Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tetrakis{μ_3-1-[(2-oxidoethyl)iminomethyl]-2-naphtholato}tetracopper(II)

Jian-Fang Dong, Lian-Zhi Li,* Tao Xu, Hui Cui and Da-Qi Wang

School of Chemistry and Chemical Engineering, Liaocheng University, Shandong 252059, People's Republic of China
Correspondence e-mail: lilianzhi1963@yahoo.com.cn

Received 13 April 2007; accepted 19 April 2007

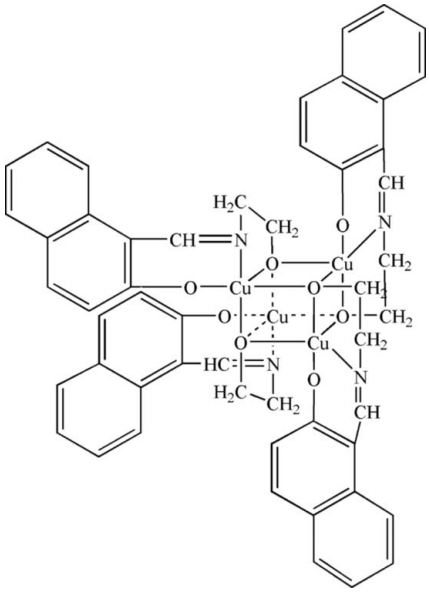
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.008 Å; R factor = 0.053; wR factor = 0.102; data-to-parameter ratio = 13.2.

In the title complex, $[Cu_4(C_{13}H_{11}NO_2)_4]$, which has crystallographic fourfold inversion symmetry, the four Cu^{II} ions are coordinated by tridentate Schiff base ligands, forming a tetranuclear cubane configuration. The Cu^{II} ions are in distorted square-pyramidal coordination environments with the Cu—O_{apical} distance significantly longer than the Cu—O_{basal} distances.

Related literature

The Cu···Cu distances in the title complex are similar to those in related structures (Si *et al.*, 2002; Mishtu *et al.*, 2002).

For related literature, see: Beinert (1980); Maggio *et al.* (1974); Oshio *et al.* (2000); Unver *et al.* (2003); Wang *et al.* (2007).



Experimental

Crystal data

$[Cu_4(C_{13}H_{11}NO_2)_4]$
M_r = 1107.11
Tetragonal, $I4_1/a$
a = 21.628 (5) Å
c = 9.858 (5) Å
V = 4611 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.88 mm^{-1}
T = 298 (2) K
0.34 × 0.21 × 0.10 mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.567, T_{max} = 0.834
9020 measured reflections
2037 independent reflections
1478 reflections with $I > 2\sigma(I)$
R_{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.102
S = 1.08
2037 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.900 (3)	Cu1—O1	1.964 (3)
Cu1—N1	1.921 (4)	Cu1—O1^{ii}	2.439 (3)
Cu1—O1^{i}	1.949 (3)		
O2—Cu1—N1	92.44 (14)	N1—Cu1—O1^{ii}	112.74 (13)
O2—Cu1—O1^{i}	96.73 (14)	O1^{i}—Cu1—O1^{ii}	74.27 (11)
N1—Cu1—O1^{i}	167.39 (14)	O1—Cu1—O1^{ii}	81.11 (12)
O2—Cu1—O1	176.91 (13)	Cu1^{iii}—O1—Cu1	107.05 (13)
N1—Cu1—O1	84.51 (13)	Cu1^{iii}—O1—Cu1^{ii}	90.92 (11)
O1^{i}—Cu1—O1	86.36 (13)	Cu1—O1—Cu1^{ii}	98.18 (11)
O2—Cu1—O1^{ii}	99.68 (12)		

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

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

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

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2368).

