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A mixed-valence copper coordination polymer generated by hydrothermal metal/ligand redox reactions†

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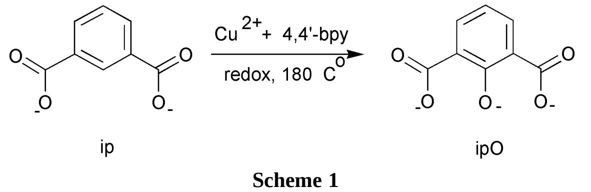
A novel coordination polymer of mixed-valence copper(I,II) with 4,4′-bipyridine and *in situ* oxidized isophthalate, [Cu_2(ipO)(4,4′-bpy)] (ipOH = 2-hydroxyisophthalate), was hydrothermally synthesized and crystallographically characterized to be a laminated structure *via* weak copper(II)–oxygen interactions.

Extended frameworks of coordination polymers, based on complexes of transition metals and multifunctional bridging ligands, are of great research interest.[1] The hydro(solvo)thermal method has been a promising technique in preparing highly stable, infinite metal–ligand frameworks.[2] It has been found that *in situ* reactions,[3] such as ligand oxidative coupling, hydrolysis, substitution and redox process of copper, can occur under hydro(solvo)thermal conditions. These reactions represent promising new routes for constructing novel coordination polymers. We have shown that mixed organic ligands[4] can be used to construct unusual molecular architectures under hydrothermal conditions and wish to extend this to mixed-valence copper complexes. Copper(I) compounds are of great biological importance and mixed-valence Cu^ICu^{II} species can be formed, in which the two states are readily interconverted as well as phenol catalytically generated.[5]

It is surprising that mixed-valence Cu^ICu^{II} species and *in situ* synthesis of 2-hydroxyisophthalate (ipOH) are simultaneously generated under the hydrothermal reaction of isophthalate (ip) and 4,4′-bipyridine (4,4′-bpy) with $Cu(NO_3)\cdot 3H_2O$ (Scheme 1). To the best of our knowledge, this is the first mixed-valence coordination polymer with *in situ* ligand synthesis, although one mixed-valence copper coordination polymer[3f] and two polynuclear mixed-valence copper compounds, with hydroxylated bipyridyl ligands,[3g] have been recently reported. In this communication, we report the synthesis and structure of the mixed-valence complex [Cu_2(ipO)(4,4′-bpy)] (ipOH = 2-hydroxyisophthalate) (**1**) and its magnetic properties.

The hydrothermal reaction of copper(II) salt with the dicarboxylate and 4,4′-bpy, in molar ratio 1 : 1 : 1, at 180 °C (80 h) led to the formation of dark blue **1**.‡ This resulted in the *in situ* synthesis of 2-hydroxyisophthalate. Cu^{II} ions may act as an oxidative agent to promote the formation of the phenoxo group. The reaction mechanism is different from that of the phenoxo formation, catalyzed by Cu^I, in the presence of dioxygen.[3g,6]



Scheme 1

Single-crystal X-ray analysis§ has revealed that there are two crystallographically independent metal atom centers in the crystal structure (Fig. 1). Cu1 is primarily coordinated to four oxygen atoms in a distorted square geometry, of which two belong to two endogenous phenoxo groups and the other two to carboxylate groups of the two ipO ligands. The metal atom (Cu1) is slightly deviated from the plane (0.14 Å). In addition, Cu1 weakly interacts with the O4B atom (2.594(4) Å), which belongs to the ipO ligand in the adjacent layer; therefore Cu1 has a square-pyramidal coordination geometry. It is interesting that the bis-phenoxo-bridged Cu_2O_2 core adopts a butterfly geometry and is interconnected to generate a chain-like structure through the weak Cu^{II}–carboxylate interactions (Fig. 2). Cu1, Cu1A and two ipO ligands form a $[Cu^{II}_2(ipO)_2]^{2-}$ ‘metallo-ligand’, which is coordinated to two mono-valence copper atoms in an opposite direction and in a T-shape mode. The monovalence Cu2 is trigonally coordinated by two nitrogen atoms from two 4,4′-bpy and one oxygen atom from the ipO carboxylate group.

The most striking feature of **1** is the connection of $[Cu^{II}_2(ipO)_2]_n^{2n-}$ ‘metallo-ligands’ and $[Cu^I(4,4'\text{-bpy})]_n^{n+}$

