

Synthesis and Crystal Structure of Schiff Base 2-[(3-Bromo-phenylimino)methyl]phenol and It's Copper(II) Complex

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A new Schiff base 2-[(3-bromo-phenylimino)methyl]phenol (**HL**) (**1**), derived from condensation of salicylaldehyde with *m*-bromoaniline, and its copper(II) complex (**2**) [Cu_2L_4], have been prepared and characterized by single crystal X-ray diffraction. Schiff base is in the monoclinic system, space group P2_1 with $a = 3.928(14) \text{ \AA}$, $b = 10.590(4) \text{ \AA}$, $c = 13.212(5) \text{ \AA}$, $\beta = 97.360(4)^\circ$, $M_r = 276.13$, $V = 5451(3) \text{ \AA}^3$, $D_c = 1.682 \text{ g/cm}^3$, $Z = 2$, $\mu = 3.745 \text{ mm}^{-1}$, $F(000) = 276$, $R = 0.0326$, $wR = 0.0455$. Complex belongs to the monoclinic system, space group $\text{P2}_1/n$ with $a = 13.970(9) \text{ \AA}$, $b = 11.891(7) \text{ \AA}$, $c = 15.232(9) \text{ \AA}$, $\beta = 114.876(9)^\circ$, $M_r = 1227.55$, $V = 2296(2) \text{ \AA}^3$, $D_c = 1.776 \text{ g/cm}^3$, $Z = 2$, $\mu = 4.460 \text{ mm}^{-1}$, $F(000) = 1212$, $R = 0.1801$, $wR = 0.2158$. **1** is stabilized by intermolecular C-H...O and $\pi\cdots\pi$ interaction and further linked into a 2D layer structure. But compound **2** is connected by halogen...halogen and C-H... π hydrogen bond and Cu...H interaction to form a 3D network.

Keywords: Salicylaldehyde, Schiff base, Synthesis, Crystal structure.

INTRODUCTION

Schiff bases in general have been reported as organic chelating ligands in the synthesis of metal complexes due to their hard donor-atom frameworks, stability, structural variety and easy modification. Their complexes have proved to be of significant interest in the areas of catalysis¹, photo electricity and LCD², magnetic³ and biological properties⁴⁻⁵, which caused many researcher's significant interests and more and more studies were performed in these fields to explore their relevant properties through transforming the transition metal ions in different coordination environment with different Schiff base ligands. Schiff base complexes of copper are also no exception in these respects⁶⁻⁸ because of important biochemical role of copper and some Schiff base copper complexes have been synthesized in recent years⁹⁻¹¹. Although Schiff bases derived from salicylaldehyde and various amines have extensively been used to synthesize many complexes of copper(II), but the binuclear complexes with *m*-bromoaniline as the amine counterpart of the Schiff base have no report now. In this paper, the preparation and characterization of a binuclear copper(II) by *in situ* preparation of this type of Schiff bases is report. The Schiff base and it's copper(II) complex have been characterized by single crystal X-ray diffraction study. The results showed that **1** is build up only by Schiff base molecules but **2** contains one copper(II) cation and four Schiff base ligands.

Compound **1** coordinates to Cu atoms through phenolate O and imine N and two Cu atoms are held together by two deprotonated phenolic oxygen atoms from two compound **1**, forming a Cu_2O_2 parallelogram. **1** is stabilized by intermolecular C-H...O and $\pi\cdots\pi$ interaction and further linked into a 2D layer structure. But **2** is connected by halogen...halogen and C-H... π hydrogen bond and Cu...H interaction to form a 3D network. Meanwhile, these interactions play a very important role in the formation, stabilization and crystallization of **1** and **2**.

EXPERIMENTAL

Crystal structure was determined on a Bruker APEX II CCD area diffractometer. Salicylaldehyde and *m*-bromoaniline were purchased from J&K Chemical Ltd. All other chemicals were commercial products and used without further purification.

