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Three [CuL_2] Type Complexes with Halogen-Substituted Schiff Base Ligands Containing a Pyridine Group

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Three mononuclear Schiff base copper(II) complexes, [$Cu(L^1)_2$] (1), [$Cu(L^2)_2$] (2) and [$Cu(L^3)_2$] (3) (HL^1 = 2,4-dichloro-6-[(2-chloro-3-pyridyl)iminomethyl]phenol, HL^2 = 2,4-dibromo-6-[(2-chloro-3-pyridyl)-iminomethyl]phenol, HL^3 = 2-bromo-4-chloro-6-[(2-chloro-3-pyridyl)iminomethyl]phenol), have been synthesized and characterized by elemental analyses, IR, UV–Vis spectra, and X-ray single crystal diffraction. X-ray structures reveal each crystal unit contains two molecules and the coordination environment around the copper(II) atom is tetracoordinated by two Schiff base ligands, showing a tetrahedron geometry with some distortion. Pairs of intermolecular C–H$\cdots$X (X = Cl or Br), C–H$\cdots$N and C–H$\cdots$O hydrogen bonds form many hydrogen bonding rings and play a crucial role in stabilizing the crystal structures.

Keywords copper(II) complex, crystal structure, property, synthesis, Schiff base ligand

INTRODUCTION

Compounds containing phenoxy-imine groups are a versatile class of ligands that display a truly impressive range of diverse applications spanning from bioinorganic chemistry to coordination chemistry, chemical catalysis, and materials related applications.[1–6] Meanwhile, Schiff base type complexes play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism, and molecular architectures.[7–8] On the other hand, copper element is very important for human beings and has been know as an essential bioelement for some time, but its biological role has been recognized only in the last decades due to the rapid development of bioinorganic chemistry, a successful interaction between model complexes and protein biochemistry, as well as the biological role of copper is primarily in redox reactions and as a biological catalyst.[9–12] In light of the importance of Schiff base compounds and the copper element, herein, the authors report the syntheses, characterization and crystal structures of three Cu(II) complexes **1**, **2**, and **3** derived from an important class of Schiff base ligand HL by the condensation of halogen-substituted salicylaldehyde and 2-chloropyridin-3-amine in 1:1 molar ratio.

EXPERIMENTAL

Materials and Instruments

Commercially available 3,5-dichlorosalicylaldehyde, 3,5-dibromosalicylaldehyde and 3-bromo-5-chlorosalicylaldehyde from Acros Organics as well as 2-chloropyridin-3-amine from Alfa Aesar were purchased. Solvents were AR grade from Tianjin Chemical Reagent Factory and used without further purification.

Elemental analysis for copper was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. Carbon, hydrogen, and nitrogen analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a VERTEX 70 FT-IR spectrophotometer, with samples prepared as KBr (500 ∼ 4000 cm^{-1}) and CsI (100 ∼ 500 cm^{-1}) pellets. UV–Vis spectra were taken on a Shimadzu UV–240 spectrophotometer. Electrolytic conductance measurements were made with a DDS–11A type conductivity bridge using a 1.0×10^{-3} mol·L^{-1} solution in DMF at room temperature. X-ray single crystal structures were determined on a Bruker Smart APEX CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike instrument limited company, and the thermometer was uncorrected.

Syntheses of Schiff base Ligands HL^1, HL^2, and HL^3

The synthetic route for three N, O-bidentate ligands is given in Scheme 1.

2,4-Dichloro-6-[(2-chloro-3-pyridyl)iminomethyl]phenol (HL^1).

To a warm pale-yellow ethanol solution (4 mL) of 3,5-dichlorosalicylaldehyde (185.3 mg, 0.970 mmol), the colorless

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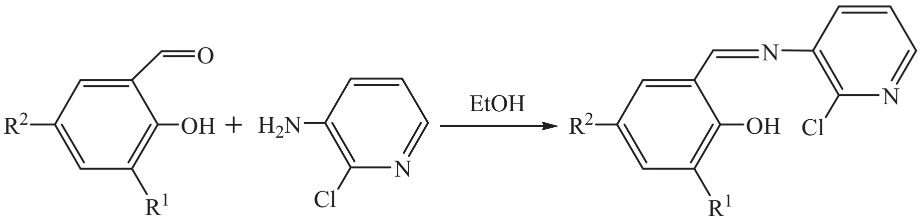


HL^1: R^1=3-Cl, R^2=5-Cl; HL^2: R^1=3-Br, R^2=5-Br;
HL^3: R^1=3-Br, R^2=5-Cl.

