

# A 2D brick wall metal-organic framework constructed from quasi-tetracopper(II) SBUs: Crystal structure and magnetic property

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## Abstract

A coordination polymer,  $[\text{Cu}_2(2,2',3,3'\text{-odpa})(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})$  ( $2,2',3,3'\text{-odpa} = 2,2',3,3'\text{-oxydiphthalic acid}$ ) (**1**), has been obtained. Single crystal X-ray diffraction analysis indicated that **1** has a 2D distorted brick wall structure ( $6^3$ -nets) constructed from tetracopper(II) SBUs. The relationship between its magnetic property and structure also has been investigated.

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The construction of coordination polymers has developed rapidly in recent years, owing to their interesting molecular topologies and crystal packing motifs along with potential applications as functional materials [1,2]. In general, structural motifs of these hybrid compounds are closely related to the geometry and the number of coordination sites provided by organic ligands [3]. As an important family of multidentate O-donor ligands, organic aromatic polycarboxylate ligands, such as 1,2-benzenedicarboxylate, 1,3-benzenedicarboxylate, 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, and 1,2,4,5-benzenetetracarboxylate, have been extensively employed in the preparation of metal-organic complexes that are possessed of multidimensional networks and interesting properties [4]. Now, searching for new polycarboxylates ligands is very important and deserved to be attentive for investigating new topology and various functional materials [3,5].

Among the many types of bridging conformations a carboxylate group can adopt, the triatomic *syn-syn*, *anti-anti*, and *syn-anti* conformations are the most typical examples, which are often closely related to the magnetic

properties of the corresponding complexes [6]. In order to make clearer of the difference in magnetic behaviors that resulted from structural factors, more examples of these kinds of complexes are needed.

With the aim of understanding the coordination chemistry of  $2,2',3,3'\text{-H}_4\text{odpa}$  and preparing new materials with interesting structural topology and excellent physical properties, we have recently engaged in the research of coordination polymers based on this and related ligands [7]. Herein, we present a 2D metal-organic framework based on a novel  $\text{Cu}_4$  cluster and its magnetic property.

Complex **1** was synthesized hydrothermally in a 23 ml Teflon-lined autoclave by heating a mixture of 0.1 mM  $2,2',3,3'\text{-H}_4\text{odpa}$ , 0.1 mM  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  and one drop of  $\text{Et}_3\text{N}$  at 120 °C for two days [8].

The X-ray diffraction study [9] for **1** reveals that it crystallizes in space group  $P\bar{1}$ , and each molecular unit consists of one  $2,2',3,3'\text{-odpa}^{4-}$  ligand, two copper atoms, three coordinated and one solvent water molecule (Figs. 1a and b). Selected bond lengths for **1** are listed in Table S1 in Supplementary materials. As shown in Fig. 1,  $\text{Cu}^{\text{II}}$  ions have two different coordination environment. At first glance,  $\text{Cu1}$  adopts a five-coordinated square-pyramidal geometry, coordinated by O1 of 2-carboxylate, O9 of 3'-carboxylate from the neighboring molecular, O4 of 3-carboxylate from

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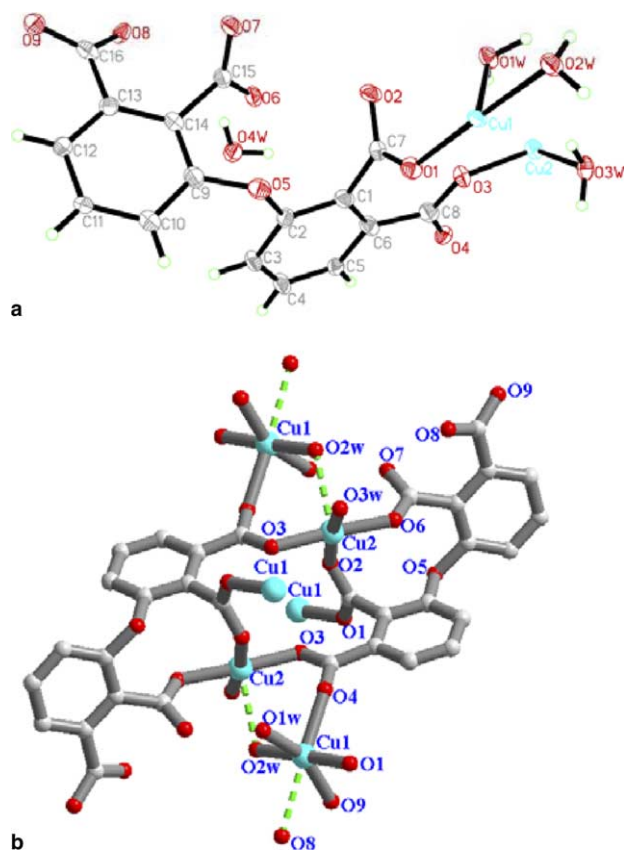


Fig. 1. (a) The asymmetric unit of **1**; (b) the coordination environments of Cu1 and Cu2.