Synthesis of 2-[(3-bromo-phenylimino)-methyl]phenol (HL): As shown in **Scheme-I**, 2-[(3-bromo-phenylimino)-methyl]phenol has been synthesized by dissolving 5 mmol of salicylaldehyde and an equimolar quantity of *m*-bromoaniline in 50 mL of methanol. The reaction mixture was heated to 50 °C for 1 h and then cooled to room temperature followed by concentrating the resulting mixture to a yellow solid product. The yield was 1.20 g (87 %). Yellow block single crystals suitable for single crystal X-ray diffraction were grown in methanol by slow evaporation.

Synthesis of Cu₂L₄: Copper(II) nitrate (1 mmol) in methanol (10 mL) was added drop wise to HL (0.55 g, 2 mmol) in methanol (50 mL) and the resultant brown reaction mixture was stirred at room temperature for 1 h and then filtered. The filtrate was left in air to evaporate the solvent and brown crystals were obtained after 7 days. The product was collected by filtration, washed with cooled methanol and then dried in air. The yield was 0.33 g (54 %). Brown plate single crystals suitable for single crystal X-ray diffraction were grown in methanol by slow evaporation.

X-ray crystal structure determination: Crystal structure determination of **1** and **2** were carried out on a Bruker APEX

II CCD area diffract meter equipped with graphite-monochromatized MoK α ($\gamma = 0.71073 \text{ \AA}$) using ϕ - ω scan technique at 153(2) K. The structures were solved by direct methods and refined on F² by full-matrix least-squares methods using SHELX-97^{12,13}. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. The crystal data, experimental details, refinement results and details of structure determinations are shown in Table-1. Selected bond lengths and bond angles are listed in Table-2. CCDC: 917479 and 917480.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT FOR THE COMPOUNDS

Parameter	Value	
	HL	Cu ₂ L ₄
CCDC No.	917479	917480
Empirical formula	C ₁₃ H ₁₀ BrNO	C ₃₂ H ₂₆ Br ₄ Cu ₂ N ₄ O ₄
Formula weight	276.13	1227.55
Crystal size/mm	0.54 × 0.28 × 0.09	0.49 × 0.29 × 0.12
Crystal system, space group	monoclinic, P2 ₁	monoclinic, P2 ₁ /n
a, b, c/Å	3.9280(14), 10.59(4), 13.212(5)	13.97(9), 11.891(7), 15.232(9)
α , β , γ (°)	$\beta = 97.360(4)$	$\beta = 114.876(9)$
V/Å ³	5451(3)	2296(2)
Dc/g cm ⁻³ , Z	1.682, 2	1.776, 2
μ /mm ⁻¹	3.745	4.460
F(000)	276	1212
Index ranges (H, k, l)	-5 ≤ h ≤ 5, -14 ≤ k ≤ 13, -16 ≤ l ≤ 17	-14 ≤ h ≤ 19, -16 ≤ k ≤ 12, -20 ≤ l ≤ 20
μ range/(°)	2.47 to 29.12	2.35 to 29.07
Reflections collected/unique	4683/2605	19146/6076
R, wR[I ≥ 2 σ (I)]	0.0326, 0.0455	0.1801, 0.4629
R, wR[all data]	0.0435, 0.0472	0.2158, 0.4705
GOF on F ²	0.978	1.405
($\delta\rho$) _{max} , ($\delta\rho$) _{min} /(e nm ⁻³)	740, -561	4335, -1232

Final weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0013P)^2 - 0.1P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **1**; $w = 1/[\sigma^2(F_o^2) + (0.130P)^2 + 63.696P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **2**

