

## Synthesis and Crystal Structure of a New Copper Complex: [Cu(Phen)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>]

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A novel copper complex [Cu(Phen)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>] was synthesized and characterized by IR spectra and single-crystal X-ray analysis. The crystal structure analysis shows that the Cu(II) has five coordinates in square-pyramid geometry. The complex forms bimolecular chains through hydrogen bonding interactions. In addition, an intermolecular  $\pi$ - $\pi$  interaction is observed between the two parallel 1,10-phenanthroline rings of the neighboring molecules. The crystal is monoclinic and has space group C2/c with the following unit cell parameters:  $a = 14.9269(15)$  Å,  $b = 13.8821(13)$  Å,  $c = 7.0490(8)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 108.6190(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1384.2(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $M_r = 375.84$ ,  $D_c = 1.803$  Mg/cm<sup>3</sup>,  $\mu = 1.760$  mm<sup>-1</sup>,  $F(000) = 764$ ,  $T = 298(2)$  K,  $R = 0.0358$ ,  $wR = 0.0875$  for 1220 reflections with  $I > 2\sigma(I)$ .

**Key Words:** Copper(II) complex, Crystal structure,  $\pi$ - $\pi$  Interaction.

### INTRODUCTION

Copper complexes are used for a wide range of applications and it is important to continue making new copper-containing complexes to study their biological activity, pharmaceutical application and catalytic chemistry<sup>1-6</sup>. The copper complexes can have different number of coordinates, generally from 2 to 6 and a variety of structures. Bhat *et al.*<sup>7</sup> synthesized copper(II) complexes from 2-naphthylimidazol-phenanthroline and acetyl acetone for fluorescent labeling. Tschulik *et al.*<sup>8</sup> synthesized a 3D complex of copper and found that it has interesting magnetic property. Moreover, the relationship of magnetic property with the structure was discussed. Similarly, Reger's group<sup>9</sup> also carried out study of the magnetic properties of the copper complexes. Complexes of copper and phenanthroline interact and degrade macromolecules like DNA<sup>10</sup>. Mixed complexes of copper phenanthroline and other biological ligands were investigated to understand the biological roles of copper in organisms<sup>11</sup>. Herein, we report a mononuclear complex in the formula of [Cu(phen)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>] and discuss the structure of the complex and the central metal ion coordination environment.

### EXPERIMENTAL

All reagents were of AR grade and used without further purification. Infrared spectra (4000-400 cm<sup>-1</sup>) were recorded with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks.

**Synthesis:** To a stirred solution of 1,10-phenanthroline (2 mmol) in 10 mL ethanol and water (1:1), the solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (1.0 mmol) in sodium acetate (10 mL) was added. The reaction was stirred at a PTFE lined autoclave, placed in an oven and the reaction proceeded at 150 °C for 72 h. The blue transparent quadrilateral type columnar crystals were obtained (yield: 50 %). IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3423 (w), 1423 (m), 1107 (s), 619 (m).

**Crystal structure determination:** A single crystal of compound with dimensions of 0.46 × 0.19 × 0.11 mm was selected for crystallographic data collection at 298(2) K and structure determination on a Siemens SMART CPB area-detector diffractometer with graphite-monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). A total of 3440 reflections were collected in the range of  $2.06^\circ \leq \theta \leq 25.02^\circ$ , of which 1220 reflections were unique with  $R_{\text{int}} = 0.0574$ . Lp effects and empirical absorption were applied in data corrections. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 102 variable parameters for 1220 reflections with  $I > 2\sigma(I)$  and converged with unweighted and weighted agreement factors of

$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} = 0.0358 \quad (1)$$

and

$$wR_2 = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right\}^{1/2} = 0.0875 \quad (2)$$

where  $w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.0000P]$  and  $P = (F_o^2 + 2F_c^2)/3$ .

The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.537 and -0.491 e/Å<sup>3</sup> (CCDC No. 908706), respectively.

## RESULTS AND DISCUSSION

The structure of the title compound consists of [Cu(phen)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cations and SO<sub>4</sub><sup>2-</sup> anions. An ORTEP drawing of the structure around the copper(II) with the atom numbering is shown in Fig. 1. Selected bond lengths, bond angles and hydrogen bond distances are presented in Tables 1 and 2.