SCH. 1. Syntheses of *N*, *O*-bidentate ligands HL^1, HL^2 and HL^3.

ethanol solution (4 mL) of 2-chloropyridin-3-amine (115.4 mg, 1.0 mmol) was added dropwise, and the color of the mixture turned into brown. The mixture solution was maintained under reflux for 6 h, and a saffron yellow powder product was obtained. It was filtered off, washed with ethanol and ethanol/hexane (1:4, V/V) (3 × 4 mL), respectively, then dried under reduced pressure yielding 0.1396 g powder. Yield, 52%. m.p. 186 ∼ 187°C. Anal. calcd. for $C_{12}H_7Cl_3N_2O$ (%): C, 47.8; H, 2.3; N, 9.3. Found: C, 47.7; H, 2.3; N, 9.4.

2,4-Dibromo-6-[(2-chloro-3-pyridyl)iminomethyl]phenol (HL^2).

To a warm pale-yellow ethanol solution (4 mL) of 3,5-dibromosalicylaldehyde (201.9 mg, 0.721 mmol), the colorless ethanol solution (4 mL) of 2-chloropyridin-3-amine (92.7 mg, 0.721 mmol) was added dropwise, and the color of the mixture turned into brown. The mixture solution was maintained under reflux for 8 h, and a white powder product was obtained. It was filtered off, washed with ethanol and ethanol/hexane (1:4, V/V) (3 × 4 mL), respectively, then dried under reduced pressure yielding yellow 0.2474 g powder. Yield, 68%. m.p. 169 ∼ 170°C. Anal. calcd. for $C_{12}H_7Br_2ClN_2O$ (%): C, 36.9; H, 1.8; N, 7.2. Found: C, 36.9; H, 1.7; N, 7.3.

2-Bromo-4-chloro-6-[(2-chloro-3-pyridyl)iminomethyl]phenol (HL^3).

The synthetic procedure was as similar as that for complex **1**. To a warm kelly ethanol solution (3 mL) of 3-bromo-5-chlorosalicylaldehyde (237.6 mg, 1.001 mmol), the colorless ethanol solution (3 mL) of 2-chloropyridin-3-amine (124.2 mg, 0.966 mmol) was added dropwise, and the color of the mixture turned into yellow. The mixture solution was maintained under reflux for 8 h, and a white powder product was obtained. It was filtered off, washed with ethanol and ethanol/hexane (1:4, V/V) (3 × 4 mL), respectively, then dried under reduced pressure yielding jacinth 0.1207 g solid. Yield, 36%. m.p. 168 ∼ 170°C. Anal. calcd. for $C_{12}H_7BrCl_2N_2O$ (%): C, 41.7; H, 2.0; N, 8.1. Found: C, 41.6; H, 2.1; N, 8.2.

Syntheses of Complexes 1, 2, and 3

*Complex **1**.*

A pale-blue ethanol solution (2 mL) of Cu(II) acetate monohydrate (2.5 mg, 0.013 mmol) was added dropwise to a pale-yellow ethyl acetate solution (4 mL) of HL^1 (7.5 mg, 0.026 mmol) at room temperature. The color of the mixing solution turned to yellow immediately then turned to brown slowly and the filtrate was allowed to stand at room temperature for about two weeks. Single crystals suitable for X-ray structural determination were obtained by the slow evaporation from ethanol and ethyl acetate solution. Anal. calcd. for $[Cu(L^1)_2]$ ($C_{24}H_{12}Cl_6CuN_4O_2$) (%): C, 43.4; H, 1.8; N, 8.4; Cu, 9.6. Found: C, 43.3; H,1.8; N, 8.5, Cu, 9.5.

*Complex **2**.*

Complex **2** was synthesized in a similar manner as described for complex **1**. A pale-blue methanol solution (2 mL) of Cu(II) acetate monohydrate (2.0 mg, 0.010 mmol) was added dropwise to a pale-yellow ethanol solution (4 mL) of HL^2 (8.0 mg, 0.020 mmol) at room temperature. The color of the mixing solution turned to yellow immediately then turned to brown slowly, and the filtrate was allowed to stand at room temperature for about several weeks. Single crystals suitable for X-ray structural determination were obtained by the slow evaporation from methanol and ethanol solution. Anal. calcd. for $[Cu(L^2)_2]$ ($C_{24}H_{12}Br_4Cl_2CuN_4O_2$) (%): C, 34.2; H, 1.4; N, 6.7; Cu, 7.5. Found: C, 34.1; H, 1.3; N, 6.8, Cu, 7.4.

*Complex **3**.*

Complex **3** was synthesized in a similar manner as described for complexes **1** and **2**. A pale-blue methanol solution (2 mL) of Cu(II) acetate monohydrate (2.2 mg, 0.011 mmol) was added dropwise to a pale-yellow methanol solution (4 mL) of HL^3 (7.8 mg, 0.022 mmol) at room temperature. The color of the mixing solution turned to yellow immediately then turned to brown slowly and the filtrate was allowed to stand at room temperature for about two weeks. Single crystals suitable for X-ray structural determination were obtained by the slow evaporation from methanol solution. Anal. calcd. for $[Cu(L^3)_2]$ ($C_{24}H_{12}Br_2Cl_4CuN_4O_2$) (%): C, 38.3; H, 1.6; N, 7.4; Cu, 8.4. Found: C, 38.1; H,1.5; N, 7.5, Cu, 8.4.