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supplementary materials

Acta Cryst. (2007). E**63**, m1501-m1502 [**doi:10.1107/S1600536807019654**]

Tetrakis{μ_3-1-[(2-oxidoethyl)iminomethyl]-2-naphtholato}tetracopper(II)

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

Comment

Considerable efforts have been devoted to the study of polynuclear Cu(II) complexes due to their importance in enzymatic systems (Beinert, 1980) and in studying the metal-metal interactions. However, very few structurally characterized multinuclear complexes containing Schiff base ligands have been reported (Oshio *et al.*, 2000). 2-Hydroxy Schiff base ligands and their copper(II) complexes play a major role in both synthetic and structural research (Maggio *et al.*, 1974). As part of a series of studies (Wang *et al.*, 2007), we report here the synthesis and crystal structure of the title compound, (I), a new tetranuclear copper(II) complex formed with a tridentate Schiff base ligand derived from the condensation of 2-hydroxy-1-naphthaldehyde and ethanolamine.

The title complex, (I) (Fig.1) contains a tetranuclear cubane core based on an approximately cubic array of alternating copper and oxygen atoms. Each Cu^{II} ion resides in a distorted square-pyramidal coordination environment consisting of 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 basical plane (formed by O1, N1, O2 and $O1^{i}$, symmetry code: (i) $y - 1/4, -x + 1/4, -z + 9/4$) by 0.0085 (25) Å, with a significantly longer Cu—O_{apical} bond distance (Table 1). In the molecular structure of (I), the Cu···Cu distances (3.1471 (11) Å, 3.3419 (13) Å) are similar to the reported values (Si *et al.*, 2002; Mishtu *et al.*, 2002), indicating no bonding interactions between the Cu^{II} ions. In the crystal structure, an intermolecular C—H···O short contact [H···O^{ii} = 2.58, C···O^{ii} 3.485 (8)Å and C—H···O^{ii} = 165°; symmetry code (ii) $1/4 + y, 1/4 - x, -3/4 + z$] (Fig. 2), may stabilize the crystal packing along with the usual van der Waals forces.

Experimental

Ethanolamine(1 mmol, 0.0597 ml) was dissolved in hot methanol (10 ml) and added dropwise to a methanol solution of 2-hydroxy-1-naphthaldehyde (1 mmol, 172.19 mg). The mixture was then stirred at 323 K for 2 h. Subsequently, an aqueous solution(2 ml) of cupric acetate monohydrate(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 green block-shaped crystals suitable for X-ray diffraction analysis were obtained.

Refinement

All H atoms were placed in geometrically calculated positions (C—H = 0.93 − 0.97 Å) and allowed to ride on their respective parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

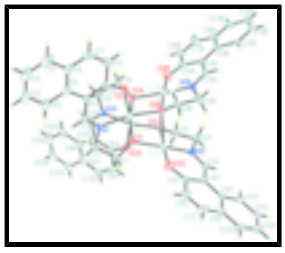


Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with the suffixes 'A', 'B' and 'C' are related by the symmetry operators ($y - 1/4, -x + 1/4, -z + 9/4$; $-x, -y + 1/2, z$ and $-y + 1/4, x + 1/4, -z + 9/4$)

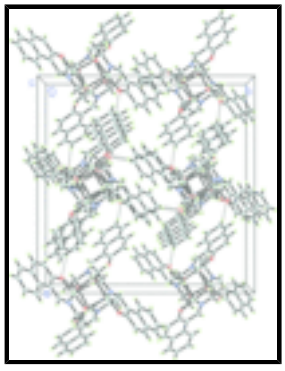


Fig. 2. Partial packing plot of the title compound with weak C—H···O hydrogen bonds shown as dashed lines.

Tetrakis{μ$_3$-1-[(2-oxidoethyl)iminomethyl]-2-naphtholato}tetracopper(II)

Crystal data

$[Cu_4(C_{13}H_{11}NO_2)_4]$	$Z = 4$
$M_r = 1107.11$	$F_{000} = 2256$
Tetragonal, $I4_1/a$	$D_x = 1.595$ Mg m^{-3}
Hall symbol: -I 4ad	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 21.628$ (5) Å	Cell parameters from 2338 reflections
$b = 21.628$ (5) Å	$\theta = 2.3$–26.2º
$c = 9.858$ (5) Å	$\mu = 1.88$ mm^{-1}
$\alpha = 90$º	$T = 298$ (2) K
$\beta = 90$º	Block, green
$\gamma = 90$º	0.34 × 0.21 × 0.10 mm
$V = 4611$ (3) Å^3	

