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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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## The Construction of a Novel Bromido- and Azido-Bridged Dinuclear Copper(II) Complex Derived From 4-Chloro-2-[(2-hydroxyethylimino)methyl]phenol

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## The Construction of a Novel Bromido- and Azido-Bridged Dinuclear Copper(II) Complex Derived From 4-Chloro-2-[(2-hydroxyethylimino)methyl]phenol

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A novel bromido- and azido-bridged dinuclear copper(II) complex,  $[Cu_2Br_2L_2] \cdot [Cu_2Br(N_3)L_2] \cdot H_2O$ , where L is the deprotonated form of the Schiff base 4-chloro-2-[(2hydroxyethylimino)methyl]phenol, has been prepared and structurally characterized by elemental analysis, IR spectra, and single crystal X-ray crystallography. Each Cu atom in the complex is coordinated by three donor atoms of Schiff base ligand and by two bridging atoms, forming a square pyramidal geometry. The bromide and azide ligands are preferred bridging groups for the construction of dinuclear copper complexes with Schiff bases.

Keywords copper complex, crystal structure, dinuclear complex, Schiff base

#### INTRODUCTION

Dinuclear complexes with bridging groups are currently attracting much attention for their interesting structures and wide applications.<sup>[1-3]</sup> The Schiff bases derived from salicylaldehyde and its derivatives are a kind of versatile ligands in coordination chemistry. The rational design and construction of dinuclear complexes with Schiff bases are of particular interest in coordination and structural chemistry. As is well known, the halide and pseudohalide groups can link two or more metal atoms, yielding various polynuclear complexes.<sup>[4-9]</sup> To our knowledge, there are no bromido-bridged dinuclear copper complexes with Schiff bases derived from salicylaldehyde and its derivatives have been reported so far. In this study, a novel dinuclear Schiff base copper(II) complex with bromide and azide bridges,  $[Cu_2Br_2L_2] \cdot [Cu_2Br(N_3)L_2] \cdot H_2O$ , where L is the deprotonated form of the Schiff base 4-chloro-2-[(2hydroxyethylimino)methyl]phenol (HL; Scheme 1), was successfully prepared and characterized.



SCH. 1. The Schiff base HL.

#### **EXPERIMENTAL**

#### **General Methods and Materials**

Starting materials, reagents and solvents with AR grade were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer (Nanjing University, China). The IR spectra were recorded on a Jasco FT/IR-4000 spectrometer (Liaoning Normal University, China) as KBr pellets in the 4000–200 cm<sup>-1</sup> region. Single crystal structural X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer (Shandong University of Technology, China).

Caution: Sodium azide is potentially explosive, only small quantity should be used and handled with great care.

#### Synthesis of the Schiff Base

To the methanolic solution (30 mL) of the 5-chlorosalicy laldehyde (1.0 mmol, 0.16 g) was added a methanolic solution (20 mL) of 2-aminoethanol (1.0 mmol, 0.06 g) with stirring. The mixture was stirred for 30 min at room temperature to give yellow solution. The solvent was evaporated to give yellow powder, which was washed with cold methanol and dried in air. Yield 83%. Characteristic IR data: 1637 cm<sup>-1</sup>. Anal. Calcd. for C<sub>9</sub>H<sub>10</sub>ClNO<sub>2</sub> (%): C, 54.2; H, 5.0; N, 7.0. Found (%): C, 54.0; H, 5.1; N, 7.1.