TABLE 1
Crystal data and structure refinement for complexes **1**, **2**, and **3**

	Complex **1**	Complex **2**	Complex **3**
Empirical formula	$C_{24}H_{12}Cl_6CuN_4O_2$	$C_{24}H_{12}Br_4Cl_2CuN_4O_2$	$C_{24}H_{12}Br_2Cl_4CuN_4O_2$
Formula weight	664.62	842.46	753.54
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/c$	$P2/c$	$P2/c$
Unit cell dimensions			
a (Å)	12.975(2)	13.130(2)	12.975(1)
b (Å)	8.5647(8)	8.688(1)	8.681(1)
c (Å)	12.953(1)	13.094(2)	12.924(1)
α (°)	90	90	90
β (°)	119.424(1)	119.095(2)	118.921(2)
γ (°)	90	90	90
Volume (Å^3)	1253.7(2)	1305.2(3)	1274.2(2)
Z, D_{calc}(Mg/m^3)	2, 1.761	2, 2.144	2, 1.964
μ (mm^{-1})	1.543	7.196	4.445
F (000)	662	806	734
Crystal size (mm)	0.26 × 0.24 × 0.11	0.23 × 0.20 × 0.10	0.18 × 0.17 × 0.07
θ (°)	1.81 to 25.02	1.77 to 25.01	1.79 to 25.02
Limiting indices	$-8 \le h \le 15, -10 \le k \le 9, -15 \le l \le 15$	$-10 \le h \le 15, -10 \le k \le 9, -15 \le l \le 7$	$-15 \le h \le 12, -10 \le k \le 9, -10 \le l \le 15$
Reflections collected /unique	6100/2129 [R_{int} =0.0284]	6329/2299 [R_{int} =0.0643]	6470/2256 [R_{int} =0.0338]
Completeness to θ	25.02, 99.9 %	25.01, 99.7 %	25.02, 100.0 %
Max. & min. transmission	0.8486, 0.6897	0.5331, 0.2884	0.7461, 0.5017
Refinement method	Full-matrix least-squares on F^2	Full-matrix least- squares on F^2	Full-matrix least- squares on F^2
Data/restraints/parameters	2229/0/168	2299/0/168	2256/0/168
GOF on F^2	1.040	0.984	0.988
R_1, wR_2 [$I > 2\sigma(I)$]	0.0310, 0.0644[a]	0.0466, 0.1141[b]	0.0267, 0.0640[c]
R_1, wR_2 (all data)	0.0485, 0.0774	0.0666, 0.1267	0.0367, 0.0670
Largest diff. peak and hole (eÅ^{-3})	0.313, –0.326	1.059, –1.257	0.476, –0.487
CCDC NO.	757716	757715	757714

[a]w = $1/[\sigma^2(F_o^2) + (0.027P)^2 + 1.2614P]$, [b]w = $1/[\sigma^2(F_o^2) + (0.0708P)^2]$, [c]w = $1/[\sigma^2(F_o^2) + (0.0379P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$

Data Collection, Structure Determination, and Refinement

Diffraction intensities for the complexes **1**, **2** and **3** were collected at 298(2) K using a Bruker SMART APEX II CCD area-detector with MoKα radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,[13] and multi-scan absorption corrections were performed using the SADABS program.[14] The structures were solved by direct method and refined against F^2 by full-matrix least-squares method using the SHELXTL program.[15] All of the non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically (C–H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.20\ U_{eq}(C)$. The crystallographic data and experimental parameters relevant to the structure determination for the complexes **1**, **2**, and **3** are summarized in Table 1.

RESULTS AND DISCUSSION

By the condensation of the aldehydes with primary amines, it can readily give rise to the corresponding Schiff base compounds, which were easily identified by their IR spectra, where replacement of the carbonyl by the imine group results in lowering of the energy of the $\nu_{(C=0)}$ stretch. The Schiff bases prepared in this way are formed in nearly quantitative yields and are of high purity. The results of the elemental analyses are in accord with the composition suggested for the Schiff base ligands and the three Cu(II) complexes.

Molar Conductances

Complexes **1**, **2**, and **3** are soluble in DMF and DMSO, slightly soluble in $CHCl_3$, but not soluble in DCM, EtOH,

TABLE 2
The most important FT-IR bands for the ligands and their complexes (cm^{-1})

Compound	$\nu_{(O-H)}$	$\nu_{(C=N)}$	$\nu_{(Ar-O)}$	$\nu_{(Cu-N)}$	$\nu_{(Cu-O)}$	$\nu_{(C=C)}$ benzene ring skeleton
HL^1	3433	1618	1215, 1198	–	–	1554, 1448, 1404
Complex **1**	–	1601	1211, 1193	474	430	1566, 1414, 1441
HL^2	3425	1622	1245, 1200	–	–	1553, 1441, 1421
Complex **2**	–	1597	1215, 1194	473	440	1564, 1503, 1435
HL^3	3437	1618	1213, 1197	–	–	1553, 1444, 1402
Complex **3**	–	1598	1211, 1194	472	422	1564, 1506, 1435

MeOH, MeCN, THF, acetone, and ethyl acetate. All complexes display good stability in air at room temperature. Meanwhile, three ligands (HL^1, HL^2, and HL^3) are soluble in aforementioned solvents. Molar conductance values of complexes **1**, **2**, and **3** of 1.0×10^{-3} mol · L^{-1} DMF solutions are 3.3, 2.7 and 2.6 S · cm^2· mol^{-1}, respectively, indicating these complexes are non-electrolytes.

