). As part of our ongoing studies (Dong *et al.*, 2007) in this area, we report here the synthesis and crystal structure of the title compound, (I), a tetracopper(II) complex with a tridentate Schiff base ligand derived from the condensation of salicylaldehyde and trihydroxymethylaminomethane. Mishtu *et al.* (2002) reported the same cluster as a hydrate in a different space group.

Compound (I) contains a tetranuclear cubane core based on an approximately cubic array of alternating copper and oxygen atoms (Fig. 1). Each Cu^{II} atom resides in a distorted square-pyramid coordination environment with one nitrogen and two oxygen atoms from one Schiff base ligand and two oxygen atoms from the neighboring units of the cubane. The Cu atom deviates from the basal plane formed by O1, N1, O2 and O2ⁱ ($i = y - 1/4, -x + 5/4, -z + 9/4$) by 0.0672 (12) Å, with a significantly longer Cu—O_{apical} bond distance (Table 1).

Within the cluster, the Cu \cdots Cu distances [3.591 (4) Å, 3.154 (3) Å] are similar to the reported values for related structures (Si *et al.*, 2002; Mishtu *et al.*, 2002), indicating no significant bonding interactions between the Cu^{II} ions in (I).

In the crystal structure, the intermolecular O—H \cdots O hydrogen bonds help to form a three-dimensional network (Fig. 2, Table 2).

Experimental

Trihydroxymethylaminomethane (1 mmol, 121.14 mg) was dissolved in hot methanol (10 ml) and added in portions to a methanol solution (3 ml) of salicylaldehyde (1 mmol, 0.11 ml). The mixture was then stirred at 323 K for 2 h. Subsequently, an aqueous solution (2 ml) of cupric acetate hydrate (1 mmol, 199.7 mg) was added dropwise and stirred for another 5 h. The solution was held at room temperature for ten days, whereupon blue blocks of (I) were obtained.

Refinement

All the H atoms were placed in calculated positions (C—H = 0.93–0.97 Å, O—H = 0.82 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}}, \text{O})$.

Figures

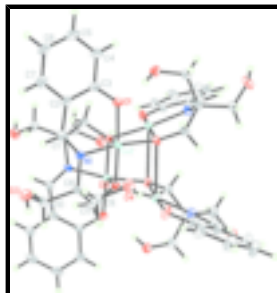


Fig. 1. The structure of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). The asymmetric atoms are labelled.

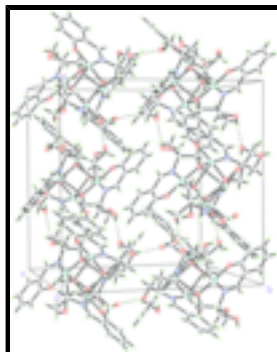


Fig. 2. Packing diagram of (I) with hydrogen bonds shown as dashed lines.

Tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]phenolato)tetracopper(II)

Crystal data

[Cu₄(C₁₁H₁₃NO₄)₄]

$M_r = 1147.06$

Tetragonal, $I4_1/a$

Hall symbol: $-I\ 4ad$

$a = 17.209\ (3)\ \text{\AA}$

$b = 17.209\ (3)\ \text{\AA}$

$c = 16.836\ (3)\ \text{\AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 4986.0\ (13)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 2352$

$D_x = 1.528\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5431 reflections

$\theta = 2.4\text{--}28.1^\circ$

$\mu = 1.75\ \text{mm}^{-1}$

$T = 298\ (2)\ \text{K}$

Block, blue

$0.53 \times 0.49 \times 0.48\ \text{mm}$

Data collection

Siemens SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298\ (2)\ \text{K}$

