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Remarkable solvent effects in the hydro- and solvothermal synthesis of copper-1,10-phenanthroline complexes

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Compound {[Cu(II)/Cu(I)]$_2$(ophen)$_4$(Htpt)}$^\bullet$2H$_2$O (1) was obtained by hydrothermal reaction. Compound 1 is a mixed-valence copper coordination complex with a different coordination environment. The X-ray structural analysis of 1 revealed two crystallographically independent dimeric [Cu$_2$(ophen)$_2$]$^+$ units bridged by two μ_1-carboxylate groups of the tpt ligand into a butterfly-shaped molecule in the crystal structure. Compound [Cu(I)$_3$(CN)$_3$(phen)$_3$] (2) was synthesized using ethanol instead of water, and consisted of an infinite helix chain formed from [Cu(I)(phen)]$^+$ units bridged by cyano groups. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: hydrothermal reaction; mixed-valence; redox; solvent effects

INTRODUCTION

Mixed-valence metal complexes have become the focus of interest over the past decade because of their large range of potential applications.[1] Specifically, of all the commonly studied transition metals, copper attracts intense interest because of the different stereo-electronic preferences of its two common oxidation states,[2–6] biological importance and electronic properties.[7–12] Recently, a few mixed-valence Cu(II)/Cu(I) complexes, such as Cu$_4$(ophen)$_4$(tp) and Cu$_4$(obpy)$_4$(tp) (ophen = ophenanthroline; obpy = obipyridine and tp = terephthalate),[14,15] have been obtained through the use of the redox reaction of Cu(II) ions with mixed ligands under hydrothermal or solvothermal conditions.[3,13]

In this paper, we obtained two very different complexes, [Cu(II)/Cu(I)]$_2$(ophen)$_6$(tpt) (tpt = trimesicate) (**1**) and Cu(I)$_3$(CN)$_3$(phen)$_3$ (**2**), through the use of different solvents. Under hydrothermal conditions, compound **1** was prepared, which contains two [Cu$^{\mathrm{I}}$/Cu$^{\mathrm{II}}$ (ophen)] units bridged by tpt, resulting in the formation of a butterfly conformation. To the best of our knowledge, **1** is a mixed-valence Cu(II)/Cu(I) compound with two copper atoms containing different coordination environments, and a shorter distance between the two copper atoms than those of reported complexes.[16,17] However, a novel compound **2** was obtained under the same conditions using ethanol instead of distilled water as the reaction medium. X-ray crystal structurial analysis, IR spectra and other physical analytical methods indicate that compound **2** consists of an infinite helix chain through formation of [Cu(phen)]$^+$ bridged by cyano. Here, we also show an example in which the cyano group was obtained by redox between phen and copper salt at high temperature and pressure.

The hydrothermal reaction of Cu(NO$_3$)$_2$ with 1,10-phen, Na$_3$tpt and water in the molar ratio 1 : 1.5 : 0.5 : 600, at 165 °C (7 days), results in the formation of dark brown [(Cu(II)/Cu(I))$_2$(ophen)$_2$(Htpt)]$^\bullet$2H$_2$O. The X-ray structural analysis of **1** revealed two crystallographically independent dimeric [Cu$_2$(ophen)$_2$]$^+$ units bridged by two μ_1-carboxylate groups of tpt ligand forming a butterfly-shaped molecule (see Fig. 1). It is expected that 1,10-phen was oxidized to 1,10-Hophen, which was bound to Cu–Cu centers forming dimeric [Cu(I)$_2$(ophen)$_2$]$^+$ units analogous to

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[Cu(II)/Cu(I) $(\text{ophen})_2]^+$ complexes,[14,15] indicating that the metals have a mixed Cu(I)–Cu(II) formulation. Furthermore, the unusual Cu–Cu distances in **1** [2.3999(8)–2.4076 Å] are shorter than those of the majority of $[\text{Cu}_2]^{3+}$ complexes determined previously.[3,8,14,15,18,19] The bond valence sums of compound **1** molecule are the copper center as a delocalized 1.5+ oxidation state or a mixed Cu(I)–Cu(II) formulation. The XPS spectrum of **1** also supports its novel mixed-valence formulation. In Fig. 2 there are four characteristic copper characteristic peaks of 937.95, 949.25, 958.8 and 968.1 eV, indicating that compound **1** contains a copper(II) center. On the other hand, the two main peaks are higher and wider than those of standard copper(II),[20] showing that compound **1** contains copper(I) ions.