IR Spectra Analyses

Some important IR absorption bands are listed in Table 2. The IR spectra of the free ligands and their corresponding Cu(II) complexes show characteristic C=N stretching bands. For the free ligand HL^1, HL^2, and HL^3, the bands appear at 1618, 1622, and 1618 cm^{-1}, respectively, while the C=N bands of complexes **1**, **2**, and **3** are observed at 1601, 1597, and 1598 cm^{-1}, respectively. The frequency towards to lower wavenumbers of the C=N absorption shift by *ca.* 17 ∼ 25 cm^{-1} because of the behavior between the free ligands and the corresponding complexes resulting in weakening the force constant of C=N bond.

The Ar–O stretching frequencies appear as a strong band within the 1245 ∼ 1193 cm^{-1} range, and the toward lower wavenumbers of the Ar–O absorption shift by 2 ∼ 30 cm^{-1}indicating that Cu–O bonds are formed between the Cu(II) ions and the oxygen atoms of the phenolic groups.[16–17] In addition, the broad OH group absorption bands centered at 3433, 3425, and 3437 cm^{-1} in the free ligands HL^1, HL^2 and HL^3, however, in the spectra of complexes **1**, **2**, and **3** disappear, further demonstrating the coordination of deprotonated phenolic oxygen atom to copper ions.

The IR spectra of complexes **1**, **2**, and **3** in the region of 500 ∼ 100 cm^{-1} show ν(Cu—N) (or ν(Cu—O)) vibrational absorption frequencies at 474, 472, and 473 (or 430, 440, and 422) cm^{-1}, respectively.[18–19] These bands are not observed in the spectra of corresponding free ligands HL^1, HL^2 and HL^3.

UV–Vis Spectra Analyses

The most UV–Vis spectra data of the ligands and complexes **1**, **2**, and **3** are shown in Table 3. The UV–Vis spectrum of the free ligand HL^1 exhibit three absorption peaks at ca. 258, 307, and 426 nm (248, 306, and 427 nm for HL^2 and 265, 308, and 428 nm for HL^3), respectively. The first absorption peak at 258 nm can be assigned to the π–π* transition of the benzene rings, the second one at 307 nm can be assigned to the intra-ligand π–π* transition of the C=N bonds, and the third one at 426 nm can be attributed to the n–π* transition in the free ligand.

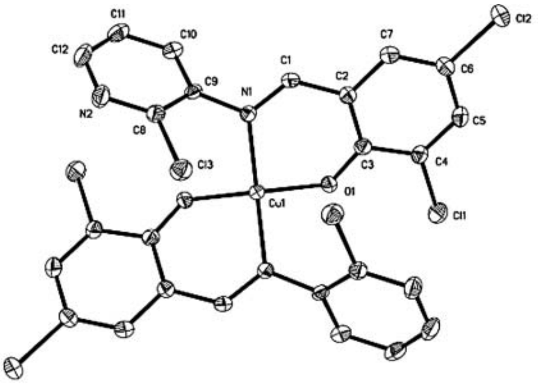
Compared with the absorption peaks of the free ligands, the corresponding absorption peaks at 254, 284, and 400 nm are observed in complex **1** (244, 283, and 401 nm for complex **2** and 263, 283, and 401 nm for complex **3**). Obviously, hypsochromic shifts of three absorption peaks are ca. 2 ∼ 4, 23 ∼ 25, and 26 ∼ 27 nm, respectively. The first value of blue shift is small but the other two ones are considerable larger up to 25 nm, indicating the coordination of Cu^{II} ions with free ligands via azomethine nitrogen and phenolic oxygen atoms.

