

## 二维网状铜(II)配合物的合成及晶体结构表征

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### Synthesis and Crystal Structure of Cu(II) Complex with Two-dimensional Network Structure

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**Abstract:** A Cu(II) complex  $[\text{Cu}(\text{L})_{1.5}(\text{OSO}_3)] \cdot 3\text{H}_2\text{O}$  (1) [ $\text{L}=1,4\text{-bis}(\text{imidazol-1-yl})\text{benzene}$ ] was synthesized by reaction of ligand L with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  using solvothermal method and its structure was determined by X-ray crystal structure analysis. The structure indicates that the complex crystallizes in triclinic, space group  $P\bar{1}$  with  $a=0.948\ 8$  (2),  $b=1.078\ 5$  (2),  $c=1.108\ 4$  (2) nm,  $\alpha=74.820$  (2),  $\beta=81.331$  (2),  $\gamma=72.638$  (2)°,  $V=1.041\ 5$  (3) nm<sup>3</sup>,  $Z=2$ ,  $D_{\text{calc}}=1.687\ \text{g} \cdot \text{cm}^{-3}$ ,  $F(000)=544$ ,  $\mu=1.205\ \text{cm}^{-1}$ , the final  $R=0.062\ 3$  and  $wR=0.132\ 8$ . The Cu(II) atom has distorted square-pyramidal environment with a  $\text{N}_3\text{O}_2$  donor set. Each L ligand links two Cu(II) atoms using its imidazole groups to form an infinite one-dimensional (1D) ladder-like chain, which further linked by  $\text{SO}_4^{2-}$  to form a two-dimensional (2D) network structure. The 2D sheets are further connected by C—H $\cdots$ O hydrogen bonds to give a three-dimensional (3D) structure. CCDC: 650388.

**Key words:** crystal structure; Cu(II) complex; synthesis

In recent years, coordination polymers obtained by reaction of multidentate organic ligands with metal salts have drawn great interests due to their novel structures, fascinating properties and potential applications<sup>[1-4]</sup>. It is known that the structures of metal organic frameworks (MOFs) are influenced by factors such as geometric requirement of metal ions, solvent system, template, counterions, and the flexibility of ligands. Many MOFs with intriguing structures have

been obtained by using bidentate ligands with two imidazole groups separated by different spacers as building block, such as 1,2-bis(imidazol-1-yl)ethane<sup>[5]</sup>, 1,1-(1,4-butanediyl)bis(imidazole)<sup>[6]</sup>. We have previously reported a Ag(I) complex with 1,5-bis(imidazol-1-yl)pentane, which has great flexibility<sup>[7]</sup>. As a part of our systematic studies on the influence of the flexibility of ligands, here, we report a Cu(II) complex with a rigidity bidentate ligand 1,4-bis(imidazol-1-yl)benzene (L) with

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rigid spacer between the two imidazole groups.

## 1 Experimental

### 1.1 General

All commercially available chemicals are of reagent grade and used as received without further purification. Solvents were purified according to the standard methods. C, H and N analyses were made on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University.

### 1.2 Synthesis of $[\text{Cu}(\text{L})_{1.5}(\text{OSO}_3)] \cdot 3\text{H}_2\text{O}$ (**1**)

An aqueous methanol solution (12 mL) of **L** (10.5 mg, 0.05 mmol),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (12.5 mg, 0.05 mmol) was sealed into a stainless steel vessel and placed in an oven at 110 °C for 3 days. After cooling to room temperature, blue crystals suitable for X-ray diffraction structural analysis were obtained. Yield: 20%. Calcd. (%) for  $\text{C}_{18}\text{H}_{21}\text{CuN}_6\text{O}_7\text{S}$ : C, 40.83; H, 3.97; N, 15.88; found (%): C, 40.89; H, 4.01; N, 16.01.

### 1.3 Structure determination

A single crystal with dimensions of 0.18 mm × 0.17 mm × 0.09 mm was selected for the experiment. The data collection was carried out on a Bruker SMART CCD at 293 K, using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.071\,07\text{ nm}$ ). The structure was solved by direct method and expanded using difference Fourier synthesis technique<sup>[8]</sup>. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on  $F^2$ <sup>[9]</sup>. The hydrogen atoms except for those of water molecules were generated geometrically. The hydrogen atoms of two of three uncoordinated water molecules were located in a difference Fourier map. Calculations were performed with the Siemens SHELXTL program package<sup>[8-10]</sup>. The crystal parameters, data collection and refinement results for the compound are listed in Table 1. The selected bond lengths and bond angles are listed in Table 2. CCDC: 650388.

