

## Synthesis and Crystal Structure of a Novel Hetero-six-nuclear Copper-iron Cluster Containing Ferrocenylphenyl Groups

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**Abstract:** A new hetero-six-nuclear cluster was synthesized and determined by X-ray diffraction technique. The four-carboxylate groups are bound to the Cu(II) atoms to form Cu(OR)<sub>4</sub>Cu paddle-wheel-type cage between two DMF as the basis for the cluster. The distance of two copper(II) atoms is 2.642 Å, and they are bridged by the carboxylate groups. A huge system plane was auto-assembled by four host molecules and two Cu (II) ions, which was observed in the crystal structure.

**Keywords:** Ferrocene, hetero-six-nuclear cluster, copper, crystal structure.

Ferrocene and the derivatives play an important role in organometallic chemistry due to their potential novel functions and applications. Of particular interest is an electron-transfer system of ion center for molecular electronics<sup>1</sup>. Several efforts have been directed towards the design and synthesis of multi-electron redox mediators that could transfer several electrons simultaneously at the same potential<sup>2</sup>. It was reported that ferrocenylphenyl group was an excellent electron transfer mediators<sup>3</sup> and could be used to evaluate the effect of the extended  $\pi$  interaction in the ligand and lowered symmetry of the molecules on the ion state<sup>4</sup>. Coordination complexes of transition metal ion containing ferrocene moiety (redox-active center) have been investigated intensively in recent years<sup>5</sup>. On the other hand, since the first report of the crystal structure of copper(II) acetate monohydrate, [Cu<sub>2</sub>(MeCO<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>6</sup>. Copper(II) complexes have been evaluated by several authors<sup>7</sup>. Coordination flexibility of copper atoms, combined with electronic and steric diversity of R groups in carboxylate anions O<sub>2</sub>CR<sup>-</sup>, still leads to a novel and interesting results in such an old-fashioned chemistry as copper carboxylate<sup>8</sup>. More interest is the fact that the nature of the structural variation and the magnetic properties is not yet clear and has provoked considerable controversy after the extensive investigation<sup>9</sup>. Advantage can be taken from the combination of the redox properties of the ferrocene moiety and the coordination ability of electron donating atoms present in the molecule tethers.

We are interested in the metal-assisted supramolecular assembly of conjugated organic ligands towards novel photonic, new bioorganometallic mediators, electroactive

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and structural materials. On base on that, a novel hetero-six-nuclear copper-ion cluster was synthesized and its crystal structure was also investigated.

## Experimental

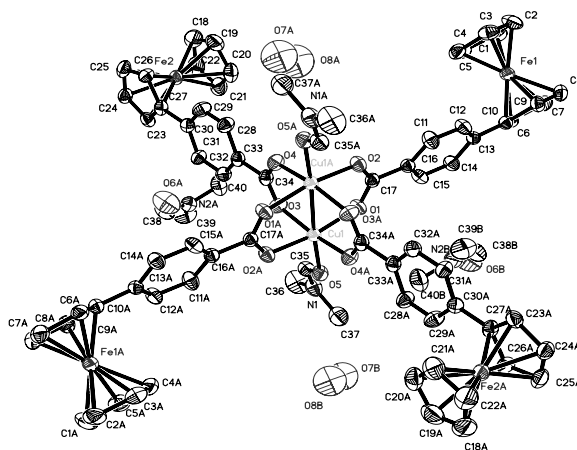
The  $\text{Cu}_2\text{Fe}_4$  hetero-six-nuclear cluster was obtained by the reaction of *p*-ferrocenylphenylformic acid with copper nitrate in ethanol. The mixture was stirring for 5 hr at room temperature and most solvent was evaporated. The green brown deposition was filtered, washed with ether three times and dried in vacuum. Then the deposition was dissolved in DMF, diluted with 95% ethanol, the resultant solution was cooled to 5~6°C in the refrigerator and dark green crystals of X-ray quality were obtained in two weeks (Yield, 25%). Anal. Calcd. for  $\text{C}_{40}\text{H}_{44}\text{CuFe}_2\text{N}_2\text{O}_8$ : C, 56.12; H, 5.18; N, 3.27; Found: C, 55.91; H, 5.40; N, 3.55. IR (KBr  $\text{cm}^{-1}$ ): 3423 (s, OH), 3101(m, Fc), 1606(s, Ar), 1545(m, C=O), 1402(s, C-O), 1106(m, Fc), 1005(w, Fc), 818 (m, Ar).