Descriptions of Crystal Structures

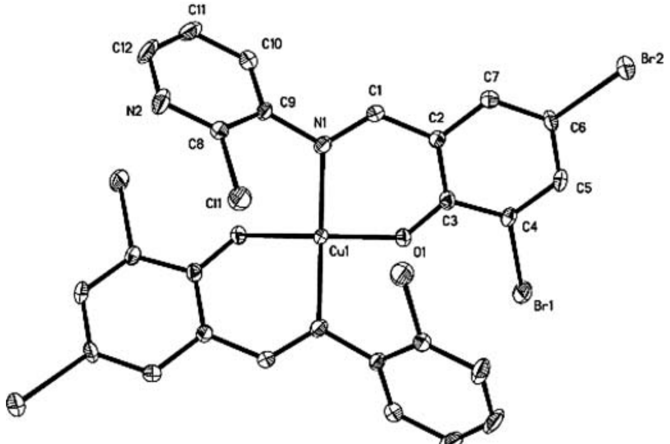
The X-ray structural studies reveal that the formation of metal complexes **1**, **2**, and **3** have 2:1 ligand to metal stoichiometries, and three complexes all crystallize in the monoclinic system and *P*2/*c* space group. In all cases, the copper atom is bonded to the oxygen and nitrogen donor atoms of the two ligand molecules in a *trans* arrangement in which the copper ion is four coordinated. The molecular structures of complexes **1**, **2**, and **3** are illustrated in Figure 1, and relevant bond lengths and angles are summarized in Table 4. Three centrosymmetric copper complexes, existing two-fold axes passing through the copper atom, all have tetrahedron geometries with some distortion around the central copper atoms, as shown in Figure. 2, which are different from the copper complexes coordinated by single-substituent ligands

TABLE 3
The UV–Vis bands for the ligands and their complexes (nm)

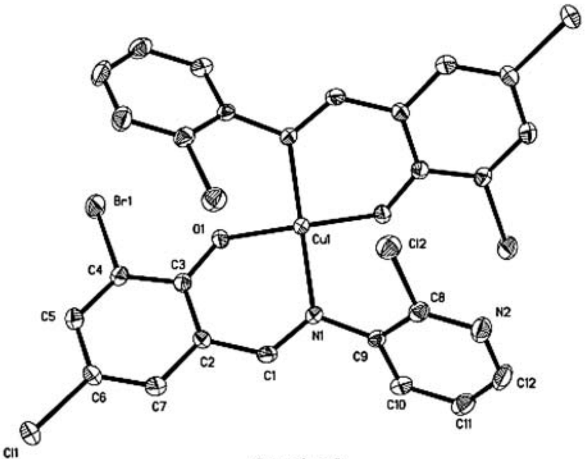
Compound	λ_1	λ_2	λ_3
HL^1	258	307	426
Complex **1**	254	284	400
HL^2	248	306	427
Complex **2**	244	283	401
HL^3	265	308	428
Complex **3**	263	283	401



Complex 1



Complex 2



Complex 3

FIG. 1. The ORTEP views of the crystal structure with thermal ellipsoids were drawn at the 30% probability for complexes **1**, **2**, and **3** and hydrogen atoms have been omitted for clarity.

TABLE 4
The selected bond lengths (Å) and bond angles (°) for complexes **1**, **2**, and **3**

Bond distance		Bond angle	
		Complex **1**	
Cu(1)–O(1)$^{\#1}$	1.892(2)	O(1)$^{\#1}$–Cu(1)–O(1)	145.4(1)
Cu(1)–O(1)	1.892(2)	O(1)$^{\#1}$–Cu(1)–N(1)$^{\#1}$	93.93(9)
Cu(1)–N(1)$^{\#1}$	1.975(2)	O(1)–Cu(1)–N(1)$^{\#1}$	94.23(9)
Cu(1)–N(1)	1.975(2)	O(1)$^{\#1}$–Cu(1)–N(1)	94.23(9)
		O(1)–Cu(1)–N(1)	93.93(9)
		N(1)$^{\#1}$–Cu(1)–N(1)	152.3(1)
		Complex **2**	
Cu(1)–O(1)$^{\#2}$	1.893(4)	O(1)$^{\#2}$–Cu(1)–O(1)	146.1(2)
Cu(1)–O(1)	1.893(4)	O(1)$^{\#2}$–Cu(1)–N(1)$^{\#2}$	93.7(2)
Cu(1)–N(1)$^{\#2}$	1.990(5)	O(1)–Cu(1)–N(1)$^{\#2}$	94.6(2)
Cu(1)–N(1)	1.990(5)	O(1)$^{\#2}$–Cu(1)–N(1)	94.6(2)
		O(1)–Cu(1)–N(1)	93.7(2)
		N(1)$^{\#2}$–Cu(1)–N(1)	151.5(3)
		Complex **3**	
Cu(1)–O(1)	1.889(2)	O(1)–Cu(1)–O(1)$^{\#3}$	145.6(1)
Cu(1)–O(1)$^{\#3}$	1.889(2)	O(1)–Cu(1)–N(1)	93.58(8)
Cu(1)–N(1)	1.979(2)	O(1)$^{\#3}$–Cu(1)–N(1)	94.80(9)
Cu(1)–N(1)$^{\#3}$	1.979(2)	O(1)–Cu(1)–N(1)$^{\#3}$	94.80(9)
		O(1)$^{\#3}$–Cu(1)–N(1)$^{\#3}$	93.58(8)
		N(1)–Cu(1)–N(1)$^{\#3}$	151.4(1)