Table 1 Crystallographic Data for Complex **1**

Empirical formula	$\text{C}_{18}\text{H}_{21}\text{CuN}_6\text{O}_7\text{S}$	$V / \text{nm}^3$	1.041 5(3)
Formula weight	529.01	$Z$	2
Temperature / K	293	$D_{\text{calc}} / (\text{g} \cdot \text{cm}^{-3})$	1.687
Crystal system	Triclinic	Absorption coefficient / $\text{cm}^{-1}$	1.205
Space group	$P\bar{1}$	$F(000)$	544
$a / \text{nm}$	0.948 8(2)	$\theta$ range / (°)	1.91~25.00
$b / \text{nm}$	1.078 5(2)	Reflections collected	5 242
$c / \text{nm}$	1.108 4(2)	Independent reflections	3 623
$\alpha / (^\circ)$	74.820(2)	Goodness of-fit on $F^2$	1.036
$\beta / (^\circ)$	81.331(2)	$R [I > 2\sigma(I)]$	0.062 3
$\gamma / (^\circ)$	72.638(2)	$wR [I > 2\sigma(I)]$	0.132 8

Table 2 Selected Bond Lengths (nm) and Bond Angles (°) for Complex **1**

Cu1-N1	0.197 7(4)	Cu1-N3	0.202 8(4)	Cu1-N5	0.199 0(4)
Cu1-O3	0.200 0(3)	Cu1-O3#1	0.233 8(4)		
N1-Cu1-N5	172.09(17)	N1-Cu1-O3	90.00(15)	N5-Cu1-O3	90.08(15)
N1-Cu1-N3	93.04(17)	N5-Cu1-N3	86.98(17)	O3-Cu1-N3	176.92(16)
N1-Cu1-O3#1	92.42(15)	N5-Cu1-O3#1	95.29(15)	O3-Cu1-O3#1	76.97(14)
N3-Cu1-O3#1	102.40(16)				

Symmetry transformation used to generate equivalent atoms: #1 1-x, 2-y, 1-z.

## 2 Results and discussion

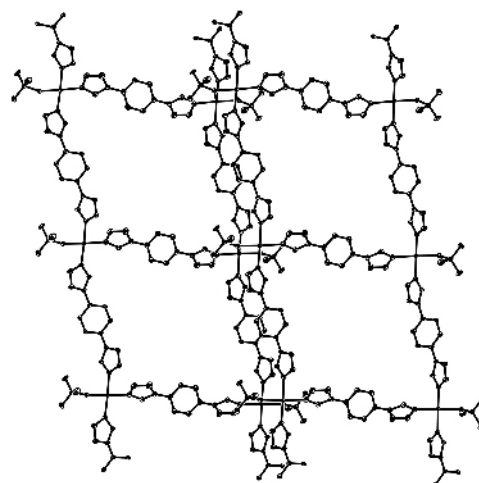
### 2.1 Structure description

The crystal structure of complex **1** is shown in Fig.

1. The asymmetric unit of complex **1** contains one copper(II) atom, one and a half **L** ligands, one sulfate ion and three lattice water molecules. The copper(II) atom has a slightly distorted square-pyramidal environment