As shown in Fig. 1, in the crystal structure of compound **1**, the coordination geometry of the Cu3 and Cu4 atoms is roughly square planar composed of a pair of nitrogen atoms [Cu–N 1.894(3)–2.064(3) Å] from an ophen ligand, a deprotonated hydroxyl group [Cu–O 1.874(2) to 1.899(2) Å] from another ophen ligand and the adjacent copper atom at the equatorial positions. However, the Cu1 and Cu4 atoms have a square-pyramidal coordination environment, which is similar to the coordination environment of Cu3 and Cu4 at the equatorial positions beside the oxygen atom at the axis from carboxylate oxygen atoms of a tpt [Cu–O 2.159(2)–2.168(2) Å]. This is a mixed-valence copper coordination complex with a different coordination environment due to two carboxyls of tpt ligand with a 120° angle, in order to decrease the influence of steric hindrance effect, leading to this result. Two $[\text{Cu}_2(\text{ophen})_2]^+$ units of compound **1** with a dihedral angle of 30.9° are not parallel to each other, as with those complexes reported.[14,15] On the other hand, there are shorter Cu–O distances [1.874(2)–1.899(2) Å] in the $[\text{Cu}_2(\text{ophen})_2]^+$ unit than those [1.921(5)–1.943(4) Å] found in mixed-valence complexes with a $[\text{Cu}_2(\text{ophen})_2]^+$ or $[\text{Cu}_2(\text{obpy})_2]^+$ unit.

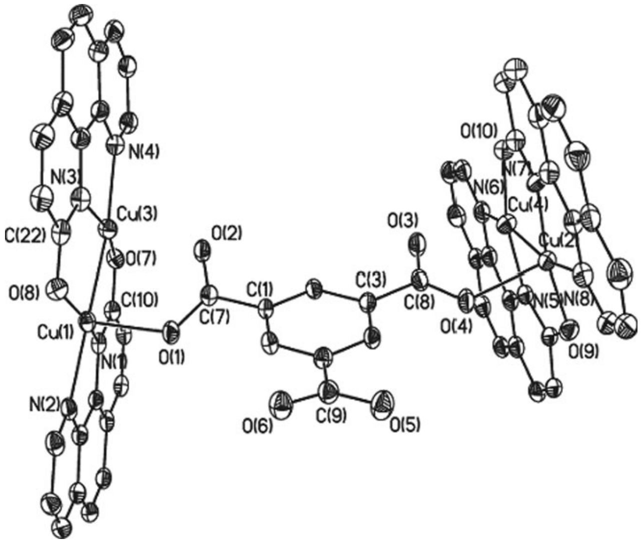

Figure 1. A view of the structure of **1**. Selected bond lengths (Å) and angles(deg): Cu1–O8, 1.899(2); Cu1–N1, 1.920(3); Cu1–N2, 2.076(3); Cu1–O1, 2.159(2); Cu1–Cu3, 2.3999(8); Cu2–O9, 1.897(3); Cu2–N7, 1.903(3); Cu2–N8, 2.060(3); Cu2–O4, 2.168(2); Cu2–Cu4, 2.4076(8); Cu3–O7, 1.874(2); Cu3–N3, 1.894(3); Cu3–N4, 2.096(3); Cu4–O10, 1.880(3); Cu4–N5, 1.894(3); Cu4–N6, 2.064(3); O8–Cu1–N1, 164.70(11); O8–Cu1–O1, 93.87(10); N1–Cu1–O1, 100.75(11); N2–Cu1–O1, 91.98(10); O1–Cu1–Cu3, 93.08(7); O9–Cu2–O4, 90.14(10); N7–Cu2–O4, 101.65(12); N8–Cu2–O4, 95.42(11); O4–Cu2–Cu4, 87.50(7).

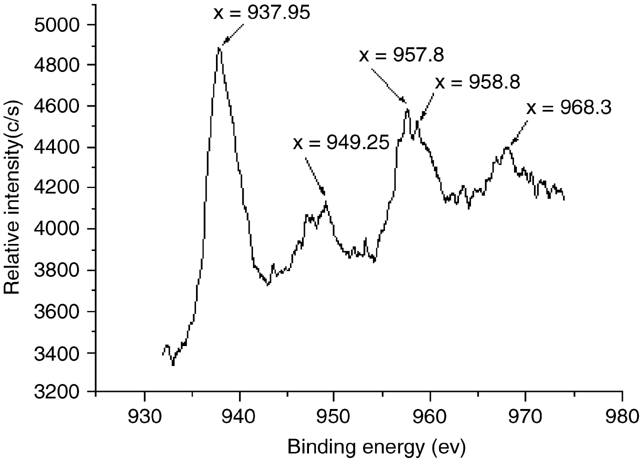

Figure 2. XPS graphic for compound **1**.