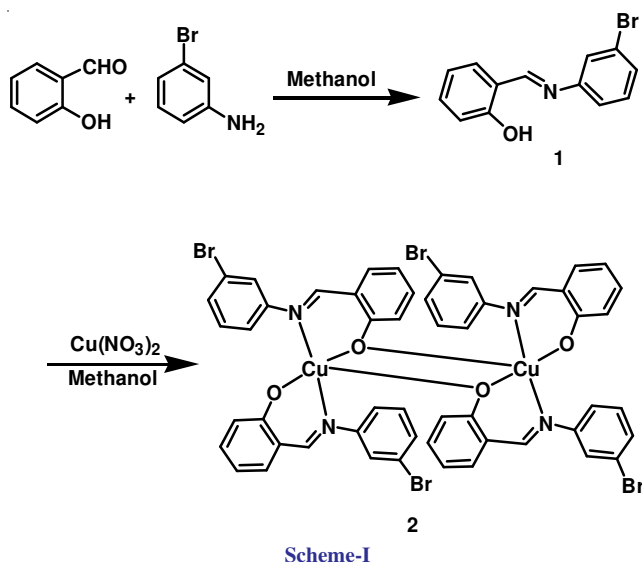
TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE COMPOUNDS

Bonds	d	Bonds	d	Bonds	D
HL					
Br(1)-C(12)	1.908(3)	O(1)-C(1)	1.360(4)	O(1)-H(10)	0.8355
N(1)-C(7)	1.285(4)	N(1)-C(8)	1.422(4)	C(6)-C(7)	1.380(4)
C(1)-C(6)	1.414(4)	C(8)-C(9)	1.394(4)	C(7)-H(7)	0.9500
Cu₂L₄					
Cu(1)-O(1)	1.904(13)	Cu(1)-O(2)	1.907(12)	Cu(1)-N(1)	2.059(16)
Cu(1)-N(2)	2.065(16)	Cu(1)-O(2) #1	2.405(13)	O(2)-Cu(1) #1	2.405(13)
Br(1)-C(12)	1.88(2)	Br(2)-C(25)	1.88(2)	O(1)-C(1)	1.28(2)
N(1)-C(7)	1.36(3)	N(1)-C(8)	1.44(2)	N(2)-C(20)	1.36(3)
N(2)-C(21)	1.44(2)	C(6)-C(7)	1.39(3)	C(19)-C(20)	1.45(3)
Angle	ω	Angle	ω	Angle	ω
HL					
C(1)O(1)H(10)	107.7	C(7)N(1)C(8)	121.5(3)	O(1)-C(1)-C(2)	118.6(3)
C(1)C(6)C(7)	122.1(3)	N(1)C(7)C(6)	122.6(3)	C(11)C(12)Br(1)	119.4(3)
Cu₂L₄					
O(1)Cu(1)O(2)	176.7(6)	O(1)Cu(1)N(1)	88.6(6)	O(2)Cu(1)N(1)	92.0(6)
O(1)Cu(1)N(2)	87.3(6)	O(2)Cu(1)N(2)	91.3(6)	N(1)Cu(1)N(2)	165.5(6)
O(1)Cu(1)O(2) #1	100.5(5)	O(2)Cu(1)O(2) #1	82.7(5)	N(1)Cu(1)O(2) #1	95.9(6)
N(2)Cu(1)O(2) #1	98.5(5)	C(1)O(1)Cu(1)	128.0(12)	C(14)O(2)Cu(1)	124.7(11)
Cu(1)O(2)Cu(1) #1	97.3(5)	C(7)N(1)Cu(1)	120.6(12)	C(20)N(2)Cu(1)	121.1(12)
O(1)C(1)C(6)	123.2(17)	N(1)C(7)C(6)	126.0(18)	N(2)C(20)C(19)	125.8(16)

Symmetry transformations used to generate equivalent atoms:^{#1} -x + 1, -y + 1, -z + 1

RESULTS AND DISCUSSION

The Schiff base (HL) was prepared in excellent yields (87 %) in absolute methanol. The compound is yellow solids and stable in air at room temperature. The Cu(II) complex was prepared by the reaction of the Schiff bases with cupric nitrate in methanol in accordance to reactions **Scheme-I**. Both the Schiff bases and the copper complex are stable in air at room temperature and soluble in common polar organic solvents, such as DMSO, methanol and ethanol.



