

## Synthesis and Characterization of a New Hybrid-metallic Complex Containing Mixed-valence Cu<sup>I</sup>/Cu<sup>II</sup> Units Generated by Hydrothermal Redox Reaction

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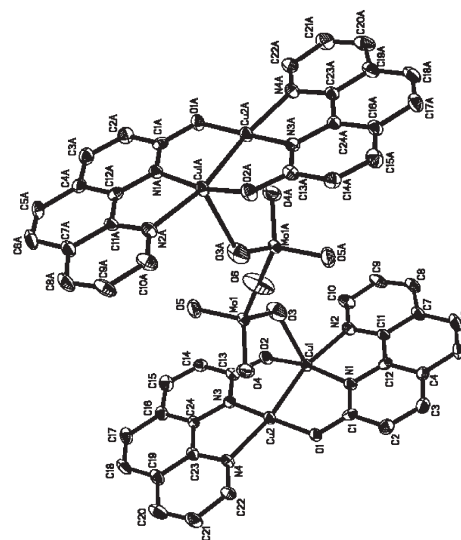
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A new hybrid-metallic complex containing mixed-valence Cu<sup>I</sup>/Cu<sup>II</sup> units, [Cu<sub>4</sub>(ophen)<sub>4</sub>(Mo<sub>2</sub>O<sub>7</sub>)] (Hophen = 2-hydroxy-1,10-phenanthroline), was hydrothermally synthesized and crystallographically characterized.

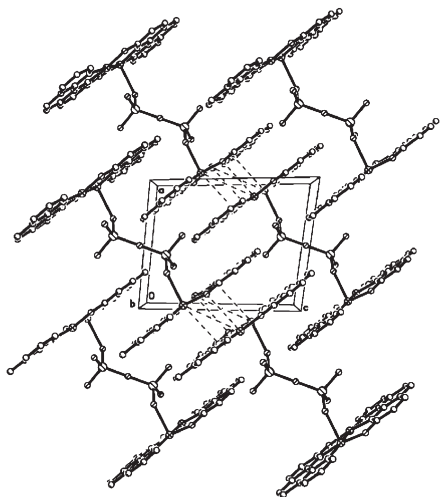
In the past decades, the design and synthesis of inorganic-organic hybrid materials have been increasingly developed.<sup>1–4</sup> The diversity in synthetic systems is derived from the great possibility of the structural construction for both variables of inorganic and organic parts. Thereinto, metal coordination chemistry is a noticeably growing field. In this field, 1,10-phenanthroline (phen) is a well-known motif to prepare a large range of strong chelating ligands for various metal ions. Besides a great number normalization complexes, a handful of so-called anomalies have been reported in reactions of their metal complexes, such as [M(phen)<sub>3</sub><sup>n+</sup>]. Thereof the hydroxylation of phen is important because it would be novel heterocyclic ligands capable of chelating and bridging ligation. On the other hand, owing to involving long-distance electron transfer, the delocalized mixed-valence Cu<sub>2</sub> centers are important in metalloprotein systems, such as cytochrome *c* oxidase and nitrous reductase.<sup>5–8</sup> Thus, the discovery of the spin-delocalized dicopper units has stimulated renewed interest in mixed-valence copper chemistry. Up to now there have been a few approaches to stabilize model complexes containing delocalized mixed-valence Cu<sub>2</sub> centers. Recently, Chen group reported their observation of hydroxylated phen and bpy ligands in the two delocalized mixed-valence Cu<sup>I</sup>/Cu<sup>II</sup> complexes: [Cu<sub>4</sub>(ophen)<sub>4</sub>(tp)] and [Cu<sub>4</sub>(obipy)<sub>4</sub>(tp)], and proposed a new route to the stable mixed-valence dicopper complexes.<sup>9</sup> But these complexes so far reported are mostly onefold metal system. Herein, we report the synthesis, structure and magnetic property of a new hybrid-metallic complex [Cu<sub>4</sub>(ophen)<sub>4</sub>(Mo<sub>2</sub>O<sub>7</sub>)](**1**). To the best of our knowledge, this is the first hybrid-metal complex containing delocalized mixed-valence Cu<sub>2</sub> units. The hydrothermal reaction of copper(II) nitrate, phen and sodium molybdate led to the formation of deep brown **1** that is air stable and insoluble in water and most organic solvents. The IR spectrum exhibited a complex pattern of bands in the range 700–900 cm<sup>-1</sup>, ascribed to ν(Mo=O) and ν(Mo–O–Mo).

