

# A Novel Copper Complex with Multibridging Coordination Mode: Synthesis, Structure, Luminescent and Magnetic Properties

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**Abstract:** A novel three-dimensional (3D) metal-organic framework (MOF),  $[\text{Cu}_5(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_4(\text{N}_3)_2(\text{SO}_4)_2]_n$  (**1**), was constructed by a hydrothermal process at 160°C. The complex **1** exhibits strong emission at 396 nm in solid state. Importantly, the variable-temperature magnetic susceptibility study indicates that there exists strong antiferromagnetic interactions between the copper atoms with  $C = 0.87 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and  $\theta = -320.2 \text{ K}$ .

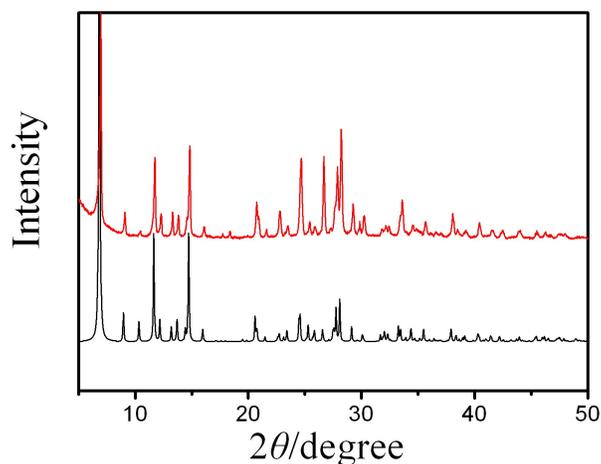
**Key Words:** Copper complex, hydrothermal synthesis, luminescent, magnetic property.

## INTRODUCTION

The metal-organic frameworks (MOFs) is now of great interest due to their intriguing topology architecture and significant potential applications in many fields such as gas storage [1-4], catalysis [5], luminescence [6, 7] and magnetism [8-11]. The mainly strategy to obtain MOFs is employ organic groups as building blocks [8, 11], therefore, the organic ligand is a vital factor in the construction of MOFs. The carboxylate group is an active block because of its eximious ability to mediate metal ions, and various complexes have been obtained [11, 12]. As an element for metal organic complex, the metal ion is very important because the resultant functionality might be determined not only the organic ligands but also the inorganic metal ions [11]. Accordingly, the selection of metal ions for MOFs is vital. As we know copper is a very attractive framework candidate to construct functional materials because of its capability to coordinate with unsaturated N-, O- atoms. So far, a great number of MOFs containing copper atoms and carboxylate group have been prepared, however, most of which display single property, either optical or magnetic property alone [11-14], so it is still a challenge to construct metal complexes with multi-functionality, e.g., magnetic and optical properties [15]. An attractive approach to obtain multi-functional materials might be design multifunctional organic ligand as building block. In this communication, a multal-property ligand, 4-(imidazol-1-yl) benzoic acid (HL) was selected, which contains an imidazole group and carboxylic acid group. The target product  $[\text{Cu}_5(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_4$

$(\text{N}_3)_2(\text{SO}_4)_2]_n$  was successfully obtained with the expected MOF and the desired luminescent and magnetic properties. Here we report its preparation, single crystal structure, thermal stability, luminescent and magnetic properties.

The complex **1** was obtained as green single crystals by the reaction of HL and copper sulfate in the presence of sodium azide *via* a hydrothermal process and a little powder product was obtained at the same time. The powder XRD experimental and computer-simulated patterns from the single crystal data using Mercury 1.4 software are shown in Fig. (1). The similarity of the powder XRD patterns indicates that the bulk synthesized materials and the as-grown crystals are homogeneous.

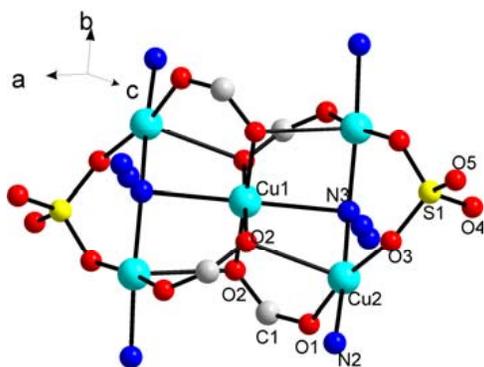


**Fig. (1).** The X-ray powder diffraction (XRD) pattern of **1**. (Upper--- experimental and Under--- computer-simulated).