The crystal structures of HL and Cu₂L₄ with the atomic numbering scheme are presented in Figs. 1 and 2, respectively. Compound HL is build up only by Schiff base molecules, but the Cu(II) complex build up by Cu(II) ion and Schiff base ligands, within which all bond lengths and bond angles of ligand are in normal ranges. Ligand (L) of compounds assigns to be E configuration with respect to the azomethine -CH=N- bond on the basis of the crystal data. The C(7) = N(1) and C(20) = N(2) distance of complex (1.36(2) Å) are longer than that of the free Schiff base ligand (1.285(4) Å). The dihedral angles of two phenyl rings from each Schiff base ligand (ring A, C(1)-C(6) and ring B, C(8)-C(13) and ring C, C(14)-C(19) and ring D, C(21)-C(26)) of complex are 39.59 and 40.53°, respectively, which is much bigger than that of free Schiff base ligand (6.24°). It can be interpreted in terms of coordination effect. Moreover, the whole molecule of free ligand is nearly coplanar, which is interpreted by conjugation effect and the stabilization of ring from intramolecular hydrogen bond. But the complex is not coplanar due to coordination effect and steric effect.

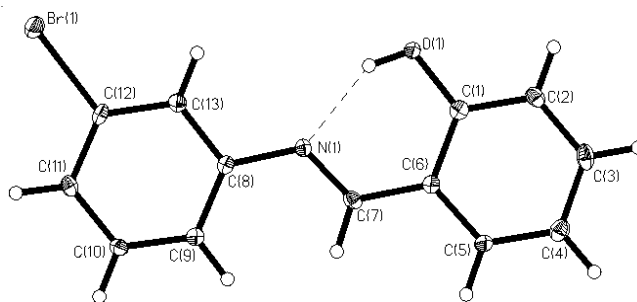


Fig. 1. Molecular structure of HL. Displacement ellipsoids are drawn at the 30 % probability level

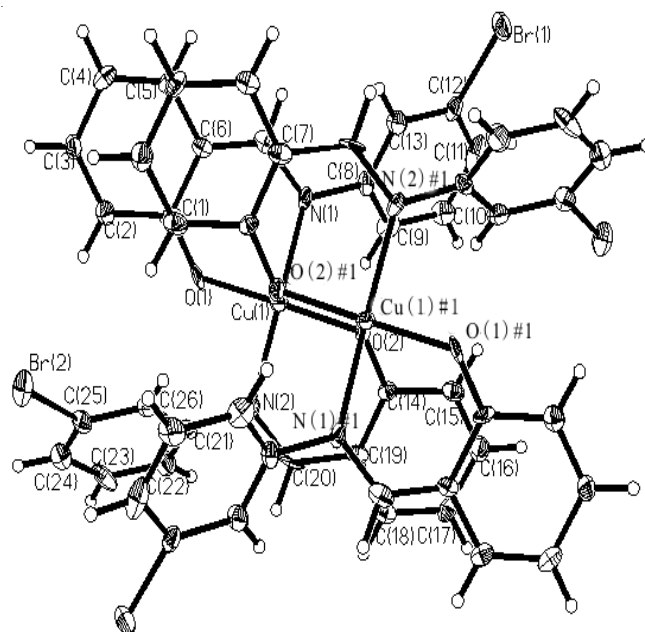


Fig. 2. Molecular structure of Cu₂L₄. Displacement ellipsoids are drawn at the 30 % probability level and the hydrogen atoms are omitted for clarity. Symmetry code: #1 -x + 1, -y + 1, -z + 1

In the crystal structure of the Schiff base, there are some intermolecular interaction C-H...O hydrogen bonds and $\pi \dots \pi$ stacking interaction in the lattice structure. Discrete monomeric molecules are held together by intermolecular hydrogen bond C(7)-H(7)...O(1), which connect the molecules to form a 1D zig-zag chain along *c*-axis (Fig. 3, Table-3).

