Burns, A. R., Cardwell, T. J. & Cattrall, R. W. (1971). *Aust. J. Chem.* **24**, 661–663.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Dexheimer, S. L., Gohdes, J. W., Chan, M., Hagen, K. S., Armstrong, W. H. & Klein, M. P. (1989). *J. Am. Chem. Soc.* **111**, 8923–8925.
Folting, K., Cox, M. M., Moore, J. W. & Merritt, J. L. L. (1968). *Chem. Commun.* pp. 1170–1171.
Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Department of Chemistry, Univ. of Glasgow, Scotland.
Goher, M. A. S., Youssef, A. A., Zhou, Z.-Y. & Mak, T. C. W. (1993). *Polyhedron*, **12**, 1871–1878.
Marguez, F., Zabala, I. & Romas, F. (1992). *J. Lumin.* **54**, 13–22.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1986). *CONTROL. An Automation Package for Rigaku AFC Single Crystal Diffractometers.* Revised 1988. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Philippa, A., Dennis, F. E. & Quero, S. (1987). *Polyhedron*, **6**, 2003–2007.
Silvia, A. R., Paul, S. T. & Donald, T. S. (1989). *Inorg. Chem.* **28**, 2471–2475.
Uma, L. & Krishnamuirthi, V. S. (1984). *Leather Sci. (Madras)*, **31**, 15–16.

Acta Cryst. (1995). C**51**, 1980–1982

Tetrameric Copper(II) Complex of 6-Hydroxy-3-methyl-1-phenyl-4-azahexa-3-en-1-one

HOONG-KUN FUN AND BOON-CHUAN YIP

X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

BAO-LIN SONG, REN-GEN XIONG AND XIAO-ZENG YOU

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

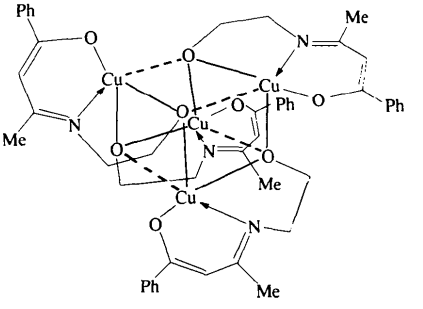
(*Received* 16 *February* 1995; *accepted* 26 *April* 1995)

Abstract

The title complex, tetrakis(μ_3-3-methyl-1-phenyl-4-azahexa-1,3-diene-1,6-diolato)tetracopper, $[Cu_4(C_{12}H_{13}NO_2)_4]$ forms a cubane-like tetramer. Within the Cu_4O_4 framework all four Cu atoms have square-pyramidal $CuNO_4$ coordination and the alkoxide O atom of each ligand is triply bridging. The Cu—O bond distances within the Cu_4O_4 framework are in the range 1.898 (9)–2.618 (7) Å, whereas the four Cu—N bond lengths range from 1.916 (9) to 1.929 (8) Å.

Comment

Schiff base compounds have found applications in many fields, being particularly excellent candidates for building a novel type of conductive organic material (Hadjoudis, Vittorakis & Moustakali-Mavridis 1987). They have also attracted broad attention because of their ferromagnetic properties (Hines & Theriot, 1991). Although the title complex (I) has been prepared previously and some of its physical properties described, its crystal structure had not been reported (Hines & Theriot, 1991).



(I)

The structure of (I) consists of cubane-like tetramers with four square-pyramidally coordinated Cu atoms and four alkoxide O atoms at the corners of the cube (Fig. 1). It can also be described as containing a folded eight-membered ring in a boat-like conformation with short Cu—O distances [1.898 (9)–1.976 (7) Å] defining the ring, which forms the cubane-like molecule through two pairs of long mutually perpendicular Cu—O interactions [2.391 (7)–2.618 (7) Å]. Compared with β-CuEIA (EIA = 7-hydroxy-4-methyl-5-azahept-4-en-2-one) (Mergehenn, Merz, Haase & Allmann, 1976), which has a similar Cu_4O_4 framework with Cu—O distances of 1.907–2.505 Å, the larger range of Cu—O distances observed in (I) shows that the cubic Cu_4O_4 framework is more distorted. The Cu atoms have distorted square-pyramidal $CuNO_4$ coordination with one N and two O atoms of the same chelate ligand plus an O atom of another ligand of the tetramer forming the base of the pyramid; an O atom of another ligand occupies the axial position. The Cu—N bond lengths are in the range 1.916 (9)–1.929 (8) Å, and are in good agreement with values reported for comparable bonds in β-CuEIA and copper phthalocyanine (Brown, 1968). Bond lengths in the ligands are unexceptional. C9*B* has a highly anisotropic displacement tensor which may indicate positional disorder.