The crystal structure of complex **1** is studied by single-crystal X-ray diffraction, and result reveals a 3D framework that crystallizes in the monoclinic space group  $C2/m$  (see supporting information). As shown in Fig. (2) the unit

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contains five Cu (II) ions, two azide anions, four imidazolyl-benzoic acid groups and two sulfate anions, where two kinds of Cu (II) ions with different coordination environments were observed. The Cu1 is coordinated with four oxygen atoms of carboxyl groups, forming an oblong geometry with the *cis*-O-Cu-O angles from 86.02(5) ° to 93.98(5) °. While the Cu2 resides in a distorted tetragonal pyramid environment with apex occupied by one benzoic oxygen atom. The base surface is formed by two oxygen atoms are offered by sulfate ion and carboxylate group, and the two nitrogen atoms are belonged to azide ion and imidazolyl, respectively. The two adjacent Cu2 are bridged by one azide anion with  $\mu$ -1,1 model (end-on model, EO model), while the distances and the angle as following: Cu2-N3 1.983(1) Å, Cu2-N3-Cu2 133.07(7) °, respectively. The two Cu2 are also linked with Cu1 by carboxylic oxygen (O2), and a triangle is formed by the metal atoms. The two metal triangles connect to each other with a vertex to give rise to a bow-tie type  $\text{Cu}_5(\text{N}_3)_2$  unit is symmetrically joined to adjacent cluster units by the bridge: imidazol-carboxylate group, the closest inerunit Cu...Cu separation is 11.876(12) Å linked by it.

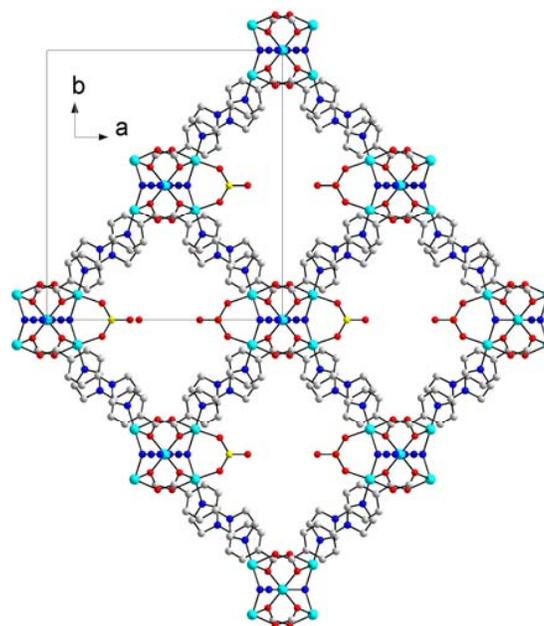


**Fig. (2).** Molecular structure and atom numbering of complex **1** (All hydrogen atoms are omitted for clarity).

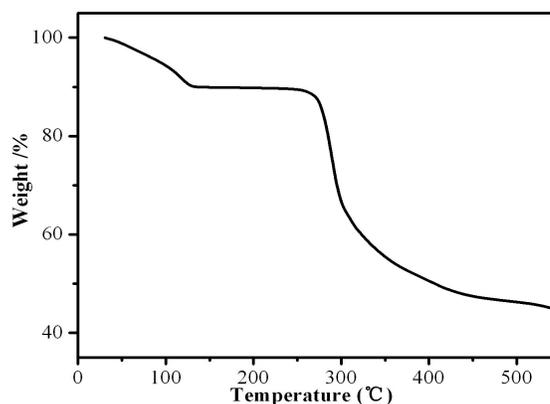
The units are further extended to a 3D porous framework through the imidazol-carboxylate spacer. Every HL is connected with four copper atoms from different units, and there are two HL between every two units, and the two bridge groups are paralleled in alternate directions. The unique feature of **1** focuses on the (*ab*) plane (Fig. (3)). It is shown that the network packs as a rhombus with the units occupied the crank points and grouped by the imidazol-carboxylate. The distance between the two central coppers is 14.12 (1) Å and the angles of the rhombus are 88.3° and 91.7°, respectively. The distances between the diagonal entry are 19.669(3) Å and 20.263(27) Å, but the difference of the apertures is obvious: the longer one is 19.669(3) Å, the shorter is 13.449(11) Å which is shortened by the sulfate anions.

To obtain the thermal stability information of **1**, the complex was heated in air with 10°C/min, and the thermogravimetric analysis (TGA) is shown in Fig. (4). The initial weight loss corresponds to the removal of water from the crystals. Then the framework remains thermally stable up to 270 °C, and then a dramatic weight loss occurs, which indicates the decomposition of  $[\text{Cu}_5(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_4(\text{N}_3)_2$

$(\text{SO}_4)_2]_n$  accompanying with gas phase formation begins at the temperature.