It is noteworthy that hydrogen-bonding, $\pi-\pi$ stacking and van der Waals interactions between molecules result in the formation of three-dimensional supramolecular arrays. In the crystal structure of **1**, there are four types of hydrogen bonds. Molecules adopting head–tail contacts are C–O···Ow hydrogen bonds [C7–O2···O1w, 2.709Å; C8–O3···O2w, 2.768 Å; C9–O5···O2w, 2.609 Å $(x, y+1, z)$; C9–O6···O1w, 2.725 Å $(x, y+1, z)$; O1w···O2w, 2.688 Å] between the carboxyl groups from ligand tpt and H_2O molecules, which form a five-number cycle (O1w, O2w, O5B, C9B, O6B) and a nine-number cycle (O1W, O2W, O3, C8, C2, C1, C7, O2), resulting in the formation of an infinite one-dimensional polymer like a channel along the *b*-axis. One-dimensional chains are further extended by strong $\pi-\pi$ stacking interactions between adjacent aromatic rings of ophen stacking in a face-to-face fashion with a separation of 3.5–3.7 Å and van der Waals interactions from the intermolecular Cu···Cu interactions (Cu···Cu 3.916–4.074 Å) into the forming two-dimensional polymer along the *c*-axis, which are held together by C–H···O hydrogen bonds [C4···O4, 2.695(4) Å; C15···O2, 3.407(4) Å; C39···O3, 3.372(4) Å] and $\pi-\pi$ stacking interactions between aromatic rings along the *a*-axis into three-dimensional supramolecular array (Figs 3 and 4).

According to the conditions for synthesis of **1**, we find that the use of uniqueous anhydrous ethanol instead of water produced one novel compound $[\text{Cu}_3(\text{CN})_3(\text{phen})_3]$

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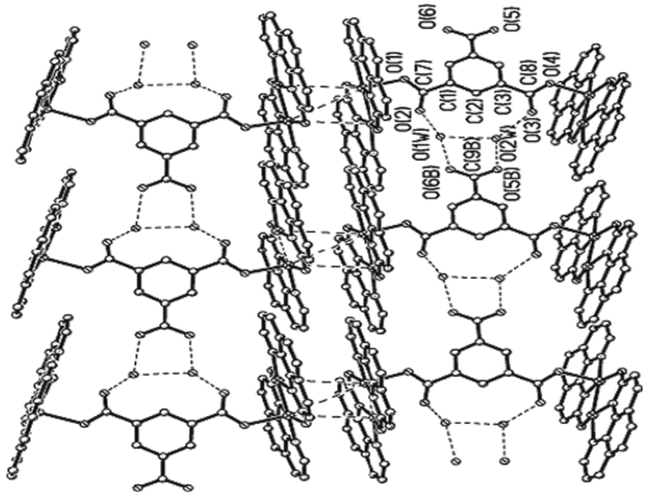

Figure 3. Along bc planar in **1** forming a two-dimensional network through hydrogen-bonding, Cu···Cu and pai–pai interaction.

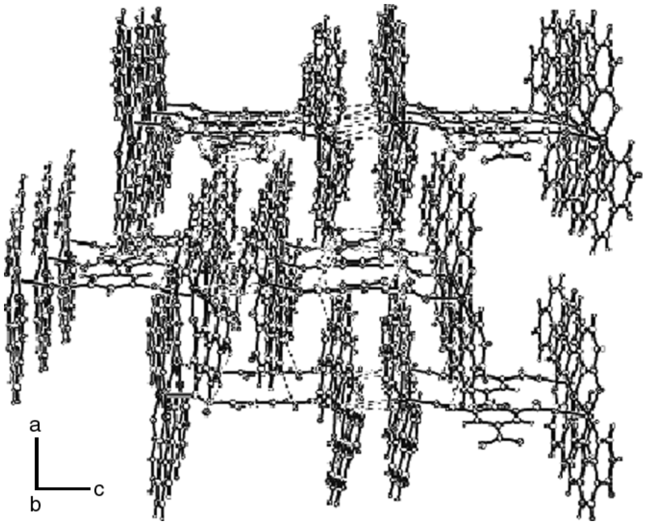

Figure 4. Molecular packing as seen along the crystallo-graphic *a* axis for **1**.