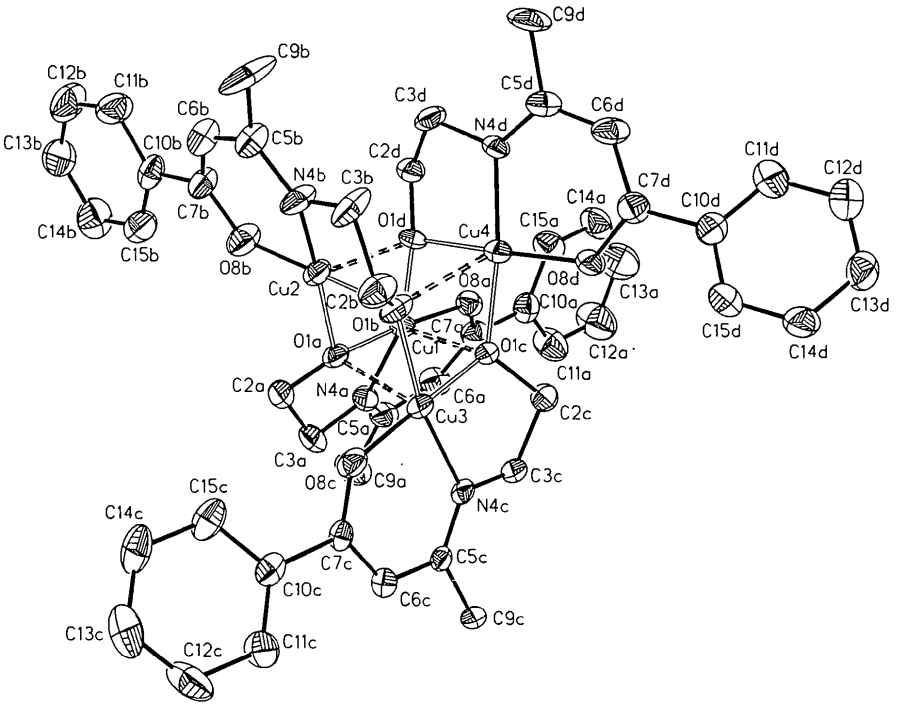


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I) with the numbering scheme, showing 30% probability displacement ellipsoids.

Experimental

The title complex was prepared by refluxing benzoylacetone, ethanol and $CuCl_2.2H_2O$ in absolute ethanol for 4 h. Recrystallization was from $CHCl_3$/MeCN.

Crystal data

$[Cu_4(C_{12}H_{13}NO_2)_4]$
$M_r = 1067.10$
Rhombohedral (hexagonal axes)
$R\bar{3}$
$a = 30.195\ (4)$ Å
$c = 14.871\ (2)$ Å
$V = 11742.1\ (3)$ Å^3
$Z = 9$
$D_x = 1.358$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 5$–$12.5°$
$\mu = 1.659$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.62 × 0.32 × 0.20 mm
Dark green

