



Synthesis and Crystal Structure of a Mononuclear Copper(II) Complex

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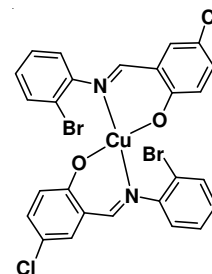
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A new mononuclear complex with the Schiff base ligand 2-[(2-bromo-phenylimino)-methyl]-4-chloro-phenol (HL), namely CuL_2 , has been synthesized and characterized by X-ray single-crystal diffraction analysis. The complex crystallizes in monoclinic system, space group $\text{P2}_1/\text{c}$ with $a = 9.568(2) \text{ \AA}$, $b = 10.853(3) \text{ \AA}$, $c = 12.047(3) \text{ \AA}$, $\beta = 105.965(7)^\circ$, $V = 1202.8(6) \text{ \AA}^3$, $M_r = 682.67$, $D_c = 1.885 \text{ Mg/m}^3$, $Z = 2$, $\mu = 4.481 \text{ mm}^{-1}$, $F_{(000)} = 670$, $R = 0.0450$ and $wR_2 = 0.1225$. The coordination geometry in the copper(II) complex is slightly distorted tetrahedral and the unit CuL_2 is linked into a three-dimensional network structure by weak halogen... halogen and C-H... π interactions and the conformation and packing is also stabilized by them.

Key Words: 5-Chlorosalicylaldehyde, Copper(II) complex, Crystal structure.

INTRODUCTION

Schiff bases and their metal complexes have been widely investigated for their structures and versatile applications in catalytic, magnetic and medicinal chemistry. The Schiff bases due to their facile $-\text{C}=\text{N}-$ and the availability of several potential donors can coordinate with metals in versatile ways^{1,2}. In recent years, there has been enhanced interest in the synthesis and characterization of Schiff bases and their metal complexes due to their important catalytic³, magnetic⁴ and biological properties^{5,6}. Copper is an essential trace element for all forms life and is important component in composing copper-dependent enzymes. Reports indicate that copper element play an important influence on the cardiovascular system, blood system, immune system, development of cancer and other diseases as well as the development of the skeletal system of infants^{7,8}. As an extension of the work on the synthesis and coordination of metal complexes with Schiff bases, the author reports here the synthesis and characterization of a new Schiff base copper(II) complex (**Scheme-I**). The structure of copper(II) complex had been established accurately from the single crystal X-ray diffraction study. The results showed that the copper(II) ion in the monomeric unit in the complex seems to reside in a distorted quadrilateral environment with a N_2O_2 donor set from the chelating Schiff base ligands, while two oxygen atom and two nitrogen atom from the Schiff base. The complex was stabilized by intermolecular and intramolecular hydrogen bonds, C-H... π stacking interaction and halogen-halogen interactions and the unit was linked into a three-dimensional network. These



Scheme-I: Structure of the Cu(II) complex

interactions play an important role in the formation, stability and crystallization of the complex.

EXPERIMENTAL

Reagents and physical measurements: Crystal structure was determined on a Bruker Smart ApexII diffractometer.

All reagents obtained from commercial sources were of AR grade and used without further purification.

Synthesis of the Cu(II) complex: 5-Chlorosalicylaldehyde (10 mmol) and an equimolar quantity of 2-bromoaniline were dissolved in ethanol (50 mL). After stirring for *ca.* 3 h at room temperature, the solution of $\text{Cu}(\text{NO}_3)_2$ (5 mmol) in 10 mL methanol was added. The mixture was stirred for 0.5 h in air at room temperature, yielding a brown solution and then filtered. The filtrate was left in air to evaporate the solvent and brown crystals were obtained after 10 days. The product was collected by filtration, washed with cooled methanol and then dried in air. yield: 63 %. Brown plate single crystals suitable

TABLE-1
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) OF THE COMPLEX

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)-O(1)#1	1.900(3)	Cu(1)-O(1)	1.900(3)	Cu(1)-N(1) #1	2.006(3)
Cu(1)-N(1)	2.007(3)	Br(1)-C(1)	1.899(4)	Cl(1)-C(10)	1.744(3)
N(1)-C(7)	1.290(4)	N(1)-C(6)	1.435(4)	O(1)-C(13)	1.303(4)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)#1-Cu(1)-N(1) #1	90.42(11)	O(1)-Cu(1)-N(1)#1	89.58(11)	O(1)#1-Cu(1)-N(1)	89.58(11)
O(1)-Cu(1)-N(1)	90.42(11)	N(1)#1-Cu(1)-N(1)	179.999(10)	O(1)#1-Cu(1)-O(1)	180.0
C(13)-O(1)-Cu(1)	123.0(2)	C(7)-N(1)-C(6)	119.0	C(7)-N(1)-Cu(1)	122.8(2)
C(6)-N(1)-Cu(1)	118.1(2)	C(2)-C(1)-Br(1)	121.3(3)	N(1)-C(7)-C(8)	125.4(3)

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

for single crystal X-ray diffraction were grown in methanol by slow evaporation. the resulting brown filtrate was left standing at room temperature for slow evaporation about one week, brown block crystals suitable for X-ray analysis obtained.