ω scans

2203 independent reflections

1821 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 1.7^\circ$

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996) $h = -20 \rightarrow 18$
 $T_{\min} = 0.457$, $T_{\max} = 0.487$ $k = -20 \rightarrow 16$
 12748 measured reflections $l = -18 \rightarrow 20$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.028$ H-atom parameters constrained
 $wR(F^2) = 0.075$ $w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 3.0697P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.06$ $(\Delta/\sigma)_{\max} = 0.002$
 2203 reflections $\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
 156 parameters $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$
 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.396178 (15)	0.739558 (15)	1.069439 (16)	0.02320 (12)
N1	0.37415 (11)	0.69497 (11)	0.96723 (11)	0.0261 (4)
O1	0.31430 (10)	0.81400 (10)	1.06436 (10)	0.0347 (4)
O2	0.48427 (9)	0.66875 (9)	1.07064 (8)	0.0235 (4)
O3	0.36321 (12)	0.57702 (11)	0.82462 (11)	0.0452 (5)
H3	0.3518	0.5309	0.8286	0.068*
O4	0.32782 (10)	0.58053 (12)	1.07332 (10)	0.0393 (5)
H4	0.3644	0.5761	1.1042	0.059*
C1	0.32492 (15)	0.72192 (14)	0.91698 (15)	0.0341 (6)
H1	0.3192	0.6951	0.8694	0.041*
C2	0.27757 (15)	0.79070 (15)	0.92818 (15)	0.0343 (6)
C3	0.27275 (14)	0.83153 (14)	1.00084 (15)	0.0293 (5)
C4	0.22008 (15)	0.89372 (15)	1.00520 (17)	0.0400 (7)
H4A	0.2151	0.9208	1.0527	0.048*

supplementary materials

C5	0.17574 (18)	0.91569 (17)	0.94118 (18)	0.0492 (8)
H5A	0.1420	0.9577	0.9459	0.059*
C6	0.18063 (19)	0.87623 (18)	0.87002 (19)	0.0543 (9)
H6	0.1508	0.8914	0.8267	0.065*
C7	0.23011 (18)	0.81440 (18)	0.86439 (17)	0.0497 (8)
H7	0.2326	0.7870	0.8168	0.060*
C8	0.40970 (14)	0.61676 (13)	0.95857 (14)	0.0262 (5)
C9	0.48709 (13)	0.61901 (14)	1.00416 (14)	0.0285 (5)
H9A	0.5000	0.5669	1.0217	0.034*
H9B	0.5279	0.6364	0.9686	0.034*
C10	0.42851 (15)	0.59321 (15)	0.87300 (15)	0.0355 (6)
H10A	0.4581	0.6347	0.8484	0.043*
H10B	0.4614	0.5475	0.8743	0.043*
C11	0.35195 (14)	0.55883 (15)	0.99569 (15)	0.0328 (6)
H11A	0.3066	0.5549	0.9617	0.039*
H11B	0.3761	0.5079	0.9980	0.039*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02486 (18)	0.02156 (18)	0.02318 (18)	0.00370 (11)	-0.00404 (12)	-0.00364 (11)
N1	0.0298 (11)	0.0224 (10)	0.0260 (10)	0.0035 (8)	-0.0045 (9)	-0.0034 (8)
O1	0.0382 (10)	0.0368 (10)	0.0291 (9)	0.0146 (8)	-0.0113 (8)	-0.0098 (8)
O2	0.0288 (9)	0.0195 (8)	0.0222 (9)	0.0043 (6)	-0.0045 (7)	-0.0024 (6)
O3	0.0653 (14)	0.0341 (11)	0.0362 (10)	0.0008 (9)	-0.0197 (10)	-0.0073 (9)
O4	0.0288 (10)	0.0581 (12)	0.0310 (10)	0.0011 (9)	0.0001 (8)	0.0036 (9)
C1	0.0433 (16)	0.0315 (14)	0.0273 (13)	0.0041 (12)	-0.0095 (12)	-0.0054 (11)
C2	0.0384 (15)	0.0309 (14)	0.0336 (14)	0.0049 (11)	-0.0102 (12)	0.0015 (11)
C3	0.0303 (14)	0.0229 (12)	0.0346 (14)	0.0016 (10)	-0.0066 (11)	0.0009 (11)
C4	0.0381 (16)	0.0364 (15)	0.0456 (16)	0.0106 (12)	-0.0080 (13)	-0.0057 (13)
C5	0.0496 (18)	0.0366 (16)	0.061 (2)	0.0180 (13)	-0.0146 (15)	0.0033 (14)
C6	0.061 (2)	0.0534 (19)	0.0489 (19)	0.0191 (16)	-0.0243 (15)	0.0073 (15)
C7	0.064 (2)	0.0486 (18)	0.0360 (16)	0.0164 (15)	-0.0187 (14)	-0.0041 (14)
C8	0.0288 (13)	0.0239 (12)	0.0258 (12)	0.0027 (10)	-0.0032 (10)	-0.0069 (10)
C9	0.0254 (13)	0.0289 (13)	0.0312 (14)	0.0042 (10)	-0.0018 (11)	-0.0075 (11)
C10	0.0441 (16)	0.0339 (15)	0.0287 (14)	0.0027 (12)	-0.0008 (12)	-0.0082 (11)
C11	0.0323 (14)	0.0298 (14)	0.0364 (15)	0.0016 (10)	-0.0008 (11)	-0.0002 (11)