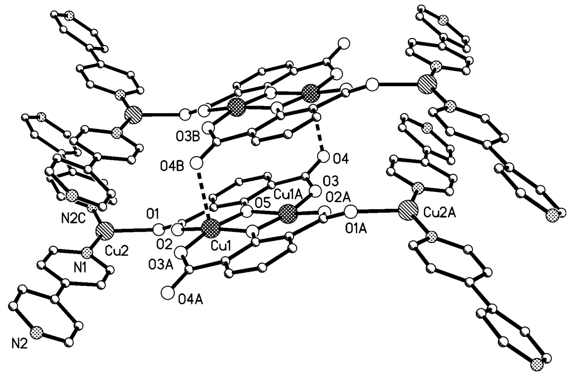


Fig. 1 The coordination environment of the copper atoms in **1**. Selected bond distances (Å) and angles (°): Cu1–O2 1.904(4), Cu1–O5 1.928(4), Cu1–O3A 1.892(4), Cu1–O5A 1.925(4), Cu1··Cu1A 2.970(2), Cu2–N1 1.935(5), Cu2–N2A 1.953(5), Cu2–O1 2.163(5); O2–Cu1–O3A 94.6(2), O2–Cu1–O5 92.3(2), O3A–Cu1–O5A 92.8(2), O5–Cu1–O5A 79.1(2), O2–Cu1–O4B 94.3(2), O5–Cu1–O4B 89.0(2), O3A–Cu1–O4B 98.7(2), O5–Cu1–O4B 93.9(2), Cu1–O5–Cu1 100.9(2), O2–Cu1–O5A, 168.0(2), O3A–Cu1–O5 169.2(2), N1–Cu2–O1 118.8(2), N2C–Cu2–O1 97.3(2), N1–Cu2–N2C 143.9(2), Cu1–O5–Cu1A 100.9(2). Symmetry codes: A) −*x*, −*y*, −*z*; B) *x* +1/2, −*y*, −*z*; C) *x* −3/2, −*y* +1/2, *z* +1/2.

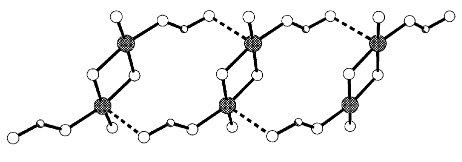


Fig. 2 Perspective view of the chain-like Cu_2O_2 cores.

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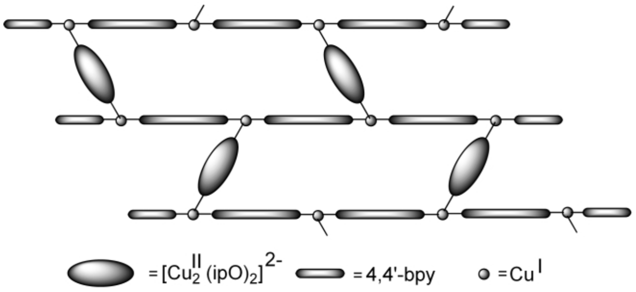
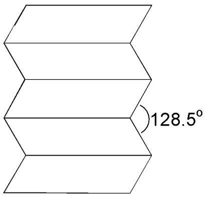
† Electronic supplementary (ESI) available: the effective molar magnetic moment μ_{eff} of **1** *vs. T*. See http://www.rsc.org/suppdata/cc/b2/b203301a/

chains to form an infinite two-dimensional layer in a herringbone (6,3) net, as shown in Scheme 2. This two-dimensional layer is puckered with $[Cu^{II}_2(ipO)_2]^{2-}$ groups lying in each plane, and each pair of the adjacent planes (dihedral angle 128.5°) is linked to one another by sharing $[Cu^{I}(4,4'\text{-bpy})]_n^{n+}$ chains (Scheme 3). Adjacent puckered layers are interconnected by the weak Cu^{II}–carboxylate interactions to form a three-dimensional laminated structure in the solid state.



Scheme 2



Scheme 3

Preliminary magnetic study of **1** (Fig. 1S, ESI†) shows that upon cooling, the $\chi_M T$ value decreases rapidly from 300 to 150 K, and then increases to a maximum at *ca*. 22 K before decreasing again. This behavior is very unusual and interesting, indicative of a very strong antiferromagnetic interaction admixture with a weak ferromagnetic interaction.[7]

In summary, this hydrothermal redox reaction and *in situ* ligand synthesis provide a new strategy for the construction of coordination polymers with promising physico-chemical properties. Further investigation of magnetic properties is in progress.

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Notes and references

‡ Anal. Calc. for $C_{18}H_{11}Cu_2N_2O_5$ **1**: C, 46.76; H, 2.40; N, 6.06%. Found: C, 46.62; H, 2.39; N, 5.72%. IR (KBr, cm^{-1}): 3421m, 3108w, 3045w, 1600vs, 1538s, 1484w, 1436s, 1415m, 1355s, 1281m, 1250w, 1213w, 1150w, 1102w, 1071w, 928w, 873w, 815m, 754m, 712w, 630m, 476w.

§ *Crystal data* for **1**: $C_{18}H_{11}Cu_2N_2O_5$, M_r = 462.37, monoclinic, space group $P2_1/n$ (no. 14), a = 5.331(1), b = 22.863(7), c = 13.088(4) Å, β = 91.54(3)°, V = 1594.6(8) Å^3, Z = 4, D_c = 1.926 g cm^{-3}, μ = 2.70 cm^{-1}. Data collections ($2 \leqslant 2\theta \leqslant 27°$) were performed at 293 K on a Siemens R3m diffractometer (Mo-Kα, λ = 0.71073 Å). The structure was solved with direct methods and refined with full-matrix least-squares (SHELX-97),[8] giving a final R_1 value of 0.0546 for 245 parameters and 2438 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.1546 for all 3644 reflections for **1**. CCDC reference number 183240. See http://www.rsc.org/suppdata/cc/b2/b203301a/ for crystallographic data in CIF or other electronic format.

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