X-Ray crystallographic determination of the complex:

A brown block crystal with dimensions of 0.25 mm × 0.21 mm × 0.19 mm was selected for measurement. Diffraction data were collected at 153(2) K on a Bruker Smart ApexII diffractometer equipped with a graphite-monochromatic MoK α radiation ($\lambda = 0.71073$ Å). A total of 10002 reflections were collected in the range of $2.9 \leq \theta \leq 29.1^\circ$ by using an ϕ - ω multi-scan mode, of which 3161 were unique with $R_{\text{int}} = 0.033$ and 2310 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELX-97 program package⁹. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were fixed at their ideal positions. The final $R = 0.040$, $wR = 0.103$ ($w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.067$, $(\Delta\rho)_{\text{max}} = 0.001$, $(\Delta\rho)_{\text{max}} = 1.60$ and $(\Delta\rho)_{\text{min}} = -0.60$ e/Å³. The crystals used for the diffraction study showed no decomposition during data collection. Selected bond lengths and bond angles are listed in Table-1 and the hydrogen bond parameters in Table-2.

TABLE-2
PARAMETERS OF HYDROGEN BONDS AND HALOGEN-HALOGEN INTERACTION OF THE COMPLEX

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(1)-Br(1)---Cl(1) ^{#2}	1.899	3.532	3.490	153.0
C(1)-Br(1)---Br(1) ^{#3}	1.899	3.612	3.490	136.9
C(5)-H(5)...Cg	0.950	2.853		125.4

Note: Cg is center of the plane of the C8-C13 ring. Symmetrycodes: #2: -x + 1, y-1/2, -z + 1/2; #3: -x + 2, -y+1, -z + 1; Cg: x, -y + 3/2, z-1/2.

RESULTS AND DISCUSSION

As shown in Fig. 1, the present Cu(II) complex is composed of one copper(II) ion and two Schiff base ligands, within which all bond lengths and bond angles of ligand are in normal ranges. The C(7) = N(1) distance of 1.290(4) Å and the dihedral angle of two phenyl rings (ring A, C(1)-C(6) and ring B, C(8)-C(13)) is 46.90(13)°, which is not coplanar, all which could be interpreted in terms of coordination effect. The bromine atom at phenyl ring is slightly twisted out of phenyl ring with the torsion angle Br(1)-C(1)-C(2)-C(3) = 176.3(3)° in the structure of the complex. The hydroxyl group nearly oriented out of the oriented phenyl ring, as indicated

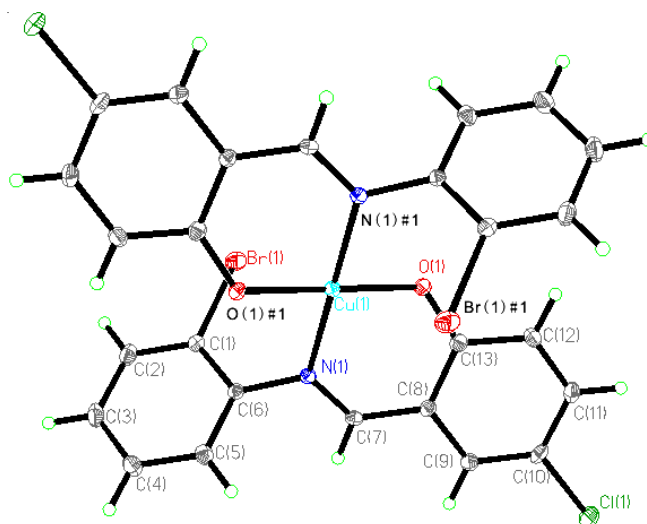


Fig. 1. Molecular structure of the Cu(II) complex. Displacement ellipsoids are drawn at the 30 % probability level and the hydrogen atoms are omitted for clarity. Symmetry code: #1: -x + 1, -y + 1, -z + 1

by the torsion angle C(9)-C(8)-C(13)-O(1) = -173.9(3)°, all which is due to the p- π conjugate effect of atom which possess the unshared electron pair and phenyl ring.

In the complex, the four-coordinated copper(II) ion are bonded to the oxygen and nitrogen donor atoms of the two bidentate Schiff base ligands in the usual *trans* arrangement. The geometry around copper(II) is in a slightly distorted tetrahedral environment with O(1)Cu(1)N(1), N(1)Cu(1)N(1A) and O(1)Cu(1)O(1A) angles of 89.53(14), 180.0 and 180.0°, respectively. The distances of Cu(1)-O(1) and Cu(1)-N(1) are 1.900(3) and 2.006(3) Å, respectively. The distances are approach to the values found in reported copper complex¹⁰. The phenyl ring plane (ring B) and the chelate ring (O(1)/Cu(1)/N(1)/C(7)/C(8)/C(9), RMS deviation of fitted atoms is 0.1680) are nearly coplanar with a dihedral angle of 9.79 (11)°. This is true of the corresponding planes which were generated by symmetry.