with a  $\text{N}_3\text{O}_2$  donor set. The three nitrogen atoms are from the imidazole groups of three different L ligands with the Cu-N bond lengths in the range of 0.197 7(4) ~ 0.202 8(4) nm. The additional two sites are completed by two oxygen atoms from two sulfate ions which connect another copper(II) atom to form  $\text{M}_2(\text{OSO}_3)_2$  with the Cu-O bond lengths of 0.200 0(3) and 0.233 8(4) nm, respectively. The Cu-O distance is similar to that observed in complex  $[\text{Cu}_4(\text{TPPNOL})_2(\text{SO}_4)_2](\text{ClO}_4)_2$  (TPPNOL = *N, N, N*-tris-(2-pyridylmethyl)-1, 3-diaminopropan-2-ol and the Cu-O distance are 0.194 7(2) and 0.235 7(2) nm)<sup>[10]</sup>. The Cu-O-Cu bond angle is 103.0° and the Cu...Cu distance is 0.340 nm. The copper(II) lies 0.006 nm out from the N1-N3-N5-O3 plane toward the O3A atom. Each L ligand links two copper(II) atoms to form an infinite non-interpenetrated ladder-like chain, and the  $\text{SO}_4^{2-}$  anions link the adjacent ladders to form a 2D network structure (Fig.2). There are face-to-face interactions between the imidazole rings of adjacent molecular ladders since the two imidazole ring planes are strictly parallel each other with a centroid-to-centroid distance of 0.363 nm. In addition, the 2D sheets are further linked by one of the lattice water molecule and  $\text{SO}_4^{2-}$  anions to generate 3D framework through the C-H...O hydrogen bonds as exhibited in Fig.3. The hydrogen bonding data are summarized in Table 3. The result indicates that the hydrogen bonds play important role in stabilizing the whole structure of

complex **1**.



Hydrogen atoms and solvent molecules are omitted for clarity

Fig.2 2D network structure of complex **1**

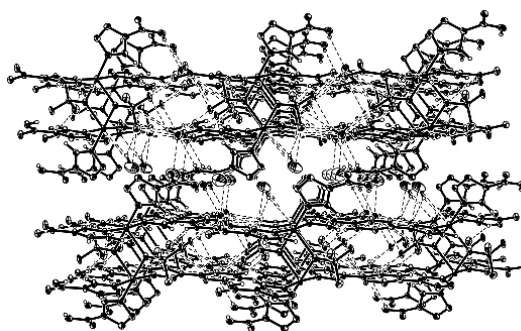


Fig.3 Crystal packing diagram of complex **1** with hydrogen bonds indicated by dashed lines

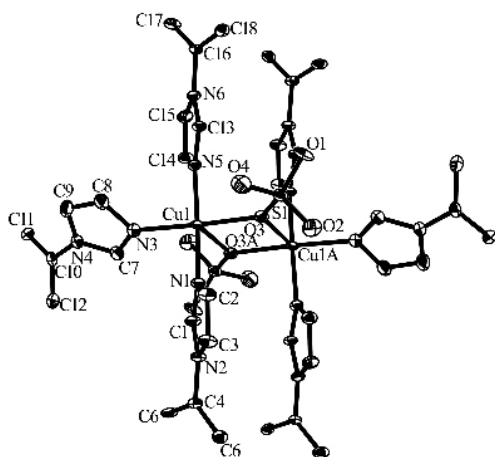
Table 3 Hydrogen Bonding Data for Complex **1**

D-H...A	Distance of D...A / nm	Angle of D-H-A / (°)
O5-H5C...O1	0.278 4(6)	162
O6-H6B...O4	0.273 6(11)	127
C1-H1A...O1#1	0.319 2(7)	158
O5-H5B...O4#2	0.284 6(6)	165
C6-H6A...O2#3	0.311 0(7)	155
C7-H7A...O1#1	0.334 6(7)	154
C12-H12A...O5#1	0.319 9(8)	134
C14-H14A...O2#1	0.324 6(7)	155
C15-H15A...O2#4	0.314 7(7)	157

Symmetry transformation used to generate equivalent atoms: #1 1-x, 2-y, 1-z; #2 1-x, 2-y, -z; #3 -x, 2-y, 1-z; #4 1+x, y, z.

## 2.2 Luminescent Properties

The luminescent properties of L and complex **1** in the solid state were measured at ambient temperature. The emission with a maximum at 406 nm was observed for the free ligand under the excitation



Hydrogen atoms and solvent molecules are omitted for clarity.

Symmetry code: #1 1-x, 2-y, 1-z.

Fig.1 Structure of complex **1** with ellipsoids at 30% probability

wavelength of 356 nm, while no clear photoluminescence was observed for complex **1**. The copper ions quench the fluorescence of the ligand. This result indicates that the photoluminescence properties of the metal-organic complexes depend on the nature of the organic ligand as well as the metal ions.

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