Symmetry transformations used to generate equivalent atoms: #1, #2, and #3 all are –x+1, y, –z+1/2 for complex **1**, **2**, and **3**, respectively.

on the aromatic ring, showing lightly distorted square-planar coordination spheres.[20–21] Besides, in the analogous $\{$2-[1-(2,6-diethylphenylimino)ethyl]phenoxy$\}_2$Cu(II), $\{$2-[1-(2,6-dimethyl-phenylimino)ethyl]phenoxy$\}_2$Cu(II) and $\{$2-[1-(2-methylphenylimino)ethyl]phenoxy$\}_2$Cu(II) complexes where a phenyl substituent is attached to the imine nitrogen,[22] the geometry is square planar too. By contrast, the geometry of bis-bidentate Schiff base copper(II) complexes can be the result of steric and electronic effects, which result in various intermediate geometries between square planar and tetrahedral.[23–25] Furthermore, each crystal unit of three complexes is consisting of one divalence Cu(II) ions and two deprotonated N, O-bidentate L$^-$ units.

The coordination environment around the central Cu(II) ion is tetra-coordinated by two imino nitrogen atoms (N1 and N1$^\#$) and two deprotonated phenolic oxygen atoms (O1 and O1$^\#$) from two deprotonated L$^-$ units. The coordination spheres of complexes **1**, **2**, and **3** (bond lengths and angles) are compared in Table 4, and found rather similar. A slight shortening of the Cu-O bond lengths is observed on passing from complexes **1** $\sim$ **3**. These structural features, which favor steric hindrance of the L$^-$ fragments, can account for the distortion of the ligands in the complexes. Indeed, the dihedral angels between two metal chelating rings (the plane defined by Cu1N1O1C1C2C3 and the other plane defined by Cu1N1$^\#$O1$^\#$C1$^\#$C2$^\#$C3$^\#$) for complexes **1**, **2**, and **3** are 42.83(2), 43.96(4), and 44.86(3)°, respectively. The six membered chelate ring formed through O1 and N1 shows a fold about the O1$\cdots$N1 vector and Cu1 are displaced *ca* 0.400, 0.418, and 0.435 Å for respective complexes **1**, **2**, and **3** from their corresponding mean-plane of the O1–C1–C2–C3–N1 group. These observations suggest a variety negative, versus that of the free HL ligand.

The coordinated bonds Cu1–N1 and Cu1–O1 in complexes **1** ∼ **3**, have similar lengths and are in the same range to those reported for similar Bis{(*E*)-4-bromo-2-[(2-chloro-3-pyridyl)- iminomethyl]phenolato-$\kappa^2 N, O$} copper(II) and Bis{(*E*)-4-chloro-2-[(2-chloro-3-pyridyl)imino-methyl-κN]phenolato-κO} copper(II) complexes, i.e., Cu–N distances in the range 1.972(3) to 1.994(3) Å, while Cu–O distances have values between 1.882(2) to 1.897(3) Å.[20–21] Owing to the presence of the distortion the for ∠N–Cu–O bond angles at the copper center in all complexes are also marginally different from the ideal value of 90° [O(1)–Cu(1)–N(1) and O(1)$^{\#}$–Cu(1)–N(1) are 93.93(9)° and 94.23(9)° for complex **1**; 93.7(2)° and 94.6(2)° for complex **2**; 93.58(8)° and 94.80(9)° for complex **3**], while the diagonal angles [O(1)$^{\#}$–Cu(1)–O(1) and N(1)$^{\#1}$–Cu(1)–N(1) are 145.4.1(1)° and 152.3(1)° for complex **1**; 146.1(2)° and 151.5(3)° for complex **2**; 145.6(1)° and 151.4(1)° for complex **3**] are also significantly deviated from the expected value of 180°. It is worthy to note that there exist similar bond distances and bond angles among three copper complexes, suggesting the different substituted groups on the aromatic ring having almost no effect on the coordination of the copper complexes. Interestingly, the dihedral angels between aromatic ring and pyridine ring for complexes **1**, **2**, and **3** are 70.64(3), 71.73(2), and 73.05(5)°, respectively, indicating that substituted pyridine group in the complexes have a weaker steric crowding in order to form centrosymmetric compounds.

For complex **1**, as shown in Figure 3, four pairs of intermolecular C–H· · ·Cl, C–H· · ·O and C–H· · ·N hydrogen bonds (Table 5) linked adjacent four complex **1** molecule units into a tetra-polymeric structure. Besides, a pair of C12–H12· · ·Br2 hydrogen bonding interaction between carbon of the pyridine ring and the substituted chlorine group on the aromatic ring produces a twenty-six membered ring with a graph motif of $R_2^2(26)$. Two intermolecular C10–H10· · ·O1 and C11–H11· · ·O1 hydrogen bonds between aromatic carbon and phenolic oxygen also form a seven membered ring with a graph motif of $R_2^2(7)$. Furthermore, a pair of C1–H1· · ·N2 hydrogen bonds between azomethine carbon and pyridine nitrogen also form a twelve-membered ring with a graph motif of $R_2^2(12)$. Above-mentioned hydrogen bonds play an import role in stabilizing the crystal structure. In conclusion, with the help of hydrogen bonds and van der Waals forces, the packing diagrams of complex **1** show a network-like structure along the *b* axis, and form an intramolecular hexagon cave occupying the central position of the unit cell between neighboring molecular layers via carbon atom and chlorine atom along the *c* axis, as illustrated in Figure 4.