(**2**) (see Fig. 5). Compound **2** is a copper(I) coordination complex according to its red color. The XPS spectrum of **2** also supports their single valence function. There are two characteristic peaks, indicating that compound **2** only contains a copper(I) center (Fig. 6). IR absorption characteristic peaks of cyano were observed for both complexes in the region 2100–2160 cm^{-1}. Furthermore, structural evidence for this comes from the natural C–N, Cu–N (C) and N (C)–Cu–C (N) distances and angles of 1.162(6) and 1.898(5)–1.909(5) Å and 124.85(18)–137.4(3)°, respectively. These are consistent with the majority of Cu(CN) complexes determined previously. Thus it is thought that **2** is the same compound as $Cu_3(CN)_3(phen)_3$, which consists of an infinite helix chain in the form of a [Cu(I)(phen)]$^+$ unit bridged by cyano.[21]

In the formation of **2**, it is unique for this reaction to produce cyano at high temperature and pressure. However, nothing containing cyanide was added to this reaction, so the cyano could only come from the products of 1,10-phen oxidized by Cu(II) ions. Although the reaction mechanism between organo-amino and copper salts in the hydrothermal has been put forward and authenticated,[1,14,15] the solvothermal mechanism has never been described. Thus this is the first time that cyano has been successfully isolated from the oxidized products of 1,10-phen.

In conclusion, we discuss how solvent reagents affect the redox reaction between copper and organoamino at high temperatures and pressures. Through changing the

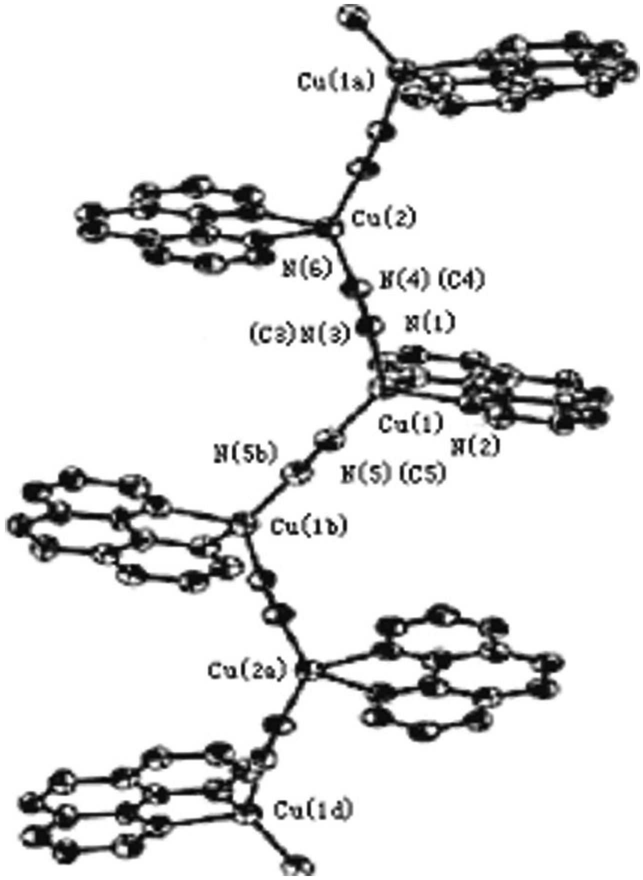

Figure 5. A view of the structure of **2**. Selected bond lengths (Å) and angles (deg): Cu1–N5, 1.891(4); Cu1–N3, 1.898(5); Cu1–N2, 2.034(4); Cu1–N1, 2.079(4); Cu2–N4, 1.909(5); Cu2–N4, 1.909(5); Cu2–N6, 2.162(4); Cu2–N6, 2.162(4); N5–Cu1–N3, 124.85(18); N5–Cu1–N2, 118.29(17); N3–Cu1–N2, 107.83(17); N5–Cu1–N1, 108.18(17); N3–Cu1–N1, 109.07(17); N2–Cu1–N1, 78.65(16); N4–Cu2–N4, 137.4(3); N4–Cu2–N6, 104.17(17); N4–Cu2–N6, 109.23(17); N4–Cu2–N6, 109.23(17); N4–Cu2–N6, 104.17(17); N6–Cu2–N6, 75.7(3).