Data collection

Siemens *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Sheldrick, 1990)
$T_{min} = 0.869$, $T_{max} = 1.000$
4758 measured reflections
3979 independent reflections
3329 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0401$
$\theta_{max} = 25.0°$
$h = -21 \rightarrow 23$
$k = -25 \rightarrow 21$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity decay: $< 4\%$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.134$
$S = 1.036$
3979 reflections
532 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0945P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: $\chi = 0.00\ (2)$ (Flack, 1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cu1	0.49716 (5)	0.97990 (5)	0.37790 (8)	0.0445 (3)
O1A	0.5460 (3)	1.0351 (3)	0.4537 (4)	0.047 (2)
C2A	0.5506 (5)	1.0163 (5)	0.5379 (7)	0.056 (3)
C3A	0.5508 (5)	0.9683 (5)	0.5230 (7)	0.060 (3)
N4A	0.5112 (4)	0.9374 (4)	0.4552 (5)	0.052 (3)
C5A	0.4927 (5)	0.8892 (6)	0.4486 (8)	0.062 (4)
C6A	0.4581 (5)	0.8608 (5)	0.3777 (8)	0.063 (3)
C7A	0.4421 (5)	0.8780 (5)	0.3076 (7)	0.054 (3)
O8A	0.4533 (3)	0.9251 (3)	0.2973 (5)	0.050 (2)
C9A	0.5055 (7)	0.8593 (6)	0.5133 (9)	0.091 (5)
C10A	0.4067 (3)	0.8420 (4)	0.2366 (5)	0.060 (3)
C11A	0.4047 (4)	0.7959 (4)	0.2185 (7)	0.091 (5)
C12A	0.3728 (5)	0.7640 (4)	0.1512 (8)	0.128 (7)
C13A	0.3428 (4)	0.7783 (5)	0.1018 (7)	0.125 (8)
C14A	0.3448 (4)	0.8245 (5)	0.1198 (7)	0.088 (5)
C15A	0.3768 (4)	0.8563 (4)	0.1872 (7)	0.067 (4)
Cu2	0.53195 (6)	1.09196 (6)	0.44157 (8)	0.0490 (4)

O1*B*	0.5813 (3)	1.1175 (3)	0.3429 (5)	0.056 (2)
C2*B*	0.6064 (6)	1.1714 (5)	0.3459 (9)	0.067 (4)
C3*B*	0.5668 (6)	1.1870 (6)	0.3577 (9)	0.075 (4)
N4*B*	0.5323 (4)	1.1553 (4)	0.4294 (7)	0.061 (3)
C5*B*	0.5003 (5)	1.1673 (5)	0.4702 (9)	0.062 (3)
C6*B*	0.4681 (6)	1.1362 (5)	0.5420 (8)	0.070 (4)
C7*B*	0.4608 (6)	1.0905 (5)	0.5705 (8)	0.059 (3)
O8*B*	0.4845 (4)	1.0677 (4)	0.5382 (6)	0.069 (3)
C9*B*	0.4985 (7)	1.2138 (6)	0.4472 (13)	0.118 (7)