Another, the Schiff base skeletons of **1** are stacked into column. A π - π interaction dimmer is formed between the adjacent Schiff bases with an parallel manner, of which the dihedral angles being 0.00°, the intercentroid distances of two rings A and two rings B in two neighboring molecules are same 3.928 Å. The corresponding perpendicular distances of them are 3.4685 and 3.3984 Å, respectively. All the inter-centroid and interplanar distances are comparable to the

TABLE-3
PARAMENTS OF HYDROGEN BONDS AND HALOGEN-HALOGEN INTERACTION FOR THE COMPOUNDS

Compound	D—H...A	d(D—H)	d(H...A)	$\angle$ (DHA)
1	C(7)-H(7)...O(1) ⁱ	0.950	2.773	167.0
	C(25)-Br(2)...Br(2) ^{#2}	1.888	3.835	129.2
2	C(12)-Br(1)...H(10) ^{#3}	1.871	2.995	123.3
	C(5)-H(5) ^{#2} ...Cu(1) ^{#3}	0.950	3.011	147.7

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

reported contact calculated from Hobza *et al.*¹⁴. Combination of these aromatic $\pi \cdots \pi$ stacking interactions generates a column along *b*-axis.

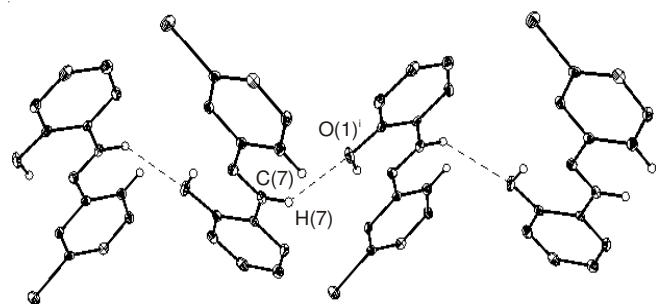


Fig. 3. A one-dimensional zig-zag chain of **1** along *b*-axis (C-H...O hydrogen bond was showed as dashed lines, hydrogen atoms were omitted for clarity: $^{-1}x + 2, 1/2 + y, -z + 1$)

Combination of the C(7)-H(7)...O(1) and the aromatic $\pi \cdots \pi$ stacking interactions linked **1** to generate a 2D network structure. These interactions also mutually strengthen and solidify the molecule.

Compound **2** is a binuclear copper(II) complex which is centrosymmetric and two copper(II) atoms in similar coordi-

nation environment. Each copper(II) atom is five-coordinated by two imino N atoms and three phenolic O atoms from three Schiff base ligands, forming a square taper geometry. The distances of Cu-O and Cu-N are in range of 1.904–2.405 and 2.59–2.065 Å, which are comparable to those in similar Schiff base copper(II) complexes¹⁵. The angles subtended at the Cu(II) atom are in the range 82.7(5)°–176.7(6)°, indicating that square tape coordination is distorted. The ligand forms two kinds of five-membered cheated rings with bite angles of 88.6(6)° and 91.3(6)°.

The two Cu(II) atoms are held together by two deprotonated phenolic oxygen atoms from two different Schiff base ligands, forming a Cu₂O₂ parallelogram ($\angle \text{Cu}(1)\text{-O}(2)\text{-Cu}(1)^{\#1} = 97.3(5)^\circ$, which very close to 100.57° in $\{[\text{Cu}(\text{py})(\text{L}_1)\text{UO}_2]_2 \cdot 2\text{py}\}$ ¹⁶; $\angle \text{O}(2)\text{-Cu}(1)\text{-O}(2)^{\#1} = 82.7(5)^\circ$, the torsion angle of $\text{O}(2)^{\#1}\text{-Cu}(1)\text{-O}(2)\text{-Cu}(1)^{\#1}$ is 0.00°) plane with Cu...Cu distance being 3.253 Å which is in agreement with that of 3.032(2) Å in a reported complex¹⁷.

