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Bis{μ-6,6′-dimethoxy-2,2′-[propane-1,2-diylbis(iminomethylene)]diphenolato}bis[aquacopper(II)] dihydrate

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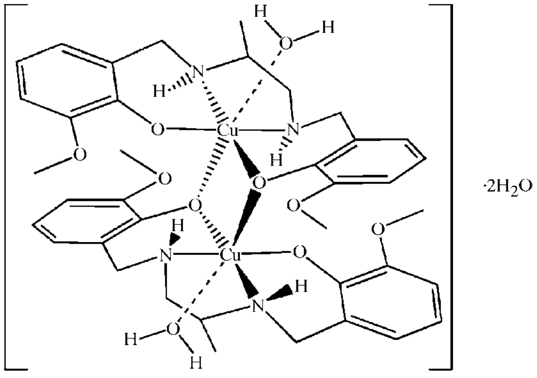
In the title compound, $[Cu_2(C_{19}H_{24}N_2O_4)_2(H_2O)_2]\cdot 2H_2O$, the asymmetric unit consists of one half of the bis{μ-6,6′-dimethoxy-2,2′-[propane-1,2-diylbis(iminomethylene)]diphenolato}bis[aquacopper(II)] complex and two water molecules. Two Cu^{II} centres are bridged through a pair of phenolate groups, resulting in a complex with a centrosymmetric structure, with the centre of inversion at the middle of the Cu_2O_2 plane. The Cu atoms are in a slightly distorted square-pyramidal coordination environment (τ = 0.07). The average equatorial Cu—O bond length and the axial Cu—O bond length are 1.928 (3) and 2.486 (3) Å, respectively. The Cu—O(water) bond length is 2.865 (4) Å, so the compound could be described as having a weakly coordinating water molecule at each Cu^{II} ion and two solvent water molecules per dimetallic unit. The Cu···Cu distance and Cu—O—Cu angle are 3.0901 (10) Å and 87.56 (10)°, respectively. The molecules are linked into a sheet by O—H···O and C—H···O hydrogen bonds parallel to the [001] plane.

Comment

Binuclear transition metal complexes have attracted much attention because of their potential applications, for example, as active sites in metalloproteins and enzymes (Elmali *et al.*, 2004) and as new inorganic functional materials showing molecular ferromagnetism (Gupta *et al.*, 2005). Among these binuclear transition metal complexes, OH^-, RO^-, RCO_2^-, Cl^-, Br^- and other groups are often used as bridging ligands (Christou *et al.*, 2000). In particular, magnetostructural correlations in dicopper(II) complexes bridged by pairs of phenoxide or alkoxide groups show that the major factors controlling the intramolecular spin coupling between the metal centres are the bridged Cu—O—Cu angle (Elmali *et al.*, 2004) and other factors, such as the distortion index (τ) of the Cu^{II} atoms, which can also affect the spin coupling between the Cu^{II} centers of some diphenoxide-bridged dicopper(II) complexes (Xie *et al.*, 2003). These complexes are able to stabilize the Cu_2O_2 core by forming square-pyramidal CuO_2N_3 coordination sites or square-planar CuO_2N_2 coordination sites (Herres *et al.*, 2005). In the light of this, we have synthesized some new ligands with diamino groups (Xia *et al.*, 2006; Xia, Liu, Yang & Wang, 2007). 6,6′-Dimethoxy-2,2′-[propane-1,2-diylbis(iminomethylene)]diphenol (H_2L) is a versatile ligand that, due to its conformational flexibility, can form a tetradentate chelating mode through its N and O atoms (Liu *et al.*, 2007; Xia, Liu, Wang & Yang, 2007) or a bridging coordination mode towards many metals, resulting in complexes with different stereochemistries. In this paper, we report the synthesis and structure of the title phenoxide-bridged dicopper(II) H_2L complex, (I).