The treatment of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O and phen in aqueous solution yields crystal suitable for X-ray diffraction.<sup>10</sup> Single-crystal X-ray analysis<sup>11</sup> has revealed that the complex **1** is centrosymmetric geometric configuration the center of which is the oxygen atom from carboxyl group of the molybdate dimer Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> (Figure 1). There are two Cu<sub>2</sub><sup>3+</sup> units that are bridged by the dimer Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup>. It is interesting that



**Figure 1.** ORTEP drawings of **1** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (°): Cu1–O2 1.885(5), Cu1–O3 2.395(6), Cu1–N1 1.925(6), Cu1–N2 2.064(6), Cu2–O1 1.884(5), Cu2–N3 1.903(6), Cu2–N4 2.048(6), Cu1–Cu2 2.4304(15), Mo1–O6 1.8524(8), C13–O2 1.314(8), C1–O1 1.308(9), O3–Cu1–Cu2 82.34(17), O2–Cu1–Cu2, 92.24(15), N1–Cu2–O2 101.7(2), N1–Cu1–N2 83.0(2), O2–Cu1–O3 86.8(2), N3–Cu2–Cu1 82.79(17), N4–Cu2–Cu1 166.31, O5–Mo1–O4 108.0(3), Mo1–O6–Mo2 180.0(17), C1–O1–Cu2 118.5(4).

the two copper atoms of every unit adopt different coordination surroundings, which are remarkably dissimilar to that found in the mixed-valence compound [Cu<sub>4</sub>(ophen)<sub>4</sub>(tp)],<sup>9</sup> [Cu<sub>4</sub>(tp)<sub>3</sub>-(4,4-bipy)<sub>2</sub>]<sup>12</sup> and other analogous complexes in which the two copper adopt the same coordination geometry. A copper atom adopts distorted quadrilateral coordination geometry and is coordinated by two nitrogen atoms and an oxygen atom of a deprotonated hydroxy group from the ophen ligand, and by metal–metal bond connected with another copper atom that adopts square pyramidal coordination geometry. Alike, defined by two nitrogen donors, an oxygen atom and a copper atom in the basal plane, the copper atom is connected by an oxygen donor of molybdate in the apical position. The unusually short Cu–Cu bond length (2.4304(15) Å) with the necessity to balance charge indicates that complex **1** is delocalized mixed-valence dicopper(I,II) complex. The Cu(I)–Cu(II) distance in **1** is similar to those in fully delocalized mixed-valence dicopper(I,II) complexes.<sup>12–16</sup> Through a μ<sub>2</sub>-O bridge, two tetrahedral molybde-

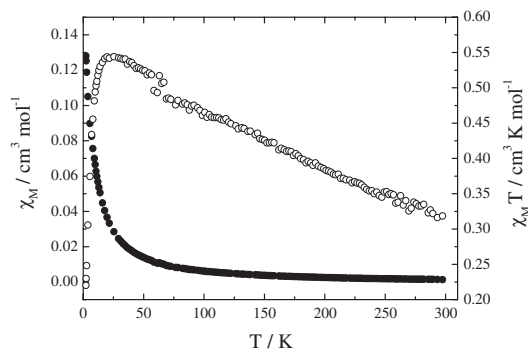


**Figure 2.** Packing of complex **1**, along the *b* axis of the unit cell. The interactions are shown by the broken lines.

num atoms form a dimer which play a role of  $\mu_2$ -bridge ligand combined a pair of the dinuclear cores to form a centrosymmetric neutral tetranuclear copper complex. The bond distance between the sharing  $\mu_2$ -O and Mo (Mo–O, 1.8524(8) Å) is obviously longer than the distance of other Mo–O (about 1.7 Å), which indicate the two molybdenum adopting distort tetrahedral configuration.