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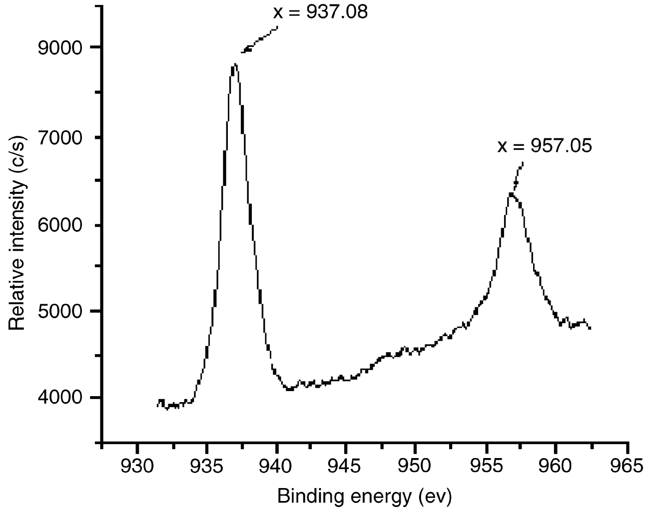

Figure 6. XPS graphic for compound **2**.

solvent, we obtained two absolute different compounds **1** and **2**.

EXPERIMENT

Materials and methods

All commercially available chemicals were of reagent grade and used as received without further purification. C, H, N analyses were carried out on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. IR spectra were recorded on a Vector 22 Bruker spectrophotometer with KBr pellets in the 5000–400 cm^{-1} region. All XPS were recorded on an ESCALB MK-II spectrometer.

X-ray crystallography

Parameters for data collection and refinement of complexes **1** and **2** are summarized in Table 1. The data collection was carried out on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatic Mo K_α radiation ($\lambda = 0.71073$ Å) at room temperature. Data were reduced using the Bruker SAINT program. Empirical absorption was done using the SADABS program. Crystal structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by means of the full-matrix least-square method on F^2_{obs} using the SHLXTL-PC software package. The hydrogen atom positions were fixed geometrically and allowed to ride on the attachment. Crystallographic data (excluding structure factors) for the structure of complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication; CCDC numbers for **1** and **2** are 227639 and 227640, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for complexes **1** and **2**

	1	2
Experimental formula	$C_{57}H_{33}Cu_4N_8O_{11}$	$C_{36}H_{24}Cu_3N_{12}$
Formula weight	1260.07	815.29
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/c	C222(1)
a (Å)	17.138(5)	16.562(1)
b (Å)	9.664(3)	8.500(1)
c (Å)	28.909(8)	24.473(1)
β (deg)	91.730(5)	90
V (Å^3)	4786(2)	3445.2(5)
Z	4	4
D_{calc}(g cm^{-3})	1.749	1.572
μ (mm^{-1})	1.831	1.881
T (K)	293(2)	293(2)
F(000)	2540	1644
Reflections collected	23063	3289
Unique reflections	5268	2263
R_{int}	0.0337	0.0387

Synthesis

{[Cu(II)/Cu(I)]$_2$(ophen)$_4$(Htpt)}$^\bullet$2H_2O (**1**) was prepared as block crystals from the hydrothermal reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (150 mg 0.60 mmol), trimesicate natrium (28.00 mg, 0.10 mmol), phen (118.00 mg, 0.60 mmol) and H_2O (20 ml, 1.11mol) in a Parr acid digestion vessel of 23 ml volume and heated at 165 °C for 7 days. It was then cooled to room temperature. A mixture of block crystals of **1** was obtained in 46.21% total yield. Calcd (%) for **1**: C, 54.29; H, 2.62; N, 13.97; found: C, 54.01; H, 2.38; N, 13.76.

$Cu_3(CN)_3(phen)_3$ (**2**) was prepared as red-back block crystals from the hydrothermal reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (150.00 mg 0.60 mmol), trimesicate natrium (28.00 mg, 0.10 mmol), phen (118.00 mg, 0.60 mmol) and uniqueous anhydrous ethanol (20 ml) in a Parr acid digestion vessel of 23 ml volume and heated at 165 °C for 5 days; yield: 38.03%. Calcd (%) for **2**: C, 52.99; H, 2.94; N, 20.61; found: C, 52.86; H, 3.03; N, 20.48.

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