Discrete monomeric molecules of the title complex are held together by Br---Cl from the adjacent molecule at (-x + 1, y-1/2, -z + 1/2), with the distance of 3.532 Å and C-H--- π hydrogen bond (Fig. 2) from molecule at (x, -y + 3/2, z-1/2) with the distances of H--- π and C--- π are 2.853 and 3.490 Å, respectively and C-H--- α = 125.4°, which connect the molecules to form a two-dimensional network (Fig. 3, Table-2) and further linked to form a three-dimensional network by Br---Br interactions from molecule at (-x + 2, -y + 1, -z + 1) with the distance of 3.612 Å (Fig. 4, Table-2).

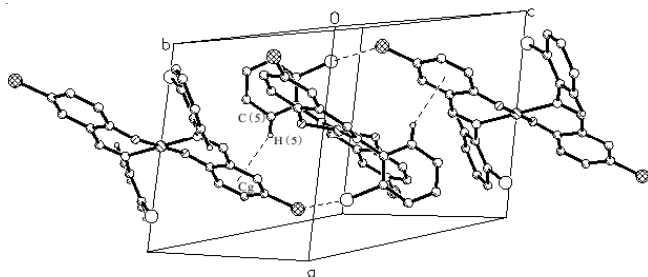


Fig. 2. Part of the complex, showing the formation of the C-H... π interaction (other hydrogen atoms are omitted for clarity. Symmetry code: Cg: $x, -y + 3/2, z - 1/2$)

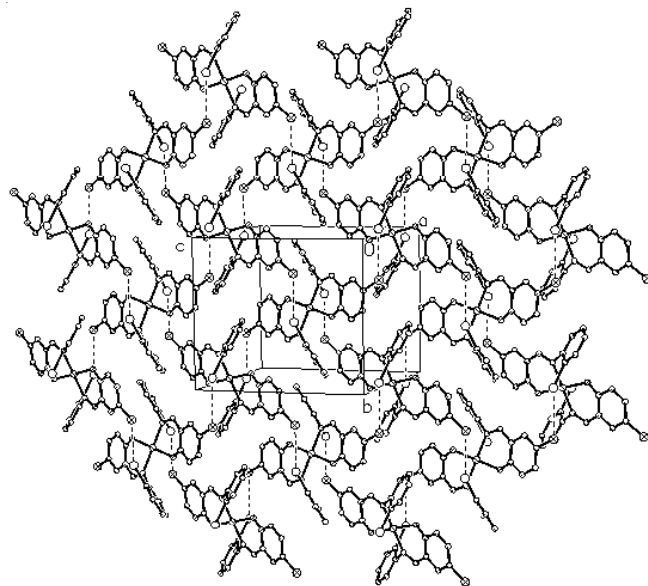


Fig. 3. Two-dimensional layer structure of 2 along the a-axis, Br...Cl interactions are shown as dashed lines (hydrogen atoms were omitted for clarity)

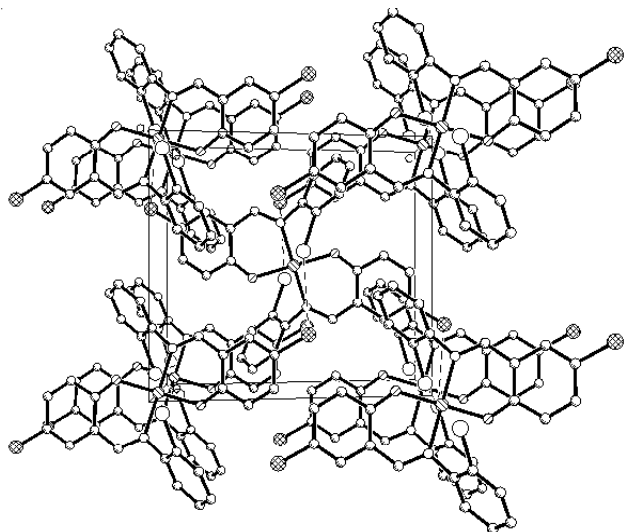


Fig. 4. Packing of 2 viewed along the a-axis, Halogen-halogen (Br...Cl and Br...Br) interactions are shown as dashed lines (hydrogen atoms were omitted for clarity)

Conclusion

In this work, a new three-dimensional supramolecular architecture of copper(II) complex has been synthesized successfully and the structure of the complex were determined by X-ray crystallography diffraction. The complex was connected by halogen-halogen and C-H... π hydrogen bond to form a three-dimensional network. Meanwhile, these interactions play a very important role in the formation, stability and crystallization for the complex.

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