(I)

In compound (I), two Cu^{II} atoms are bridged by a pair of phenoxide O atoms, with each Cu^{II} atom five-coordinated by two N and three O atoms (Fig. 1). The coordination polyhedron around the Cu^{II} atom may be described as square-based pyramidal. The distortion index τ (Addison *et al.*, 1984) is 0.07 (where τ = 0 for square-pyramidal geometry and τ = 1 for trigonal–bipyramidal geometry), with an apical Cu1—O1*A* distance of 2.486 (3) Å. The basal plane is formed by atoms O1, N1, N2 and O3. Atom Cu1 is shifted by 0.0752 (16) Å from the basal plane toward apical atom O1*A*.

The distance between water atom O5 and atom Cu1 is 2.865 (4) Å, and atom O5 is situated at the apical point of a pseudo-octahedral geometry, which is similar to what was observed in another diphenoxide-bridged dicopper(II) complex, $[Cu_2L(N_3)_2]\cdot 2H_2O$ (*L* is a macrocyclic ligand; Chattopadhyay *et al.*, 2007). Thus, compound (I) can be described as having a weakly coordinating water molecule at each Cu^{II} ion and two solvent water molecules per dimetallic unit.

The two intramolecular basal planes are strictly parallel, with an interplanar spacing of 2.528 (13) Å, corresponding to a plane offset of 1.838 Å. The dihedral angles between the basal plane and benzene rings C5–C10 and C13–C18 are 31.10 (16) and 23.37 (18)°, respectively, and the dihedral angle between the square Cu_2O_2 plane and the basal plane is 87.62 (7)°. The Cu—N bond lengths range from 1.992 (3) to 2.011 (3) Å, and the average equatorial Cu1—O1 bond length is 1.928 (3) Å, whereas the axial Cu1—O1*A* bond length is 2.486 (3) Å. This axial elongation is a consequence of the Jahn–Teller effect of

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copper(II), indicating that the spin-unpaired electron is located in the $d_{x^2-y^2}$ orbital and that the d_{z^2} orbital contains spin-paired electrons. Thus, the magnetic exchange is propagated principally *via* the $d_{x^2-y^2}$ orbital of the Cu^{II} ions which interacts with the appropriate orbital of the O atoms of the bridging phenoxide groups.

The Cu···Cu separation is 3.0901 (10) Å, consistent with the value of 3.091Å reported for the diphenoxide-bridged dicopper(II) complex $[Cu_2L(H_2O)_2](SO_4)_2\cdot 2H_2O$ (where *L* are derivatives of 4-methyl-2,6-diformylphenol with 1,3-diamine-2-propanol; Venegas-Yazigi *et al.*, 2006), but longer than the value of 2.9133 (10) Å reported for another diphenoxide-bridged dicopper(II) complex, $[Cu_2L(N_3)_2]\cdot 2H_2O$ (where *L* are derivatives of 4-methyl-2,6-diformylphenol with ethane-1,2-diamine; Chattopadhyay *et al.*, 2007). The Cu—O—Cu bridging angles of 87.56 (10)° are smaller than those of the two diphenoxide-bridged dicopper(II) complexes mentioned above [104.08 and 99.65 (15)°, respectively]. It is well known that the strength of antiferromagnetic coupling depends mainly on the Cu—O—Cu bridging angle in dicopper(II) complexes equatorially bridged by a pair of phenoxide O atoms (Thompson *et al.*, 1996). Magnetostructural correlation of such complexes has been reported by Thompson *et al.* using macrocyclic ligands. They predicted that the antiferromagnetism of such an equatorial–equatorial interaction of tetragonally distorted dicopper(II) complexes should prevail until the Cu—O—Cu angle is as small as 77°. The title compound is an axial–equatorial interaction of tetragonally distorted dicopper(II) complexes, and the Cu—O—Cu angle is much smaller than that found in the systems studied by Thompson *et al.* (99–105°), but it would still be predicted to be antiferromagnetic in nature.