Data collection

Siemens SMART CCD diffractometer	2037 independent reflections
Radiation source: fine-focus sealed tube	1478 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.072$
$T = 298$(2) K	$\theta_{max} = 25.0$º
φ and ω scans	$\theta_{min} = 1.9$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -25 \rightarrow 11$

T_{min} = 0.567, T_{max} = 0.834
9020 measured reflections
k = −25→25
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.102
S = 1.08
2037 reflections
154 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 10.1433P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.07676 (3)	0.24123 (2)	1.01961 (5)	0.0294 (2)
N1	0.09211 (17)	0.27275 (16)	0.8405 (4)	0.0307 (9)
O1	0.02178 (13)	0.31305 (13)	1.0370 (3)	0.0282 (7)
O2	0.13040 (15)	0.17273 (15)	0.9926 (3)	0.0463 (9)
C1	0.0370 (2)	0.3589 (2)	0.9401 (5)	0.0361 (12)
H1A	0.0717	0.3834	0.9720	0.043*
H1B	0.0021	0.3863	0.9259	0.043*
C2	0.0537 (2)	0.3266 (2)	0.8086 (5)	0.0421 (13)
H2A	0.0165	0.3136	0.7619	0.050*
H2B	0.0762	0.3547	0.7499	0.050*
C3	0.1335 (2)	0.2538 (2)	0.7581 (5)	0.0321 (11)
H3	0.1396	0.2772	0.6801	0.039*
C4	0.1713 (2)	0.2000 (2)	0.7741 (5)	0.0319 (11)
C5	0.1668 (2)	0.1626 (2)	0.8897 (5)	0.0392 (13)
C6	0.2058 (3)	0.1089 (3)	0.8993 (7)	0.0650 (18)
H6	0.2036	0.0840	0.9760	0.078*

C7	0.2456 (3)	0.0942 (3)	0.7991 (7)	0.0676 (19)
H7	0.2699	0.0590	0.8085	0.081*
C8	0.2516 (2)	0.1301 (3)	0.6810 (6)	0.0477 (14)
C9	0.2158 (2)	0.1841 (2)	0.6683 (5)	0.0383 (12)
C10	0.2255 (2)	0.2197 (3)	0.5510 (5)	0.0478 (14)
H10	0.2036	0.2564	0.5400	0.057*
C11	0.2669 (3)	0.2016 (3)	0.4512 (6)	0.0649 (18)
H11	0.2721	0.2263	0.3746	0.078*
C12	0.3002 (3)	0.1483 (4)	0.4633 (7)	0.069 (2)
H12	0.3273	0.1364	0.3948	0.083*
C13	0.2934 (3)	0.1129 (3)	0.5761 (7)	0.0671 (19)
H13	0.3165	0.0768	0.5850	0.081*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0348 (4)	0.0306 (3)	0.0230 (3)	0.0054 (3)	0.0053 (3)	0.0045 (3)
N1	0.037 (2)	0.032 (2)	0.024 (2)	0.0057 (18)	0.0047 (18)	0.0066 (17)
O1	0.0375 (18)	0.0268 (16)	0.0203 (17)	0.0042 (13)	0.0048 (14)	0.0005 (14)
O2	0.053 (2)	0.044 (2)	0.042 (2)	0.0185 (18)	0.0189 (18)	0.0141 (17)
C1	0.043 (3)	0.030 (3)	0.035 (3)	0.008 (2)	0.008 (2)	0.010 (2)
C2	0.055 (3)	0.042 (3)	0.029 (3)	0.015 (3)	0.007 (3)	0.012 (2)
C3	0.036 (3)	0.040 (3)	0.021 (3)	−0.004 (2)	0.003 (2)	−0.002 (2)
C4	0.025 (2)	0.038 (3)	0.033 (3)	0.000 (2)	0.007 (2)	−0.007 (2)
C5	0.035 (3)	0.039 (3)	0.044 (3)	0.007 (2)	0.007 (3)	0.001 (3)
C6	0.069 (4)	0.055 (4)	0.071 (4)	0.025 (3)	0.022 (4)	0.015 (3)
C7	0.059 (4)	0.051 (4)	0.092 (5)	0.023 (3)	0.023 (4)	0.001 (4)
C8	0.031 (3)	0.053 (3)	0.060 (4)	−0.001 (3)	0.013 (3)	−0.016 (3)
C9	0.026 (3)	0.050 (3)	0.039 (3)	−0.009 (2)	0.001 (2)	−0.014 (3)
C10	0.028 (3)	0.078 (4)	0.037 (3)	−0.001 (3)	0.004 (2)	−0.011 (3)
C11	0.038 (3)	0.116 (6)	0.040 (4)	−0.008 (4)	0.006 (3)	−0.008 (4)
C12	0.039 (4)	0.109 (6)	0.058 (5)	−0.007 (4)	0.017 (3)	−0.033 (4)
C13	0.039 (3)	0.075 (5)	0.087 (5)	0.002 (3)	0.019 (4)	−0.035 (4)