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

Cu1—O1	1.9063 (16)	C3—C4	1.404 (3)
Cu1—N1	1.9218 (19)	C4—C5	1.374 (4)
Cu1—O2 ⁱ	1.9438 (15)	C4—H4A	0.9300
Cu1—O2	1.9451 (16)	C5—C6	1.380 (4)
Cu1—O2 ⁱⁱ	2.5930 (16)	C5—H5A	0.9300
N1—C1	1.284 (3)	C6—C7	1.366 (4)
N1—C8	1.486 (3)	C6—H6	0.9300
O1—C3	1.321 (3)	C7—H7	0.9300

O2—C9	1.410 (3)	C8—C10	1.531 (3)
O2—Cu1 ⁱⁱⁱ	1.9438 (15)	C8—C9	1.538 (3)
O3—C10	1.416 (3)	C8—C11	1.540 (3)
O3—H3	0.8200	C9—H9A	0.9700
O4—C11	1.421 (3)	C9—H9B	0.9700
O4—H4	0.8200	C10—H10A	0.9700
C1—C2	1.449 (3)	C10—H10B	0.9700
C1—H1	0.9300	C11—H11A	0.9700
C2—C7	1.410 (4)	C11—H11B	0.9700
C2—C3	1.413 (3)		
O1—Cu1—N1	94.72 (7)	C6—C5—H5A	119.6
O1—Cu1—O2 ⁱ	91.99 (7)	C7—C6—C5	118.8 (3)
N1—Cu1—O2 ⁱ	169.85 (7)	C7—C6—H6	120.6
O1—Cu1—O2	176.00 (7)	C5—C6—H6	120.6
N1—Cu1—O2	85.00 (7)	C6—C7—C2	122.3 (3)
O2 ⁱ —Cu1—O2	88.83 (7)	C6—C7—H7	118.9
N1—Cu1—O2 ⁱⁱ	113.99 (7)	C2—C7—H7	118.9
O2 ⁱ —Cu1—O2 ⁱⁱ	72.12 (6)	N1—C8—C10	114.8 (2)
O2—Cu1—O2 ⁱⁱ	76.28 (6)	N1—C8—C9	106.55 (18)
C1—N1—C8	122.3 (2)	C10—C8—C9	107.05 (19)
C1—N1—Cu1	125.16 (17)	N1—C8—C11	106.31 (19)
C8—N1—Cu1	111.62 (14)	C10—C8—C11	110.29 (19)
C3—O1—Cu1	126.14 (15)	C9—C8—C11	111.9 (2)
C9—O2—Cu1 ⁱⁱⁱ	128.79 (14)	O2—C9—C8	112.44 (18)
C9—O2—Cu1	113.51 (13)	O2—C9—H9A	109.1
Cu1 ⁱⁱⁱ —O2—Cu1	108.40 (7)	C8—C9—H9A	109.1
C10—O3—H3	109.5	O2—C9—H9B	109.1
C11—O4—H4	109.5	C8—C9—H9B	109.1
N1—C1—C2	125.5 (2)	H9A—C9—H9B	107.8
N1—C1—H1	117.3	O3—C10—C8	115.2 (2)
C2—C1—H1	117.3	O3—C10—H10A	108.5
C7—C2—C3	118.8 (2)	C8—C10—H10A	108.5
C7—C2—C1	117.6 (2)	O3—C10—H10B	108.5
C3—C2—C1	123.5 (2)	C8—C10—H10B	108.5
O1—C3—C4	118.7 (2)	H10A—C10—H10B	107.5
O1—C3—C2	123.7 (2)	O4—C11—C8	113.1 (2)
C4—C3—C2	117.5 (2)	O4—C11—H11A	109.0
C5—C4—C3	121.8 (3)	C8—C11—H11A	109.0
C5—C4—H4A	119.1	O4—C11—H11B	109.0
C3—C4—H4A	119.1	C8—C11—H11B	109.0
C4—C5—C6	120.8 (3)	H11A—C11—H11B	107.8
C4—C5—H5A	119.6		
N1—Cu1—O2—O1	86.3 (9)		