#### Synthesis of the Complex

To the methanolic solution (5 mL) of HL (0.1 mmol, 0.020 g) was added a methanolic solution (5 mL) of CuBr<sub>2</sub> (0.1 mmol, 0.022 g) and an aqueous solution (1 mL) of NaN<sub>3</sub> (0.1 mmol, 0.006 g) with stirring. The mixture was stirred for 10 min at room temperature, and then transferred to a stainless steel bomb,

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Crystal data for the complex		Selected bond lengths (Å) and angles (°)		
Formula	C <sub>36</sub> H <sub>38</sub> Br <sub>3</sub> Cl <sub>4</sub> Cu <sub>4</sub> N <sub>7</sub> O <sub>9</sub>	Cu(1)-O(1)	1.914(7)	Cu(1)-O(2)
Mr	1348.4	Cu(1)-N(1)	1.938(9)	Cu(1)-N(5)
<i>T</i> (K)	298(2)	Cu(1)-Br(1)	2.766(2)	Cu(2)-O(3)
Crystal shape/color	Block/blue	Cu(2)-O(4)	2.015(6)	Cu(2)-N(2)
Crystal size (mm <sup>3</sup> )	$0.30 \times 0.27 \times 0.27$	Cu(2)-N(5)	2.005(8)	Cu(2)-Br(1)
Crystal system	Monoclinic	Cu(3)-O(5)	1.905(7)	Cu(3)-O(6)
Space group	$P2_1/n$	Cu(3)-N(3)	1.933(9)	Cu(3)-Br(2)
<i>a</i> (Å)	17.267(3)	Cu(3)-Br3	2.432(2)	Cu(4)-N(4)
$b(\dot{A})$	13.119(3)	Cu(4)-O(7)	1.910(7)	Cu(4)-O(8)
c (Å)	20.549(3)	Cu(4)-Br(2)	2.384(2)	
$\beta$ (°)	91.746(2)	O(1)-Cu(1)-N(1)	92.7(4)	O(1)-Cu(1)-O(2)
$V(Å^3)$	4652.7(15)	N(1)-Cu(1)-O(2)	83.0(4)	O(1)-Cu(1)-N(5)
Z	4	N(1)-Cu(1)-N(5)	168.0(4)	O(2)-Cu(1)-N(5)
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.925	O(1)- $Cu(1)$ - $Br(1)$	93.4(2)	N(1)-Cu(1)-Br(1)
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	4.668	O(2)-Cu(1)-Br(1)	94.9(2)	N(5)-Cu(1)-Br(1)
<i>F</i> (000)	2656	O(3)-Cu(2)-N(2)	95.0(3)	O(3)-Cu(2)-N(5)
Independent reflections	9933	N(2)-Cu(2)-N(5)	167.1(3)	O(3)-Cu(2)-O(4)
Observed reflections $(I > 2\sigma(I))$	4177	N(2)-Cu(2)-O(4)	81.8(3)	N(5)-Cu(2)-O(4)
Min. and max. transmission	0.335 and 0.365	O(3)-Cu(2)-Br(1)	100.1(2)	N(2)-Cu(2)-Br(1)
Parameters	574	N(5)-Cu(2)-Br(1)	88.4(2)	O(4)-Cu(2)-Br(1)
Restraints	9	O(5)-Cu(3)-N(3)	93.7(3)	O(5)-Cu(3)-O(6)
Goodness-of-fit on $F^2$	0.964	N(3)-Cu(3)-O(6)	82.1(3)	O(5)-Cu(3)-Br(3)
$R_1, wR_2 [I \ge 2\sigma(I)]^a$	0.0695, 0.1692	N(3)-Cu(3)-Br(3)	169.9(3)	O(6)-Cu(3)-Br(3)
$R_1, wR_2$ (all data) <sup>a</sup>	0.1879, 0.2339	O(5)-Cu(3)-Br(2)	96.9(2)	N(3)-Cu(3)-Br(2)
		O(6)-Cu(3)-Br(2)	88.8(2)	Br(3)-Cu(3)-Br(2)
${}^{a}R_{1} = F_{o} - F_{c}/F_{o}, wR_{2} = \left[\sum w(F_{o}^{2} - Fc^{2})/\sum w(F_{o}^{2})^{2}\right]^{1/2}.$		O(7)-Cu(4)-N(4)	94.3(3)	O(7)-Cu(4)-O(8)

