

Bis[μ -4-fluoro-6-hydroxymethyl-2-(2,5,8-triaza-oct-1-enyl)phenolato]dicopper(II) bis(perchlorate) methanol solvateLei Chen,^a Hong Zhou,^{a,b}
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Key indicators

Single-crystal X-ray study

 $T = 292$ KMean $\sigma(\text{C}-\text{C}) = 0.005$ Å R factor = 0.047 wR factor = 0.104

Data-to-parameter ratio = 15.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title dinuclear complex, $[\text{Cu}_2(\text{C}_{12}\text{H}_{17}\text{FN}_3\text{O}_2)_2](\text{ClO}_4)_2 \cdot \text{CH}_4\text{O}$, was synthesized by condensation between diethylenetriamine and 2-formyl-4-fluoro-6-hydroxymethylphenol in the presence of copper(II). It contains two similar units, which are linked by Cu—O bonds. The approximate planes of the two units are parallel to each other, and π – π interaction exists between the two units.

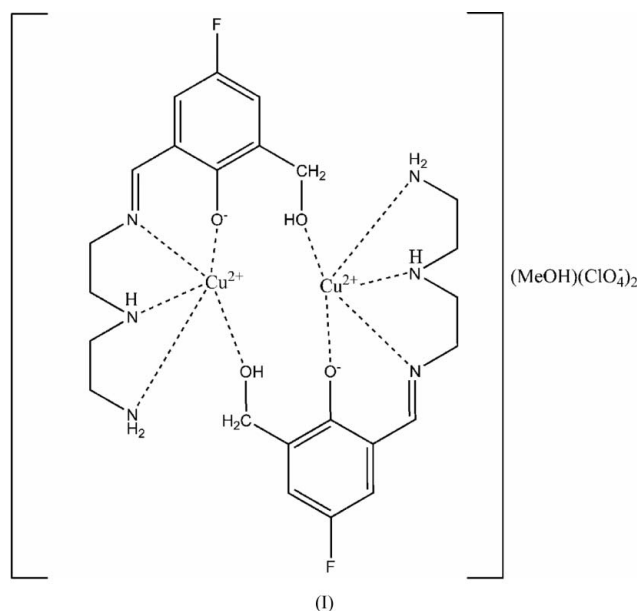
Comment

Dinuclear metal complexes, especially those of diphenol-derived Schiff bases, have attracted much attention because they have contributed significantly to the understanding of the chemical behaviour of coupled systems. This factor is very important in coordination chemistry and biological mimicry (Pilkington & Robson, 1970; Mohanta *et al.*, 1998; Wang *et al.*, 1997; Brianese *et al.*, 1999; Gao *et al.*, 2001). Complexes synthesized by the condensation between 2,6-diformyl-4-*R*-phenol and alkylenepolyamines have been obtained by the template reaction ($R = \text{CH}_3$, *n*-butyl and Cl; Shangguan *et al.*, 2000; Zhou *et al.*, 2005; Wang *et al.*, 1997), but few complexes containing fluorine substituents have been reported. In this work, the synthesis of a new complex, (I), containing fluorine substituents, is reported.

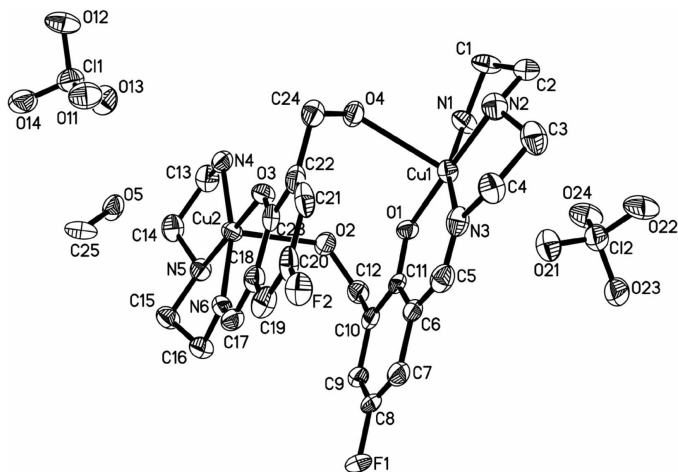
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A perspective view of the title complex is given in Fig. 1. Selected bond distances and angles relevant to the Cu^{II} coordination environments are listed in Table 1. The dinuclear cation contains two similar copper(II) units with one ligand L


Figure 1

A view of the title complex, showing the labelling of the non-H atoms and 30% probability ellipsoids. H atoms have been omitted.