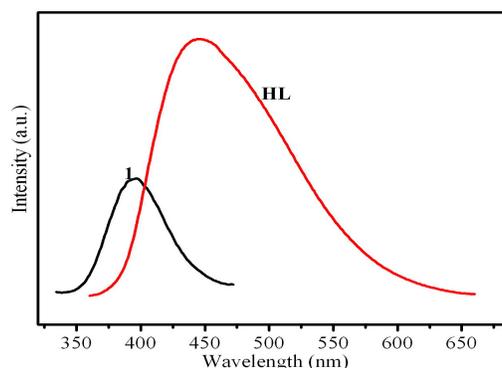


**Fig. (3).** The feature of complex **1** in the (*a b*) plane (All hydrogen atoms are omitted for clarity).



**Fig. (4).** The TG plot of complex **1**.

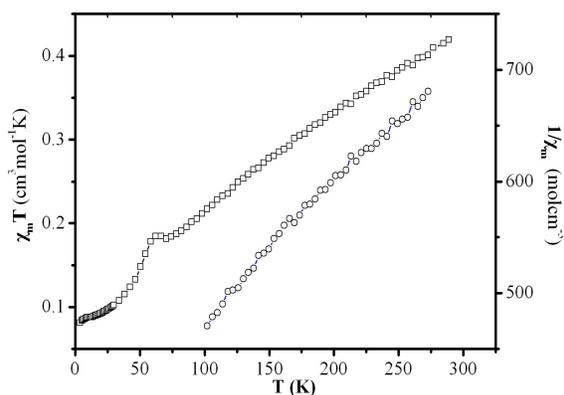
The emission spectra of complex **1** and the ligand are given in Fig. (5). The complex shows an intense blue fluorescence emission band centering at 396 nm, which might be due to the intraligand  $\pi$ - $\pi^*$  transitions, LMCT (ligand-to-metal-charge transfer) or MLCT (metal-to-ligand



**Fig. (5).** The emission spectra of complex **1** and the ligand.

charge transfer). Compared with that (444 nm) of pure ligand, the band is blue-shifted by 48 nm with the obvious decrease of luminescent intensity, which reveals that the rigidity of the ligand is inflected by the metal atoms. An explanation has been given in our previous paper [15].

On particular interest is the capacity of bridging mode of azide to mediate magnetic interactions between the Cu ions bound to it. Thus, variable-temperature magnetic susceptibility measurement was carried out on a crystalline sample of the bridged complex from 4 to 300 K within a constant magnetic field of 100 Oe, the results are represented in Fig. (6), in the form of  $\chi_M T$  and  $1/\chi_M$  versus  $T$  plots. The value of  $\chi_M T$  per Cu(II) at 300 K is  $0.39 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , slightly greater than isolated Cu(II) ion ( $0.38 \text{ cm}^3 \text{ K mol}^{-1}$  and  $S=1/2$ ). They are almost equal. The  $\chi_M T$  value then starts to decrease dramatically with an increasingly pronounced slope, down to  $0.16 \text{ cm}^3 \text{ K mol}^{-1}$  at 70 K. This shows that the system is dominated by antiferromagnetic interactions between the metal ions. Furthermore, the susceptibility data are fitted with modified Curie-Weiss law, with Curie constant  $C = 0.88 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and Weiss constant  $\theta = -320.2 \text{ K}$ . The negative value of Weiss constant  $\theta$  further indicates the intensive antiferromagnetic interactions between  $\text{Cu}^{2+}$  ions. However, the value of  $\chi_M T$  increases slightly around 60 K indicating a very weak ferromagnetic state due to spin canting of the antiferromagnetically coupled Cu(II) ions [16]. The antiferromagnetic behavior between copper atoms has been predicted in the EO series as soon as the Cu-N-Cu valence angle is sufficiently large ( $>104^\circ$ ) [17], which has also been experimentally confirmed [18], and the antiferromagnetic interactions between metal atoms are also observed in our previous work [15]. Accordingly, the bridging action strengthens the antiferromagnetic interactions between the metal atoms. At the same time, the organic group is distorted to connect the Cu5 units in the complex, which reduces the rigidity of the ligand, and thus give rise to the blue-shift of photoluminescence.



**Fig. (6).** Plots of both the magnetic susceptibility  $\chi_M T$  ( $\square$ ) and  $1/\chi_M$  ( $\circ$ ) versus temperature (K) of **1**.

In brief, a magneto-optical complex is successfully prepared *via* a hydrothermal method. The single-crystal X-ray diffraction indicates the complex is a 3D framework. The magnetic measurement reveals there are antiferromagnetic interactions between the metal atoms are bridged by azide

and imidozal-carboxylate, and the fluorescent measurement indicates the complex emits blue fluorescence at 396 nm. Therefore, it is a feasible method to obtain multi-functional materials by select multi-proprieted organic ligand as building blocks.

## ACKNOWLEDGEMENT

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