In crystal structure of **2**, discrete monomeric molecules are held together by halogen-halogen (Br...Br) interaction, C-Br...H hydrogen bonding and Cu...H interaction, forming a 3D network structure (Fig. 4). The hydrogen bonding data are summarized in Table-3. The results reveal that these interactions not only play an important role in the formation,

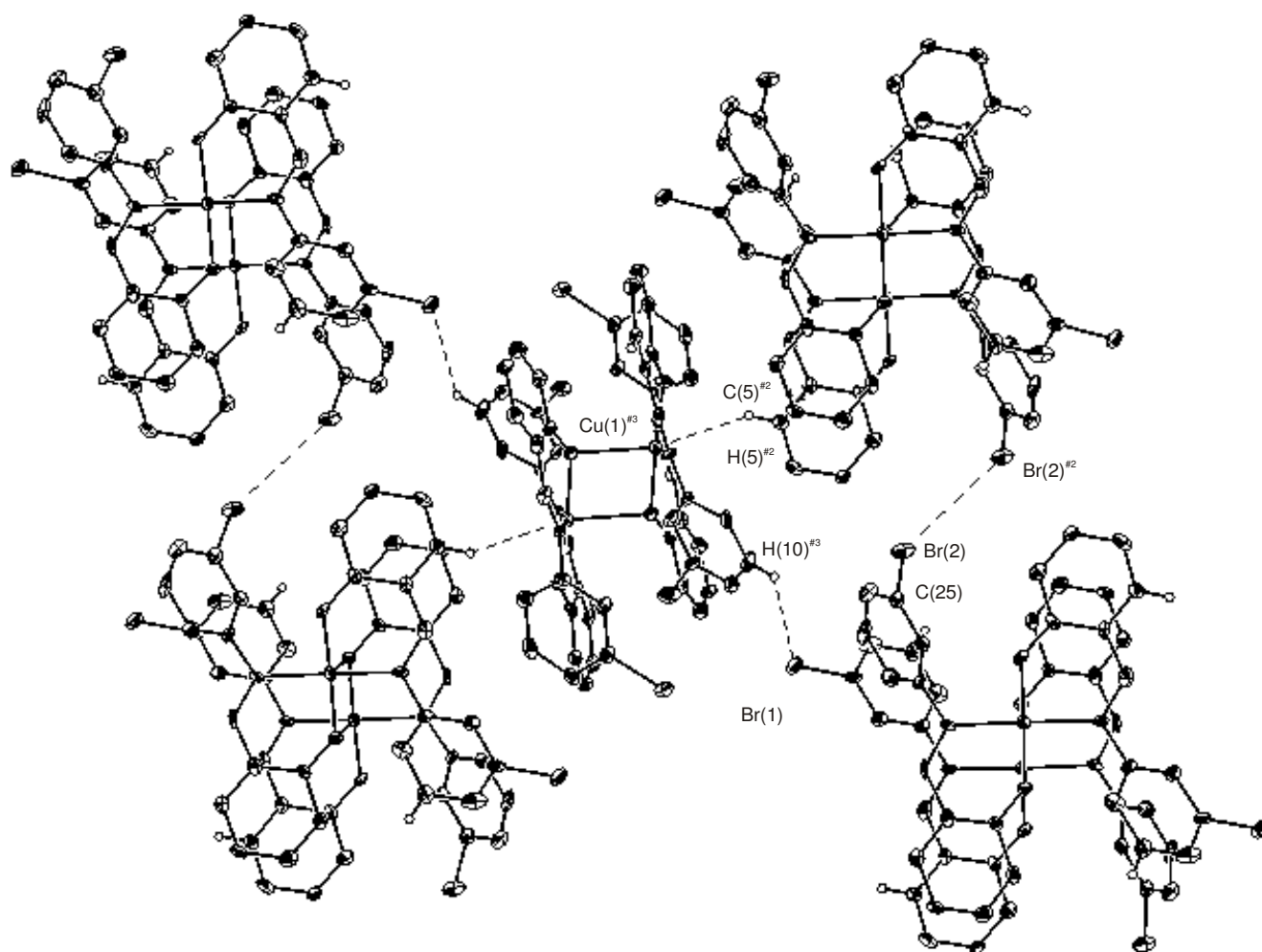


Fig. 4. Molecular packing of Cu₂L₄ complex. Some interaction are drawn as dashed lines. (Other hydrogen atoms are omitted for clarity. Symmetrycode: $^{\#2} -x, -y + 1, -z + 1$; $^{\#3} 1/2 + x, -y + 1/2, z + 1/2$)

stability and crystallization of complex, but also connect the independent molecular to a three-dimensional network.

Conclusion

A new Schiff base (**1**) was prepared by the condensation of salicylaldehyde with *m*-bromoaniline. Using the Schiff base, a new binuclear Cu(II) complex (**2**) was prepared and structurally characterized. The Schiff base coordinates to Cu atoms through phenolate O and imine N and two Cu atoms are held together by two deprotonated phenolic oxygen atoms from two different Schiff base ligands, forming a Cu₂O₂ parallelogram. **1** is stabilized by intermolecular C-H...O and $\pi\cdots\pi$ interaction and further linked into a 2D layer structure. But **2** is connected by halogen...halogen and C-H... π hydrogen bond and Cu...H interaction to form a 3D network.

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REFERENCES