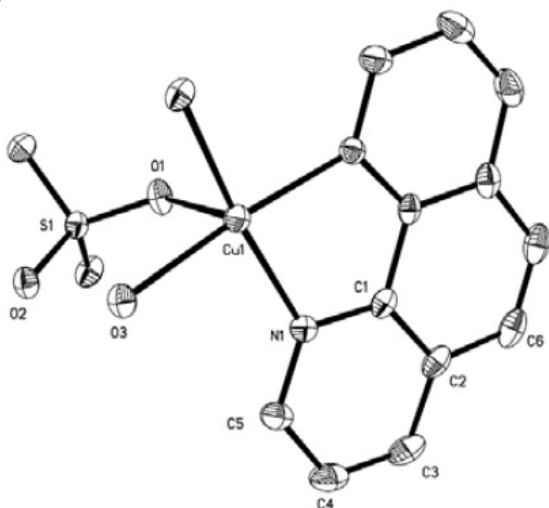


Fig. 1. Molecular structure of the title compound

TABLE-1  
SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Cu(1)-O(3) # 1	1.9749(19)	O(3)-Cu(1)-N(1)#1	173.86(9)
Cu(1)-O(3)	1.9749(19)	N(1)-Cu(1)-N(1)#1	82.01(14)
Cu(1)-N(1)	2.012(2)	O(3)#1-Cu(1)-O(1)	92.91(8)
Cu(1)-N(1)#1	2.012(2)	O(3)-Cu(1)-O(1)	85.85(8)
Cu(1)-O(1)	2.481(2)	N(1)-Cu(1)-O(1)	88.86(9)
O(3)#1-Cu(1)-O(3)	93.96(12)	N(1)#1-Cu(1)-O(1)	92.50(9)
O(3)#1-Cu(1)-N(1)	173.86(9)	Cu(1)-O(3)-H(3C)	101.6
O(3)-Cu(1)-N(1)	92.03(9)	Cu(1)-O(3)-H(3D)	117.5
O(3)#1-Cu(1) N(1) #1	92.03(9)		

#1 -x+1, y, -z+3/2

TABLE-2  
HYDROGEN BOND DISTANCES (Å) AND ANGLES (°)

D-H	D(D-H)	D(H..A)	<DHA	D(D..A)	A
O3-H3C	0.850	1.766	175.02	2.614	O2
O3-H3C	0.850	2.561	118.30	3.057	O1
O3-H3C	0.850	2.668	150.52	3.433	S1
O3-H3D	0.850	1.839	175.19	2.687	O2 [X, -Y, Z+1/2]
O3-H3D	0.850	2.908	150.07	3.670	S1 [-X+1, -Y, -Z+1]

In the complex each Cu(II) ion is coordinated by two nitrogen atoms of phenanthroline ligand and one oxygen atoms of sulfate ion as well as two coordinated water molecules. The coordination geometry of the complex is square-pyramid ( $\tau = 0$ ). Additionally, two nitrogen atoms of phenanthroline ligand and two coordinated water molecules are obviously coplanar (360°). The length of the bond between the copper atom with nitrogen (1,1#) and three oxygen (1,3,3#) atom are as follows: Cu(1)-N(1), 2.012(2); Cu(1)-N(1)#1, 2.012(2), Cu(1)-O(1),

2.481(2); Cu(1)-O(3), 1.9749(19); Cu(1)-O(3)#1, 1.9749(19). The bond angle of O(3)#1-Cu(1)-O(3) is 93.96(12)°, O(3)#1-Cu(1)-N(1) is 173.86(9)°, O(3)-Cu(1)-N(1) is 92.03(9)°, O(3)#1-Cu(1)-N(1)#1 is 92.03(9)°, O(3)-Cu(1)-N(1)#1 is 173.86(9)° and N(1)-Cu(1)-N(1)#1 is 82.01(14)°.

In crystal packing (Fig. 2), it is interesting to observe that significant  $\pi$ - $\pi$  stacking interactions between the phen ligands are formed between adjacent molecules resulting in a molecular framework. Different from the N-donor bridging species, phen is a bidentate chelating reagent that not only acts as a terminal ligand but also potentially provides molecular interaction such as aromatic stacking to form interesting structures.

In addition, Fig. 2 also shows that O-H...O and O-H...O intermolecular hydrogen bonds are formed between adjacent molecules, resulting in a framework.

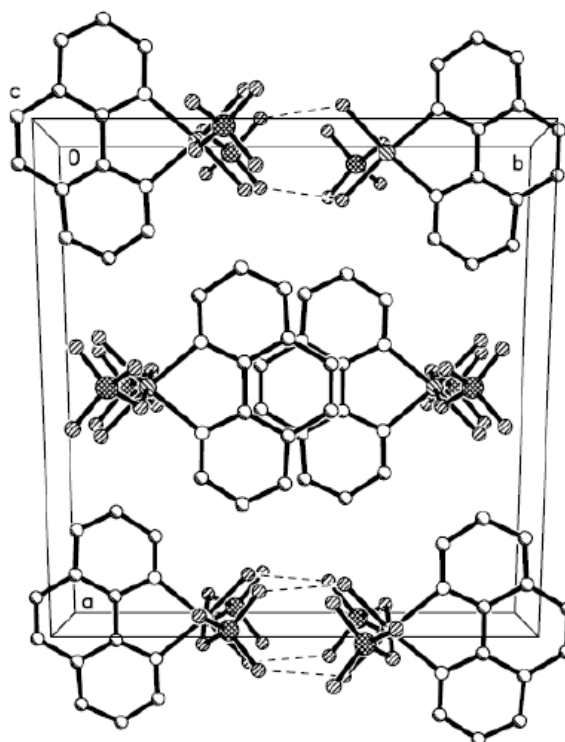


Fig. 2. View of a framework of the title complex showing the intermolecular hydrogen bonding and  $\pi$ - $\pi$  stacking

Bimolecular chains are formed through  $\pi$ - $\pi$  stacking and hydrogen bonding interactions. Three dimensional networks are formed with bimolecular chains through hydrogen bonding interactions.

## Conclusion

A novel copper(II) complex [Cu(Phen)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>] was synthesized and its crystal structure was characterized by IR and X-ray diffraction analysis. Cu(II) had five coordinates in square-pyramid geometry and the complex formed bimolecular chains through hydrogen bonding interactions.

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