C10*B*	0.4258 (3)	1.0629 (3)	0.6482 (4)	0.058 (3)
C11*B*	0.3907 (4)	1.0763 (4)	0.6792 (6)	0.080 (4)
C12*B*	0.3601 (4)	1.0513 (5)	0.7530 (6)	0.100 (6)
C13*B*	0.3646 (4)	1.0129 (4)	0.7959 (5)	0.089 (5)
C14*B*	0.3997 (4)	0.9994 (3)	0.7649 (6)	0.096 (5)
C15*B*	0.4303 (4)	1.0244 (4)	0.6910 (6)	0.074 (4)
Cu3	0.61316 (5)	1.07482 (5)	0.34385 (8)	0.0430 (3)
O1*C*	0.5593 (3)	1.0301 (3)	0.2611 (4)	0.043 (2)
C2*C*	0.5768 (5)	1.0046 (5)	0.2034 (7)	0.050 (3)
C3*C*	0.6090 (4)	0.9904 (5)	0.2594 (7)	0.048 (3)
N4*C*	0.6410 (3)	1.0309 (3)	0.3188 (5)	0.035 (2)
C5*C*	0.6801 (4)	1.0330 (4)	0.3585 (6)	0.035 (2)
C6*C*	0.7104 (4)	1.0706 (4)	0.4221 (6)	0.038 (2)
C7*C*	0.7023 (4)	1.1100 (4)	0.4529 (6)	0.037 (3)
O8*C*	0.6666 (3)	1.1180 (3)	0.4238 (5)	0.052 (2)
C9*C*	0.6954 (4)	0.9921 (4)	0.3403 (7)	0.046 (3)
C10*C*	0.7342 (3)	1.1433 (3)	0.5299 (4)	0.046 (3)
C11*C*	0.7818 (3)	1.1494 (3)	0.5504 (5)	0.071 (4)
C12*C*	0.8078 (3)	1.1765 (4)	0.6268 (6)	0.096 (5)
C13*C*	0.7862 (4)	1.1976 (3)	0.6825 (5)	0.090 (5)
C14*C*	0.7386 (4)	1.1915 (3)	0.6619 (5)	0.077 (5)
C15*C*	0.7126 (3)	1.1644 (3)	0.5856 (5)	0.065 (4)
Cu4	0.51660 (5)	1.05732 (5)	0.22107 (7)	0.0440 (3)
O1*D*	0.4784 (3)	1.0299 (3)	0.3327 (4)	0.046 (2)
C2*D*	0.4290 (5)	1.0230 (5)	0.3233 (7)	0.050 (3)
C3*D*	0.4341 (5)	1.0689 (5)	0.2766 (8)	0.056 (3)
N4*D*	0.4677 (3)	1.0787 (3)	0.1978 (5)	0.044 (2)
C5*D*	0.4671 (5)	1.1039 (5)	0.1268 (8)	0.056 (3)
C6*D*	0.4972 (5)	1.1116 (5)	0.0519 (9)	0.063 (4)
C7*D*	0.5350 (5)	1.0972 (5)	0.0417 (8)	0.055 (3)
O8*D*	0.5487 (3)	1.0774 (3)	0.1066 (4)	0.056 (2)
C9*D*	0.4315 (6)	1.1263 (6)	0.1238 (10)	0.088 (5)
C10*D*	0.5606 (3)	1.1026 (4)	−0.0461 (4)	0.055 (3)
C11*D*	0.5349 (3)	1.0977 (4)	−0.1264 (5)	0.083 (5)
C12*D*	0.5596 (4)	1.1033 (4)	−0.2080 (4)	0.084 (5)
C13*D*	0.6100 (4)	1.1138 (4)	−0.2095 (4)	0.073 (4)
C14*D*	0.6357 (3)	1.1186 (4)	−0.1292 (5)	0.076 (4)
C15*D*	0.6110 (3)	1.1130 (4)	−0.0476 (4)	0.070 (4)