each (*L* is formed by condensation between 2-formyl-4-fluoro-6-hydroxymethylphenol and diethylenetriamine). In the first unit, the Cu^{II} ion is coordinated by an N atom of one Schiff base, two amine N atoms and a phenol O atom, as well as being weakly coordinated by one perchlorate O atom which is *trans* to a methanol O atom to form an elongated octahedron. The bond distances in plane 1, comprising atoms Cu1, N1, N2, N3 and O1, are in the range 1.907 (2)–2.018 (3) Å. The Cu1–O4(HOCH₂–) bond distance is 2.471 (3) Å, and the angle between the bond and plane 1 is 81.00 (12)°. The Cu1–O21(OCIO₃) bond distance is 2.927 (3) Å, and the angle between the bond and plane 1 is 81.30 (12)°, which makes the octahedron distorted. Because the C5–N3 bond parallels the benzene plane and the sum of the angles around Cu1 is 359.67°, the Cu^{II} ion, Schiff base, phenoxide group and amide N atoms lie in an approximate plane. In the second unit, the coordination environment of atom Cu2 is similar to the first unit, except that perchlorate is displaced by methanol and the Cu2–O5 bond distance [2.925 (3) Å] is equal to the Cu1–O21 bond, which makes the relative bond distances and angles in the two units slightly different. Two Cu–O bonds (Cu2–O2 and Cu1–O4) bridge the two units and the two benzene rings are parallel to each other [the dihedral angle of the two benzene planes is 2.90 (13)°]. The distance between the two centres of the benzene planes is 3.476 Å, indicating that they form π – π stacks in the crystal structure.

Experimental

2-Formyl-4-fluoro-6-hydroxymethylphenol was prepared according to the literature method (Taniguchi, 1984; Okawa & Kida, 1972). To a mixture of Cu(OAc)₂·H₂O (0.05 g, 0.25 mmol) and 2-formyl-4-fluoro-6-hydroxymethylphenol (0.084 g, 0.5 mmol) in absolute methanol (15 ml) was added dropwise with stirring a methanol solution (15 ml) containing diethylenetriamine (0.0518 g, 0.5 mmol). The mixture was stirred for 12 h at room temperature. A dark-green solution formed. A methanol solution (15 ml) containing Cu(ClO₄)₂·6H₂O (0.093 g, 0.25 mmol) was added dropwise and stirred for 3 h at room

temperature. Black block-shaped crystals of [Cu₂(MeOH)L₂(ClO₄)]₂·ClO₄ suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the mother solution over a period of one week. IR (KBr, cm⁻¹): 3409 (O–H), 1647 (C=N), 1092 and 634 (ClO₄⁻).

Crystal data

[Cu₂(C₁₂H₁₇FN₃O₂)₂](ClO₄)₂·CH₄O
M_r = 866.59
 Monoclinic, *P*₂₁/*n*
a = 8.5227 (7) Å
b = 33.412 (3) Å
c = 12.2415 (10) Å
 β = 93.702 (2)°
V = 3478.7 (5) Å³
Z = 4

D_x = 1.655 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5049 reflections
 θ = 2.5–20.0°
 μ = 1.46 mm⁻¹
T = 292 (2) K
 Block, black
 0.40 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.71, *T_{max}* = 0.75
 28629 measured reflections

6805 independent reflections
 5377 reflections with *I* > 2σ(*I*)
R_{int} = 0.044
 θ_{max} = 26.0°
 θ_{min} = –10 → 10
 k = –40 → 41
 l = –15 → 14

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.047
wR(*F*²) = 0.104
S = 1.01
 6805 reflections
 451 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.55P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1–O1	1.907 (2)	Cu2–N5	2.003 (3)
Cu1–N3	1.918 (3)	Cu2–N4	2.003 (3)
Cu1–N2	2.014 (3)	Cu1–O4	2.471 (3)
Cu1–N1	2.018 (3)	Cu1–O21	2.927 (3)
Cu2–O3	1.901 (2)	Cu2–O2	2.462 (3)
Cu2–N6	1.935 (3)	Cu2–O5	2.925 (3)
O1–Cu1–N3	94.87 (11)	O3–Cu2–N6	94.74 (11)
O1–Cu1–N2	178.67 (12)	O3–Cu2–N5	178.59 (11)
N3–Cu1–N2	85.00 (13)	N6–Cu2–N5	84.00 (12)
O1–Cu1–N1	94.43 (10)	O3–Cu2–N4	95.39 (12)
N3–Cu1–N1	162.54 (13)	N6–Cu2–N4	165.18 (12)
N2–Cu1–N1	85.37 (12)	N5–Cu2–N4	85.74 (13)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1D···O22 ⁱ	0.90	2.37	3.251 (5)	165
N1–H1D···O23 ⁱ	0.90	2.47	3.228 (4)	142
N4–H4B···O22 ⁱ	0.90	2.20	3.086 (4)	167
N2–H2···O23 ⁱⁱⁱ	0.91	2.11	2.959 (5)	156
N5–H5···O11 ⁱⁱⁱ	0.91	2.56	3.430 (5)	161
O4–H4F···O22 ⁱ	0.85	2.54	3.185 (4)	133
O2–H2B···O1	0.85	2.18	2.762 (3)	126
O4–H4F···O3	0.85	2.20	2.779 (3)	125
O5–H5C···O11	0.85	1.91	2.756 (4)	171

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

All H atoms were placed in calculated positions, with C–H distances in the range 0.93–0.97 Å, N–H distances of 0.90 and 0.91 Å, and O–H distances equal to 0.85 Å, and included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}(\text{C,N,O})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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