TABLE 1

TABLE 2

2.000(7)2.003(8)1.898(7)1.918(8) 2.801(2)2.012(7)2.905(2)1.959(9) 2.005(7)

which was sealed, heated at 150°C for 12 h, and cooled gradually to room temperature. Blue block-shaped crystals of the complex, suitable for X-ray crystal structural determination, were formed at the bottom of the bomb. The crystals were isolated by filtration, washed three times with methanol, and dried in air. Yield 35%. Characteristic IR data (cm<sup>-1</sup>): 2089 (s), 1645 (s), 1178 (m). Anal. Calcd. for C<sub>36</sub>H<sub>38</sub>Br<sub>3</sub>Cl<sub>4</sub>Cu<sub>4</sub>N<sub>7</sub>O<sub>9</sub> (%): C, 32.1; H, 2.8; N, 7.3. Found (%): C, 30.9; H, 3.0; N, 7.1.

#### X-Ray Crystallography

Diffraction intensities for the complex were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector diffractometer (Shandong University Technology, China) with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The collected data were reduced with the SAINT program,<sup>[10]</sup> and multiscan absorption correction was performed using the SADABS program.<sup>[11]</sup> The structure was solved by direct methods, and refined against  $F^2$ by full-matrix least-squares method using the SHELXTL package.<sup>[12]</sup> All of the non-hydrogen atoms were refined anisotropically. The water H atoms in the complex were located from a difference Fourier map and refined isotropically, with O-H and H…H distances restrained to 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized

171.3(3)90.0(3) 92.8(3) 102.1(3)89.4(2)94.0(3) 169.2(3)87.7(3) 99.1(2) 90.6(2) 173.0(3)90.1(2)93.1(2) 91.1(3) 97.8(1) ) 173.0(3)O(7)-Cu(4)-N(4)O(7)-Cu(4)-O(8)94.3(3)N(4)-Cu(4)-O(8)O(7)-Cu(4)-Br(2)92.8(2) 81.6(3) O(8)-Cu(4)-Br(2) N(4)-Cu(4)-Br(2)156.0(3)93.2(2)

in Table 1. Selected bond lengths and angles are given in Table 2.

#### **RESULTS AND DISCUSSION**

#### Chemistry

The Schiff base HL was synthesized by the reaction of equimolar quantities of 5-chlorosalicylaldehyde with 2aminoethanol in methanol. The air-stable yellow product of the Schiff base is soluble in DMSO, DMF, methanol, ethanol, acetonitrile, and chloroform, and insoluble in water. The elemental analyses are in good agreement with the chemical formula proposed for the compound. The complex was synthesized by the reaction of the Schiff base with CuBr<sub>2</sub> and sodium azide in methanol at solvothermal condition.

#### Structure Description of the Complex

The molecular structure of the complex is shown in Figure 1. The asymmetric unit of the complex contains a doubly bromido-bridged dinuclear copper(II) complex molecule, a mixed bromido and azido-bridged dinuclear copper(II) complex molecule, and a water molecule of crystallization. The



FIG. 1. A perspective view of the molecular structure of the complex with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.

intramolecular Cu...Cu distances in the complex are 3.245(1) and 3.406(1) Å. The Schiff bases behave as monoanionic and tridentate ligands, which coordinate to the Cu atoms through the three NNO donor atoms. Each Cu atom in the complex is five-coordinated in a square pyramidal geometry, with the basal plane defined by the NNO donor atoms of the Schiff base ligand, and by one Br or N atom, and with the apical position occupied by another Br or N atom. The average trans angles are 169.6(2)° for Cu1, 168.2(2)° for Cu2, 171.4(2)° for Cu3, and  $164.5(2)^{\circ}$  for Cu4. The Cu atoms deviate from the least-squares planes defined by the four basal donor atoms by 0.167(1) Å for Cu1, 0.160(1) Å for Cu2, 0.137(1) Å for Cu3, and 0.174(1) Å for Cu4, toward the apical donor atoms. In the two molecules, the coordinate bond lengths related to the Cu atoms are comparable to each other and also comparable to the corresponding values observed in other similar halido-bridged copper(II) complexes with Schiff bases.<sup>[4,13–17]</sup>



FIG. 2. The molecular packing structure of the complex. Hydrogen bonds are drawn as dashed lines.