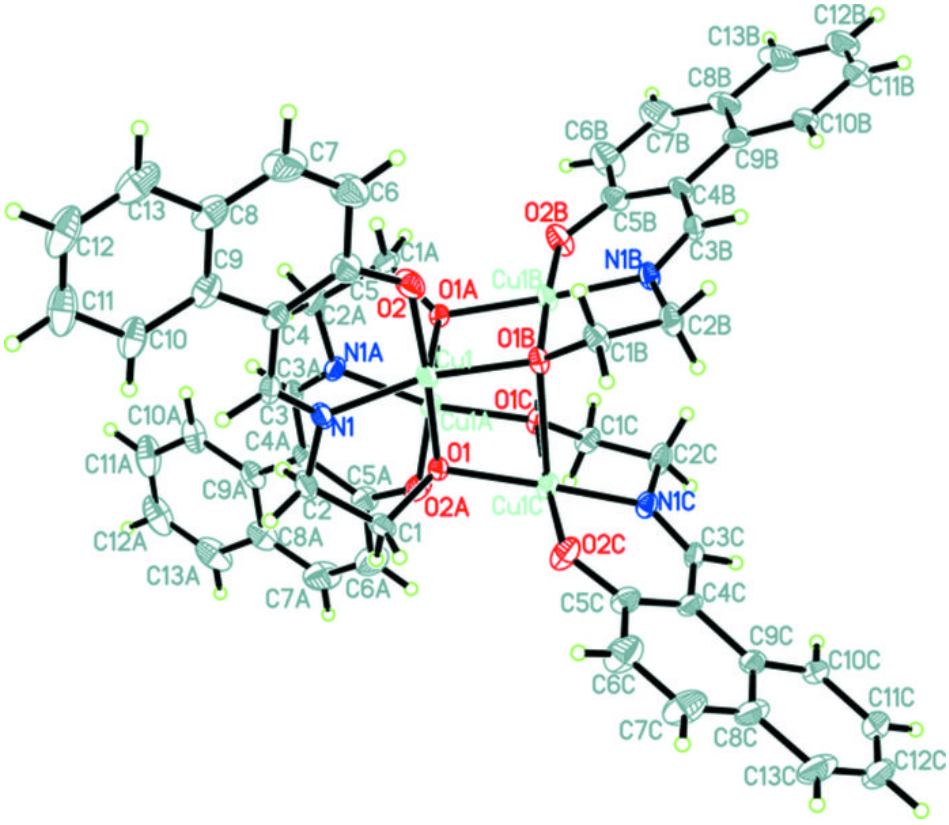
Geometric parameters (Å, °)