For complex **2**, in Figure 5, three pairs of intermolecular C–H· · ·Br, C–H· · ·O and C–H· · ·N hydrogen bonds (Table 5) linked adjacent other four complex **2** molecule units into a tetra-polymeric structure. Similar to complex **1**, two pairs of C12–H12· · ·Br2 and C1–H1· · ·N2 hydrogen bonds can also

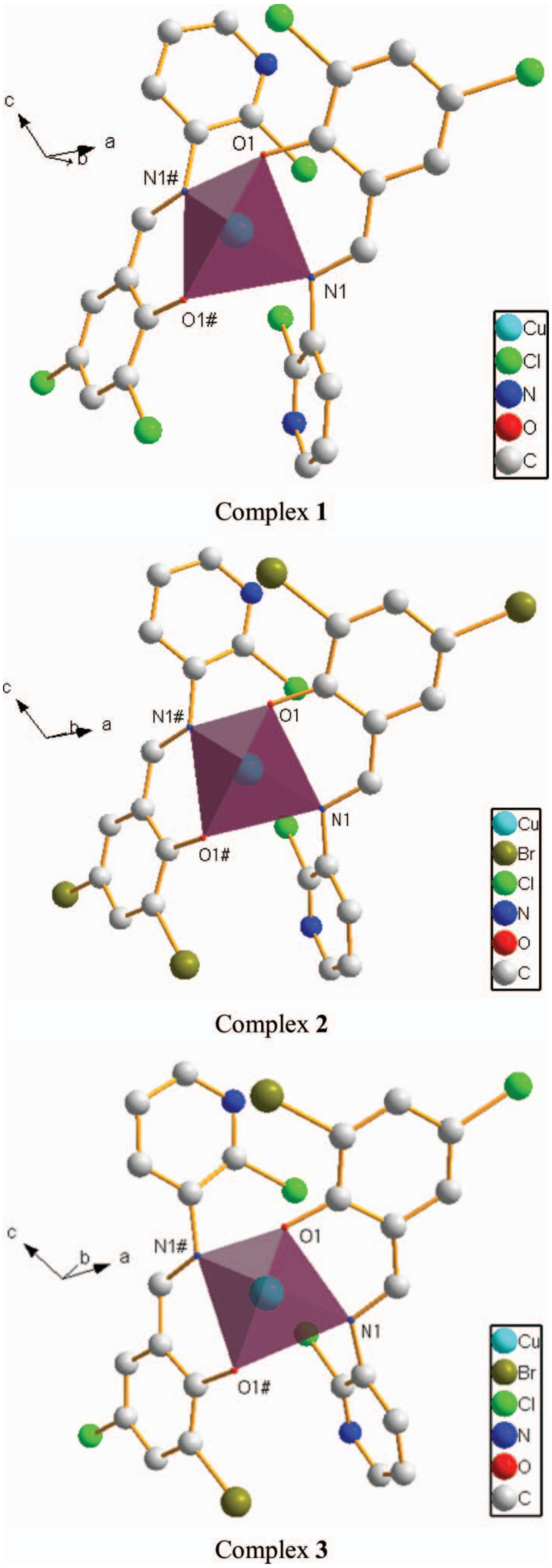


FIG. 2. The diagrams showing the coordination geometries around the Cu ion for complexes **1**, **2**, and **3**. (Figure is provided in color online.)

TABLE 5
Hydrogen bonding distances (Å) and bond angles (°) for three complexes

D–H· · ·A	D–H	H· · ·A	D· · ·A	D–H· · ·A	Symmetry code
Complex **1**					
C1–H1· · ·N2	0.93	2.80	3.176 (4)	106	1 − x, 1 − y, −z
C10–H10· · ·O1	0.93	2.66	3.513 (4)	152	x, −y, −1/2 + z
C11–H11· · ·O1	0.93	2.62	3.457 (4)	150	1 − x, −y, −z
C12–H12· · ·Cl2	0.93	2.83	3.733 (3)	165	−1 + x, y, −1 + z
Complex **2**					
C12–H12· · ·Br2	0.93	2.96	3.874 (4)	169	−1 + x, y, −1 + z
C1–H1· · ·N2	0.93	2.80	3.203 (7)	108	1 − x, 1 − y, −z
C11–H11· · ·O1	0.93	2.68	3.514 (7)	150	1 − x, − y, −z
Complex **3**					
C1–H1· · ·N2	0.93	2.77	3.164 (4)	107	1 − x, 2 − y, 1 − z
C10–H10· · ·O1	0.93	2.71	3.558 (3)	152	x, 1 − y, 1/2 + z
C11–H11· · ·O1	0.93	2.64	3.464 (4)	148	1 − x, 1 − y, 1 − z
C12–H12· · ·Cl1	0.93	2.88	3.798 (3)	170	1 + x, y, 1 + z