The coordination number 5 for copper(II) complexes is very common. The question arises as to whether the coordination polyhedra around the Cu atoms can be described as distorted square pyramid or trigonal bipyramid. Further information can be obtained by determining the structural index  $\tau^{[18]}$  that represents the relative amount of trigonality (square pyramid,  $\tau =$ 0; trigonal bipyramid,  $\tau = 1$ );  $\tau = (\beta - \alpha)/60^{\circ}$ ,  $\alpha$  and  $\beta$  being the two largest angles around the metal atom. For the present complex, the values of  $\tau$  are 0.06 (Cu1), 0.04 (Cu2), 0.05 (Cu3), and 0.28 (Cu4), indicating that all the Cu atoms in the complex adopt distorted square pyramidal coordination.

In the crystal structure of the complex, the copper complex molecules and the water molecules are linked together by

right bond distances (r) and bond digits () for the complex					
d(D-H)	$d(\mathbf{H}\cdots A)$	$d(D \cdots A)$	Angle $(D-H\cdots A)$		
0.85(1)	1.94(2)	2.790(10)	174(11)		
0.85(1)	3.00(8)	3.428(7)	113(7)		
0.85(1)	1.94(2)	2.782(9)	172(10)		
0.93	2.24	2.781(11)	116		
0.93	2.15	2.643(10)	112		
0.93	2.04	2.651(11)	122		
	d(D-H)           0.85(1)           0.85(1)           0.85(1)           0.93           0.93           0.93	$d(D-H)$ $d(H\cdots A)$ $0.85(1)$ $1.94(2)$ $0.85(1)$ $3.00(8)$ $0.85(1)$ $1.94(2)$ $0.93$ $2.24$ $0.93$ $2.15$ $0.93$ $2.04$	$d(D-H)$ $d(H\cdots A)$ $d(D\cdots A)$ 0.85(1)1.94(2)2.790(10)0.85(1)3.00(8)3.428(7)0.85(1)1.94(2)2.782(9)0.932.242.781(11)0.932.152.643(10)0.932.042.651(11)		

 TABLE 3

 Hydrogen bond distances (Å) and bond angles (°) for the complex

Symmetry codes: i) x, y, 1 + z; ii): -1/2 + x, 1/2 - y, 1/2 + z; iii): 1/2 + x, 1/2 - y, -1/2 + z; iv) x, y, -1 + z.

intermolecular  $O-H\cdots O$  and  $O-H\cdots Br$  hydrogen bonds (Table 3 and Figure 2).

#### IR Spectra

In the IR spectra of the complexes, the middle and broad band centered at 3354 cm<sup>-1</sup> is attributed to the vibration of the water molecules. The strong absorption band at 1645 cm<sup>-1</sup> can be assigned to the azomethine stretching frequencies of the Schiff base ligand, whereas for the free Schiff base the corresponding band was observed at 1637 cm<sup>-1</sup>. The shift of these bands toward lower frequencies on complexation suggests coordination to the Cu atoms through the imine N atoms. The  $\nu$ (C–O) mode is present as middle band at 1178 cm<sup>-1</sup>. The intense band at 2089 cm<sup>-1</sup> is assigned to the stretching vibration of the azide ligand. The weak bands indicative of the Cu–O, Cu–N, and Cu–Br bonds are located in the region 600–300 cm<sup>-1</sup>.

#### CONCLUSION

The present article reports the synthesis and crystal structure of a novel bromido- and azido-bridged dinuclear copper(II) complex with the tridentate Schiff base 4-chloro-2-[(2hydroxyethylimino)methyl]phenol. The bromide and azide ligands are preferred bridging groups for the construction of dinuclear copper(II) complexes with Schiff bases. The complex may serve as interesting magnetic material, which deserve further study.

#### SUPPLEMENTARY MATERIALS

CCDC 843682 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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