1. S.A. Schuetz, C.M. Silvernail, C.D. Incarvito, A.L. Rheingold, J.L. Clark, V.W. Day and J.A. Belot, *Inorg. Chem.*, **43**, 6203 (2004).
2. S. Akine, T. Taniguchi and T. Nabeshima, *Angew. Chem. Int. Ed.*, **41**, 4670 (2002).
3. M. He, Q.F. Li and T. Xie, *Chinese J. Struct. Chem.*, **29**, 582 (2010).
4. Y.N. Guo, *Russ. J. Coord. Chem.*, **38**, 121 (2012).
5. N. Raman, K. Pothiraj and T. Baskaran, *J. Mol. Struct.*, **1000**, 135 (2011).
6. S. Mandal, A.K. Rout, G. Pilet and D. Bandyopadhyay, *Transition Met. Chem.*, **34**, 719 (2009).
7. K.K. Du and S.X. Liu, *Chinese J. Struct. Chem.*, **27**, 49 (2008).
8. N.A. Negm and M.F. Zaki, *Colloids Surf. B Biointerfaces*, **64**, 179 (2008).
9. Y.N. Guo, *Chinese J. Inorg. Chem.*, **27**, 1875 (2011).
10. X.H. Pu, *Chinese J. Inorg. Chem.*, **28**, 2211 (2012).
11. Z.X. Li, *Z. Kristallogr. NCS*, **225**, 705 (2010).
12. G.M. Sheldrick, SHELXS-97. Program for Crystal Structure Determination, University of Gottingen: Germany (1997).
13. G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Refinement, University of Gottingen: Germany (1997).
14. R. Kiralj, B. Kojic-Prodic, I. Piantanida and M. Zinic, *Acta Crystallogr. B*, **55**, 55 (1999).
15. M.B. Dai, Q.L. Zhang and X.C. Zhu, *Chinese J. Inorg. Chem.*, **24**, 1381 (2008).
16. L. Salmon, P. Thuéry and M. Ephritikhine, *Polyhedron*, **22**, 2683 (2003).
17. Z. Yan-Shi, L. Qiu-Tian, Z. Hong-Ping, C. Yi-Hui and C. Chang-Neng, *Chinese J. Synth. Chem.*, **18**, 188 (2010).