Table 2. *Selected geometric parameters* (Å, °)

Cu1···Cu2	3.146 (2)	Cu2—O8*B*	1.898 (9)
Cu1···Cu3	3.271 (2)	Cu2—N4*B*	1.916 (10)
Cu1···Cu4	3.143 (2)	Cu2—O1*B*	1.954 (7)
Cu2···Cu3	3.108 (3)	Cu2—O1*D*	2.391 (7)
Cu2···Cu4	3.402 (2)	O1*B*—Cu3	1.957 (8)
Cu3···Cu4	3.252 (2)	O1*B*—Cu4	2.618 (7)
Cu1—N4*A*	1.921 (9)	Cu3—O8*C*	1.901 (8)
Cu1—O8*A*	1.933 (8)	Cu3—N4*C*	1.929 (8)
Cu1—O1*A*	1.940 (8)	Cu3—O1*C*	1.946 (7)
Cu1—O1*D*	1.976 (7)	Cu4—O8*D*	1.902 (7)
Cu1—O1*C*	2.447 (6)	Cu4—N4*D*	1.916 (9)
O1*A*—Cu2	1.971 (7)	Cu4—O1*D*	1.953 (7)
O1*A*—Cu3	2.406 (7)		
N4*A*—Cu1—O8*A*	94.8 (4)	O8*C*—Cu3—N4*C*	94.6 (3)
N4*A*—Cu1—O1*A*	84.3 (4)	O8*C*—Cu3—O1*C*	178.9 (3)
N4*A*—Cu1—O1*C*	118.7 (3)	N4*C*—Cu3—O1*C*	84.3 (3)
O8*A*—Cu1—O1*A*	175.2 (3)	O8*C*—Cu3—O1*B*	94.7 (3)
N4*A*—Cu1—O1*D*	163.1 (3)	N4*C*—Cu3—O1*B*	168.2 (3)
O8*A*—Cu1—O1*D*	96.2 (3)	O1*C*—Cu3—O1*B*	86.4 (3)
O1*A*—Cu1—O1*D*	85.8 (3)	O8*C*—Cu3—O1*A*	97.6 (3)
O1*A*—Cu1—O1*C*	82.1 (3)	N4*C*—Cu3—O1*A*	109.7 (3)
O1*C*—Cu1—O8*A*	94.3 (3)	O1*C*—Cu3—O1*A*	83.1 (3)
O1*C*—Cu1—O1*D*	73.1 (3)	O1*B*—Cu3—O1*A*	76.3 (3)
C2*A*—O1*A*—Cu1	110.8 (7)	C2*C*—O1*C*—Cu4	123.4 (6)
C2*A*—O1*A*—Cu2	122.6 (6)	C2*C*—O1*C*—Cu3	110.5 (6)
Cu1—O1*A*—Cu2	107.1 (3)	Cu4—O1*C*—Cu3	113.7 (4)
C2*A*—O1*A*—Cu3	125.1 (7)	C5*C*—N4*C*—Cu3	125.4 (7)
Cu1—O1*A*—Cu3	97.1 (3)	C3*C*—N4*C*—Cu3	111.6 (6)
Cu2—O1*A*—Cu3	89.9 (3)	C7*C*—O8*C*—Cu3	125.6 (6)
C5*A*—N4*A*—Cu1	126.8 (9)	O8*D*—Cu4—N4*D*	95.0 (3)
C3*A*—N4*A*—Cu1	111.4 (8)	O8*D*—Cu4—O1*C*	94.0 (3)
C7*A*—O8*A*—Cu1	123.9 (8)	N4*D*—Cu4—O1*C*	170.8 (3)
O8*B*—Cu2—N4*B*	94.7 (4)	O8*D*—Cu4—O1*D*	173.9 (3)
O8*B*—Cu2—O1*B*	179.4 (5)	N4*D*—Cu4—O1*D*	84.6 (3)
N4*B*—Cu2—O1*B*	85.0 (4)	O1*C*—Cu4—O1*D*	86.3 (3)
O8*B*—Cu2—O1*A*	92.5 (3)	N4*D*—Cu4—O1*B*	108.9 (3)
N4*B*—Cu2—O1*A*	169.0 (4)	O1*C*—Cu4—O1*B*	70.0 (3)
O1*B*—Cu2—O1*A*	87.6 (3)	O1*B*—Cu4—O1*D*	77.5 (3)
O8*B*—Cu2—O1*D*	97.2 (3)	O1*B*—Cu4—O8*D*	108.3 (3)
N4*B*—Cu2—O1*D*	112.5 (4)	C2*D*—O1*D*—Cu4	109.6 (6)
O1*B*—Cu2—O1*D*	83.4 (3)	C2*D*—O1*D*—Cu1	127.5 (7)
O1*A*—Cu2—O1*D*	74.6 (3)	Cu4—O1*D*—Cu1	106.2 (3)
C2*B*—O1*B*—Cu2	107.2 (7)	C2*D*—O1*D*—Cu2	115.8 (6)
C2*B*—O1*B*—Cu3	127.0 (9)	Cu4—O1*D*—Cu2	102.6 (3)
Cu2—O1*B*—Cu3	105.3 (4)	Cu1—O1*D*—Cu2	91.7 (3)
C5*B*—N4*B*—Cu2	125.8 (10)	C5*D*—N4*D*—Cu4	125.4 (8)
C3*B*—N4*B*—Cu2	111.5 (7)	C3*D*—N4*D*—Cu4	110.9 (6)
C7*B*—O8*B*—Cu2	125.5 (9)	C7*D*—O8*D*—Cu4	125.4 (7)

The structure was solved by direct methods and was completed by locating the missing atoms from successive Fourier maps. The phenyl rings of the ligands were constrained to be regular hexagons with C—C distances of 1.39 Å. All the H atoms were generated geometrically, allowed to ride on the atoms to which they are attached, and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 123-3417-2201, and the State Science and Technology Commission and National Nature Science Foundation of China, as well as the State Key Laboratory of Tribology of Tsinghua University, for a research grant for this Key Research Project.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Brown, C. J. (1968). *J. Chem. Soc. A*, pp. 2488–2494.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hadjoudis, E., Vittorakis, M. & Moustakali-Mavridis, I. (1987). *Tetrahedron*, **43**, 1345–1360.
Hines, K. & Theriot, L. T. (1991). *Synth. React. Inorg. Met. Org. Chem.* **21**, 89–97.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mergehenn, R., Merz, L., Haase, W. & Allmann, R. (1976). *Acta Cryst.* B**32**, 505–510.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.