A dark green crystal of dimensions 0.20×0.18×0.16 mm was used to determine the crystal structures of the hetero-six-nuclear cluster by X-ray diffraction technique. All calculations were performed using the *SHELXL-97* crystal graphic software package<sup>10</sup>. Crystal data for  $[(p\text{-FcC}_6\text{H}_4\text{COO})_2\text{Cu}(\text{DMF})] \cdot 2\text{H}_2\text{O} \cdot \text{DMF}$ :  $M=856.04$ , triclinic, space group *P*-1,  $a=12.052(2)$  Å,  $b=15.822(3)$  Å,  $c=10.955(2)$  Å,  $\alpha=90.33(3)^\circ$ ,  $\beta=98.06(3)^\circ$ ,  $\gamma=73.32(3)^\circ$ ,  $Z=2$ ,  $V=1979.9(7)$  Å<sup>3</sup>,  $T=291(2)$  K,  $\lambda(\text{Mo-K})=0.71073$  Å,  $F(000)=870$ , 6424 reflections measured and 4471 unique ( $R_{\text{int}}=0.0000$ ) were used in all calculations. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$ . The final *R* factor [ $I>2\sigma(I)$ ] was 0.0681 and  $wR$  0.1932.

The structural unit of the cluster is shown in **Figure 1**. The two copper ions are located at equivalent sites. The distance of copper-copper is 2.642 Å, which is short enough to allow a degree of metal-metal bonding character. Each copper atom has an octahedral coordination environment, with four oxygen atoms from the four *p*-ferrocenylphenyl carboxylate groups, which formed an equatorial plane, an oxygen atom of DMF and another copper atom sit two point of axis. The four carboxylate groups are bound to the Cu(II) atoms to form  $\text{Cu}(\text{OR})_4\text{Cu}$  paddle-wheel-type cage between two DMF as the basis for the cluster. The Cu-O distances of the carboxylate oxygen are in the range of 1.957Å to 1.986Å. The axial Cu-O distance is 2.154(5) Å. The coordination geometry around the Cu(II) ion can be regarded as a John-Teller distorted octahedron. The John-Teller effect in the cluster manifests itself as an asymmetric elongation along the axial direction. It is clear from the structure that the four oxygen atoms [O(1)-O(2)-O(1A)-O(2A)] (p1) are coplanar. The displacement of the Cu(I) atom from this plane is 0.0376 Å deviation. Another ring [O(3)-O(4)-O(3a)-O(4a)] (p2) is also coplanar and the displacement of Cu(1A) from the plane is only 0.0160 Å deviation. A huge system plane was auto-assembled by four host molecules and two Cu (II) ions. It can be seen that the two independent carboxylate groups form a good plane and the dihedral angle between them is 89.1°. The dihedral angle between the phenyl ring [C(11)-C(12)-C(13)-C(14)-C(15)-C(16)] (Ph1) and the ring plane (p1) is 14.0°, the phenyl ring [C(28)-C(29)-C(30)-C(31)-C(32)-C(33)] (Ph2) and the ring plane p2 is 7.4°, much smaller than the former. So there are two configurations in the cluster.

In one ferrocene (Fe1), the dihedral angle between the plane of Cp-ring [C(6)-C(7)-C(8)-C(9)-C(10)] (Cp1) and the plane of Ph1 is 23.5°. In another ferrocene (Fe2), the dihedral angle between the plane of Cp-ring [C(23)-C(24)-C(25)-C(26)-C(27)] (Cp2) and the plane of Ph2 is 4.0°, so the plane of Cp ring (Cp2), phenyl ring (Ph2) and the coordination ring (p2) are almost coplanar. To our knowledge, hetero-six-nuclear cluster of *p*-ferrocenylphenyl groups has not been reported, and this paper also first reports the crystallographic characterization of the title cluster.

**Figure 1** The molecular structure of the hetero-six-nuclear cluster



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