Symmetry codes: (i) $y-1/4, -x+5/4, -z+9/4$; (ii) $-x+1, -y+3/2, z$; (iii) $-y+5/4, x+1/4, -z+9/4$.

supplementary materials

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O4 ^{iv}	0.82	1.91	2.723 (3)	172
O4—H4 \cdots O1 ⁱⁱⁱ	0.82	1.85	2.668 (2)	171

Symmetry codes: (iv) $y-1/4, -x+3/4, z-1/4$; (iii) $-y+5/4, x+1/4, -z+9/4$.

Fig. 1

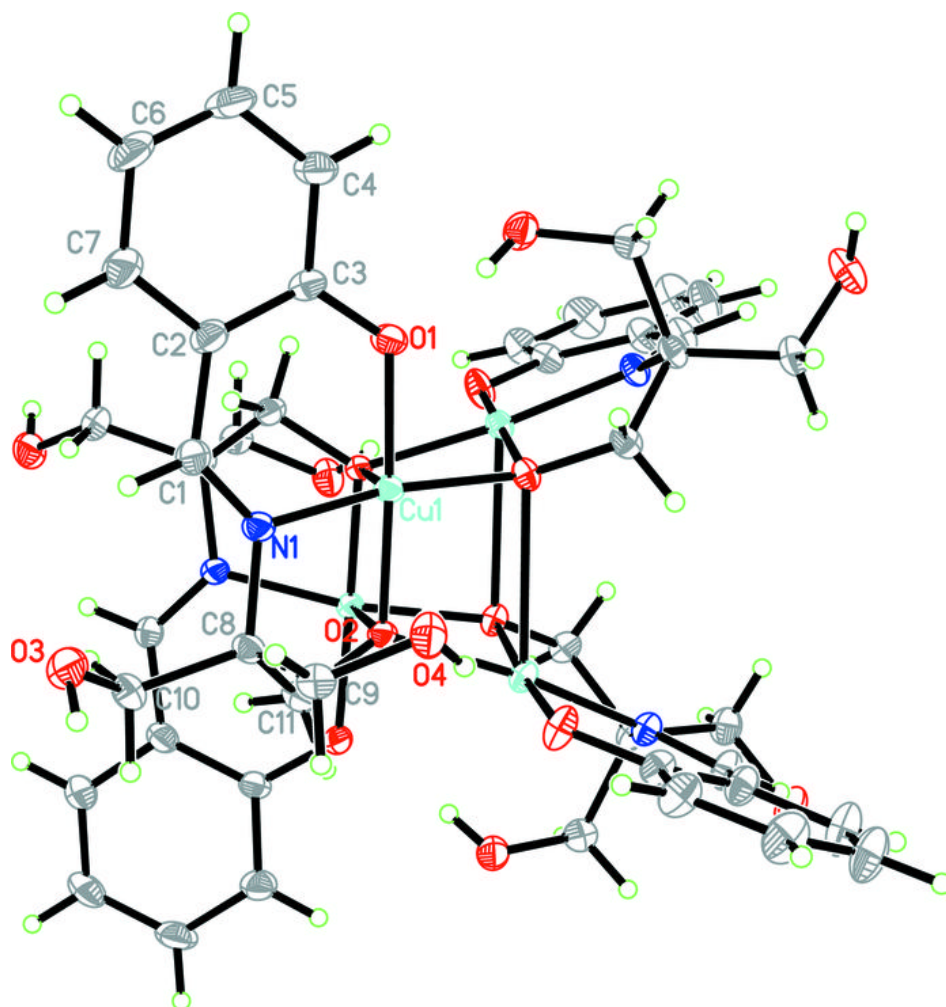


Fig. 2