Cu1—O2	1.900 (3)	C4—C5	1.401 (7)
Cu1—N1	1.921 (4)	C4—C9	1.461 (6)
Cu1—O1^{i}	1.949 (3)	C5—C6	1.438 (7)
Cu1—O1	1.964 (3)	C6—C7	1.348 (8)
Cu1—O1^{ii}	2.439 (3)	C6—H6	0.9300
N1—C3	1.277 (5)	C7—C8	1.405 (8)
N1—C2	1.465 (6)	C7—H7	0.9300
O1—C1	1.416 (5)	C8—C9	1.406 (7)
O1—Cu1^{iii}	1.949 (3)	C8—C13	1.424 (7)
O1—Cu1^{ii}	2.439 (3)	C9—C10	1.406 (7)
O2—C5	1.303 (5)	C10—C11	1.386 (7)
C1—C2	1.516 (6)	C10—H10	0.9300

C1—H1A	0.9700	C11—C12	1.364 (9)
C1—H1B	0.9700	C11—H11	0.9300
C2—H2A	0.9700	C12—C13	1.360 (9)
C2—H2B	0.9700	C12—H12	0.9300
C3—C4	1.431 (6)	C13—H13	0.9300
C3—H3	0.9300		
O2—Cu1—N1	92.44 (14)	N1—C3—H3	116.9
O2—Cu1—O1^{i}	96.73 (14)	C4—C3—H3	116.9
N1—Cu1—O1^{i}	167.39 (14)	C5—C4—C3	121.3 (4)
O2—Cu1—O1	176.91 (13)	C5—C4—C9	119.4 (4)
N1—Cu1—O1	84.51 (13)	C3—C4—C9	119.3 (4)
O1^{i}—Cu1—O1	86.36 (13)	O2—C5—C4	125.3 (4)
O2—Cu1—O1^{ii}	99.68 (12)	O2—C5—C6	116.1 (5)
N1—Cu1—O1^{ii}	112.74 (13)	C4—C5—C6	118.6 (5)
O1^{i}—Cu1—O1^{ii}	74.27 (11)	C7—C6—C5	121.2 (6)
O1—Cu1—O1^{ii}	81.11 (12)	C7—C6—H6	119.4
C3—N1—C2	121.1 (4)	C5—C6—H6	119.4
C3—N1—Cu1	126.3 (3)	C6—C7—C8	122.3 (5)
C2—N1—Cu1	112.4 (3)	C6—C7—H7	118.8
C1—O1—Cu1^{iii}	125.9 (3)	C8—C7—H7	118.8
C1—O1—Cu1	110.7 (2)	C7—C8—C9	118.8 (5)
Cu1^{iii}—O1—Cu1	107.05 (13)	C7—C8—C13	121.0 (6)
C1—O1—Cu1^{ii}	119.5 (3)	C9—C8—C13	120.1 (6)
Cu1^{iii}—O1—Cu1^{ii}	90.92 (11)	C10—C9—C8	116.5 (5)
Cu1—O1—Cu1^{ii}	98.18 (11)	C10—C9—C4	123.8 (5)
C5—O2—Cu1	127.5 (3)	C8—C9—C4	119.6 (5)
O1—C1—C2	108.0 (4)	C11—C10—C9	121.7 (6)
O1—C1—H1A	110.1	C11—C10—H10	119.1
C2—C1—H1A	110.1	C9—C10—H10	119.1
O1—C1—H1B	110.1	C12—C11—C10	121.1 (6)
C2—C1—H1B	110.1	C12—C11—H11	119.4
H1A—C1—H1B	108.4	C10—C11—H11	119.4
N1—C2—C1	108.5 (4)	C13—C12—C11	119.5 (6)
N1—C2—H2A	110.0	C13—C12—H12	120.3
C1—C2—H2A	110.0	C11—C12—H12	120.3
N1—C2—H2B	110.0	C12—C13—C8	121.0 (6)
C1—C2—H2B	110.0	C12—C13—H13	119.5
H2A—C2—H2B	108.4	C8—C13—H13	119.5
N1—C3—C4	126.3 (4)		

Symmetry codes: (i) *y*−1/4, −*x*+1/4, −*z*+9/4; (ii) −*x*, −*y*+1/2, *z*; (iii) −*y*+1/4, *x*+1/4, −*z*+9/4.

Fig. 1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C3A
C3
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Fig. 2