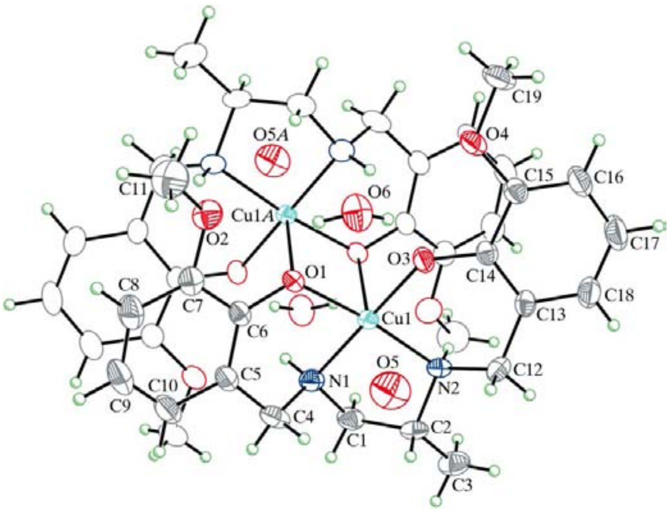

Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms and those labelled with the suffix *A* are related to labelled atoms by the symmetry code $(1 - x, -y, 1 - z)$.

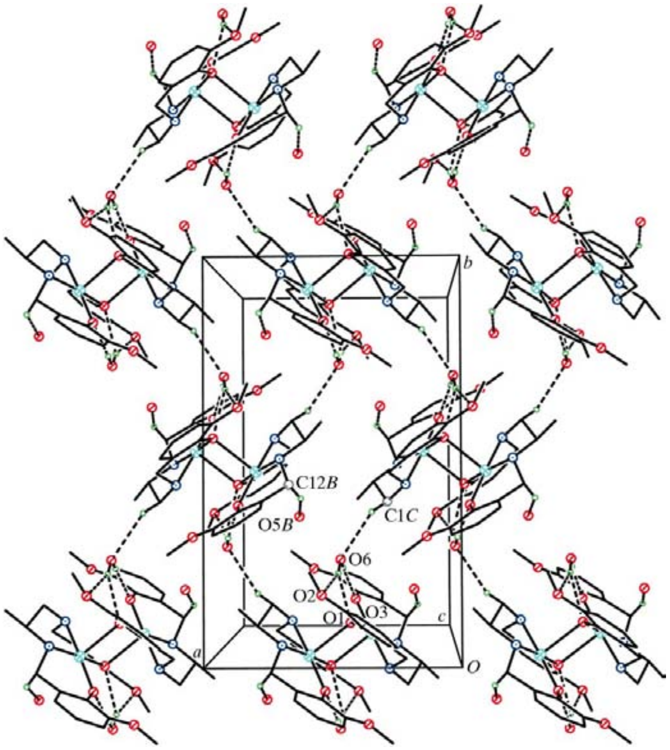

Figure 2
The crystal structure of (I), showing the formation of hydrogen-bonded sheets *via* C—H···O and O—H···O interactions. For clarity, H atoms not involved in the hydrogen bonding have been omitted. Dashed lines indicate hydrogen bonds. [Symmetry codes: (*B*) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (*C*) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.]

In the crystal structure, the molecules of compound (I) are linked into complex sheets by means of six independent O—H···O hydrogen bonds and one C—H···O hydrogen bond (Table 2), but the formation of the sheet is readily described in terms of simpler substructure motifs. Atom C1 in the molecule at $(\frac{1}{2} - x, \frac{1}{2} + y, z)$ and C12 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ act as hydrogen-bond donors to atom O6 in the molecule at (x, y, z) and atom O5 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$, respectively. Although the H atoms bonded to the O5 water molecule could not be determined reliably, it appears from the intermolecular O···O distances that atom O5 at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ acts as hydrogen-bond donor to atom O6 in the molecule at (x, y, z), with a distance of 2.722 (5) Å. At the same time, atom O6 in the molecule at (x, y, z) acts as hydrogen-bond donor to atoms O1, O2 and O3 in the molecule at (x, y, z), so forming a second ring motif, this time of $R_1^2(9)$ type. The combination of these two motifs then forms a sheet parallel to the [001] plane and generated by the *n*-glide plane at $y = \frac{1}{2}$ (Fig. 2). There are no direction-specific interactions between adjacent sheets.