It should be noted that neighboring molecules are interlaced, the  $\text{Cu}_2^{3+}$  dimer of a molecule inlays on the interspace of the two  $\text{Cu}_2^{3+}$  dimer of another molecule (Figure 2). The closest contact is observed between uncoordinated molybdate oxygen atoms and the hydrogen atom belonging to the inlayed ophen. The shortest intermolecular contact of O–H is 3.32 Å and such a contact scheme has a 1-D character for the complex **1**. Besides, the adjacent aromatic rings of ophen stack in a face-to-face fashion with a separation of about 3.54 Å, which indicates strong  $\pi$ – $\pi$  stacking interactions between the aromatic rings.

Other physical studies on **1** also support its mixed-valence formulation. The diffuse reflectance UV–vis spectrum for **1** shows broad intense absorption ( $\epsilon = 1750 \text{ M}^{-1} \text{ cm}^{-1}$ ) feature with a maximum at  $\approx 585 \text{ nm}$ . Final and conclusive evidence for the electronic structure of **1** comes from study of its temperature-dependent magnetic susceptibility. Figure 3 shows the temperature dependence of the  $\chi_M T$  measured in a field of 1 T. The room-temperature  $\chi_M T$  value of  $0.33 \text{ cm}^3 \text{ K mol}^{-1}$  is



**Figure 3.** Plots of  $\chi_M T$  and  $\chi_M$  for **1** vs *T* measured in a field of 1 T.

a little lower than the spin-only value of  $0.35 \text{ cm}^3 \text{ K mol}^{-1}$  expected for one unpaired electron per dimer. As the temperature is lowered,  $\chi_M T$  increases gradually to a maximum  $0.54 \text{ cm}^3 \text{ K mol}^{-1}$  at 25 K. This behavior of the  $\chi_M T$  curve shows that there exists ferromagnetic interaction in **1**. However, the curve drops abruptly below 25 K, indicating that an antiferromagnetic interaction exists in **1** at lower temperatures. The  $1/\chi_M$  values obey the Curie–Weiss law between 5–260 K with a Weiss constant  $\theta = +0.42 \text{ K}$ , indicating that there exist predominantly ferromagnetic interaction in **1**. According to crystal structure of **1**, it can be assumed that the magnetic behavior of **1** may be due to the supraexchange interaction of two  $\text{Cu}^{2+}$  atoms through a long pathway of Cu–O–Mo–O–Mo–O–Cu. So the magnetic couple is weak.

In conclusion, we characterized a new hybrid-metallic complex containing mixed-valence  $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$  units generated by hydrothermal metal/ligand redox reaction, which shows ferromagnetic behavior. Further investigation of magnetic properties is in progress.

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- Synthesis complex **1**: A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.291 g),  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.241 g), phen (0.198 g), and water (10 mL) in the molar ratio 1:1:1:556 is sealed in a 23-mL Telon reactor, which was heated in an oven to  $160^\circ \text{C}$  for 80 h. Cooled down to room temperature, the dark brown single crystals were obtained (yield: 42%).
- Anal. Calcd for  $\text{C}_{48}\text{H}_{28}\text{Cu}_4\text{Mo}_2\text{N}_8\text{O}_{11}$ : C, 43.06; H, 2.11; N, 8.37%. Found: 43.27; H, 2.05; N, 8.77%.
- Crystal data for **1**:  $\text{C}_{48}\text{H}_{28}\text{Cu}_4\text{Mo}_2\text{N}_8\text{O}_{11}$ ,  $M_r = 1338.82$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.884(3)$ ,  $b = 10.493(4)$ ,  $c = 12.023(4)$  Å,  $\alpha = 70.719(6)$ ,  $\beta = 76.615(6)$ ,  $\gamma = 66.387(6)^\circ$ ,  $V = 1091.8(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_{\text{calcd}} = 2.036 \text{ g/cm}^3$ ,  $\mu = 2.546 \text{ mm}^{-1}$ , Crystal size  $0.35 \times 0.20 \times 0.15 \text{ mm}^3$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $T = 293(2)$  K.  $2.26^\circ < \theta < 26.41^\circ$ ,  $R_1[I > 2\sigma(I)] = 0.0562$ ,  $wR(\text{all data}) = 0.0909$ , GOF = 0.973. Deposited in No. CCDC-212278. The crystal structure was solved by direct methods and refined on  $F^2$  using full matrix least squares with SHELXL-97 program package.
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