another neighboring molecular, and two water oxygen atoms (O1w and O2w). Cu2 should take a four-coordinated square-planar mode, coordinated by O3 from 3-carboxylate, O2 and O6 of 2- and 2'-carboxylate from the neighboring molecular, and one water oxygen atom (O3w). However, the Cu1–O8 (2.556 Å) and Cu2–O2w (2.605 Å) distances suggest nonnegligible interactions between them. Thus, Cu1 center may be regarded as distorted octahedron conformation and the surrounding of each copper ion is (4 + 2), the octahedral being elongated along O4–Cu1–O8 axis. Cu2 center can be described as square-pyramidal conformation and the surrounding of each copper ion is (4 + 1), with a long axis (Cu2–O2w = 2.605 Å). O2w acts as a bridge ligand between Cu1 and Cu2. Further investigation of the structure of **1** confirmed a novel square Cu<sub>4</sub> cluster [Cu<sub>4</sub>(COO)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] in the 2D arrangement (Fig. 2a). In the tetranuclear copper cluster, four copper(II) ions are bridged by four carboxylate groups, in which two *syn-syn* in equatorial–axial positions and two *syn-anti* carboxylate groups in equatorial–equatorial positions. Two kinds of distances are 3.832 and 5.591 Å for *syn-syn* and *syn-anti* carboxylate bridged Cu1–Cu2, respectively. Since there is a symmetry center in Cu<sub>4</sub> cluster, we can take Cu(1)–Cu(2) binuclear clusters which are bridged together through *syn-syn* carboxylate groups and O2w molecules as minimal “joints”

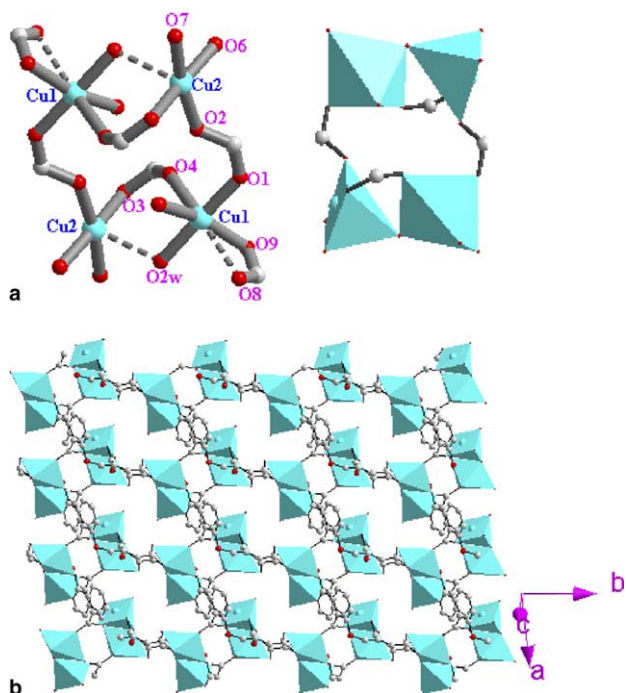


Fig. 2. (a) Cu<sub>4</sub> cluster; (b) 2D brick wall structure of **1**. Hydrogen atoms and solvent water molecules are omitted for clarity.

[4,10]. Finally, a 2D distorted brick wall architecture with 6<sup>3</sup> topology was obtained (Fig. 2b). In addition, there are some hydrogen bonds in **1**. Through these hydrogen bonds, **1** gives a 3D supramolecular structure (see Table S2 and Fig. S1 saved in Supplementary materials).

A thermogravimetric analysis of **1** displays the total weight loss of 13.11% between 25 and 230 °C corresponding to the loss of four water molecules (calculated: 13.31%). Above 230 °C, the sample starts to decompose (see Fig. S2 saved in Supplementary materials).

The magnetic behavior of the complex **1** in the form of a  $\chi T$  vs.  $T$  plot is shown in Fig. 3. The global feature is characteristic of weak ferromagnetic interaction. The value of

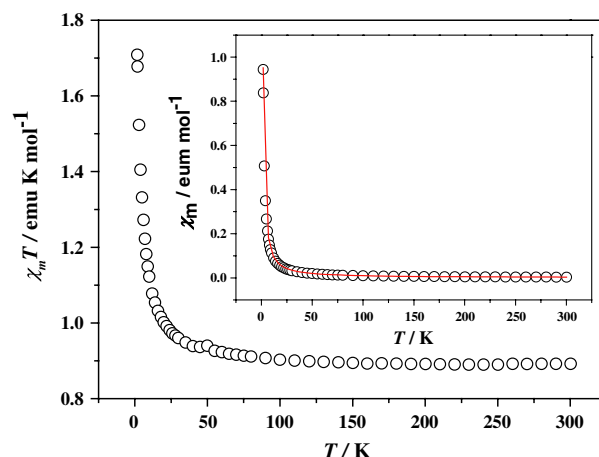


Fig. 3. Thermal variation of the molar magnetic susceptibility,  $\chi_M$  (inset) and  $\chi_M T$  product of **1**. Solid line shows the best fit to the model.

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