Experimental

The ligand was produced according to the literature method of Xia, Liu, Yang & Wang (2007). For the preparation of complex (I), the ligand (0.693 g, 2 mmol) was dissolved in ethanol (10 ml) and an aqueous solution (10 ml) of cupric chloride (0.341 g, 2 mmol) was added. The reaction mixture was stirred for 2 h at 323 K. The solution was then cooled slowly to room temperature and filtered. Green crystals suitable for X-ray diffraction were obtained by evaporation of an ethanol solution (yield 0.48 g, 51%; m.p. 514–516 K). Analysis calculated for $C_{38}H_{56}Cu_2N_4O_{12}$: C 51.40, H 6.36, N 6.31%; found: C 51.56, H 6.57, N 6.15%. IR (KBr disk, ν, cm^{-1}): 3426 (*w*), 3246 (*m*), 2932 (*w*), 1598 (*w*), 1562 (*m*), 1482 (*s*), 1452 (*s*), 1291 (*m*), 1241 (*s*), 1070 (*s*), 719 (*m*); UV–vis [λ (nm), ε (mol^{-1} cm^{-1}), CH_3OH]: 247 (27225), 284 (16575), 334 (1990), 405 (2038), 581 (510).

Crystal data

$[Cu_2(C_{19}H_{24}N_2O_4)_2(H_2O)_2]\cdot 2H_2O$
M_r = 887.95
Orthorhombic, *Pbca*
a = 10.3214 (16) Å
b = 16.474 (2) Å
c = 23.812 (2) Å
V = 4048.7 (9) Å^3
Z = 4
Mo *Kα* radiation
μ = 1.12 mm^{-1}
T = 298 (2) K
0.28 × 0.21 × 0.10 mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.745, T_{max} = 0.897
15892 measured reflections
3572 independent reflections
2280 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.118
S = 1.00
3572 reflections
259 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.911 (3)	Cu1—O1^i	2.486 (3)
Cu1—O1	1.944 (3)	Cu1—O5	2.865 (4)
Cu1—N1	1.992 (3)	Cu1—Cu1^i	3.0901 (10)
Cu1—N2	2.011 (3)		
O3—Cu1—O1	89.51 (11)	N1—Cu1—O1^i	88.89 (12)
O3—Cu1—N1	177.11 (14)	N2—Cu1—O1^i	93.51 (11)
O1—Cu1—N1	89.18 (13)	O3—Cu1—O5	78.30 (12)
O3—Cu1—N2	94.07 (12)	O1—Cu1—O5	85.92 (12)
O1—Cu1—N2	172.84 (12)	N1—Cu1—O5	99.04 (13)
N1—Cu1—N2	86.96 (14)	N2—Cu1—O5	88.73 (13)
O3—Cu1—O1^i	93.73 (11)	O1^i—Cu1—O5	171.87 (10)
O1—Cu1—O1^i	92.44 (10)		

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

All H atoms were located in difference Fourier maps, except those bonded to O5 which could not be determined reliably. H atoms bonded to C and N atoms were treated as riding atoms, with C—H distances of 0.93 (aryl), 0.96 (methyl), 0.97 (methylene), 0.98 Å (tertiary C—H) and N—H distances of 0.91 Å (amine), and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ (aryl, methylene, tertiary C—H, amine) and $1.5U_{eq}(C)$ (methyl). The H atoms bonded to O6 were refined isotropically with the bond lengths restrained to be the same and $U_{iso}(H)$ values of $1.5U_{eq}(O)$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); 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*.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*B*···O5	0.97	2.58	3.338 (6)	135
C1—H1*C*···O6^{ii}	0.97	2.56	3.427 (5)	149
O6—H6*A*···O3	0.90 (3)	1.87 (3)	2.723 (4)	158 (5)
O6—H6*B*···O2	0.89 (3)	2.20 (3)	3.036 (5)	156 (5)
O6—H6*B*···O1	0.89 (3)	2.24 (5)	2.907 (4)	131 (5)
N2—H2···O2^i	0.91	2.20	3.052 (4)	156
N1—H1···O4^i	0.91	2.43	3.155 (5)	137
N1—H1···O3^i	0.91	2.30	3.133 (4)	153

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3052). Services for accessing these data are described at the back of the journal.

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