described as graph motifs of $R_2^2(26)$ and $R_2^2(12)$. Furthermore, a pair of C10–H10· · ·O1 hydrogen bonds between aromatic carbon and phenolic oxygen produce an eighteen membered ring with a graph-motif of $R_2^2(18)$. As shown in Figure 6, the packing diagram of complex **2** shows the stacking structures is similar to those of complex **1**.

For complex **3**, as shown in Figure 7, four pairs of intermolecular C–H· · ·Cl, C–H· · ·O and C–H· · ·N hydrogen bonds

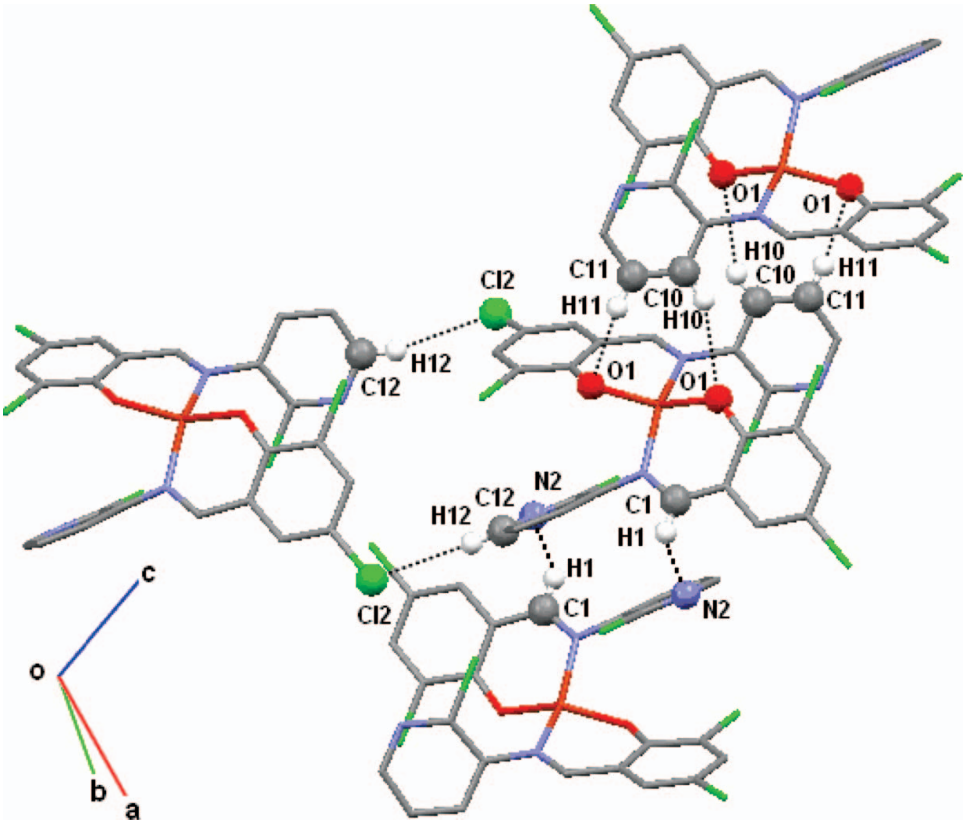


FIG. 3. The diagram showing intermolecular hydrogen bonds in complex **1.** (Figure is provided in color online.)

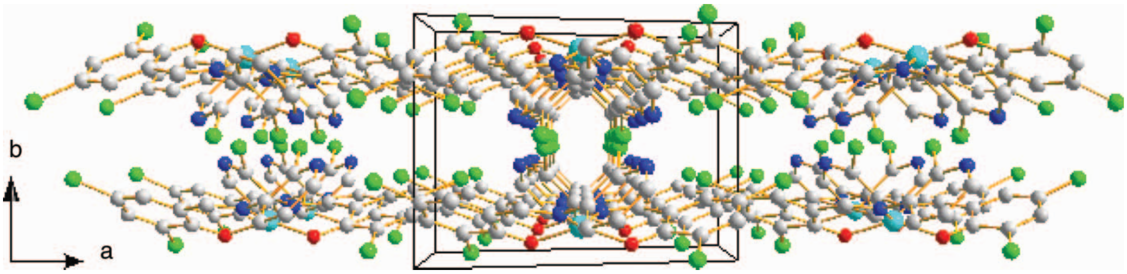


FIG. 4. The packing diagram along the *c*-axis for complex **1.** (Figure is provided in color online.)

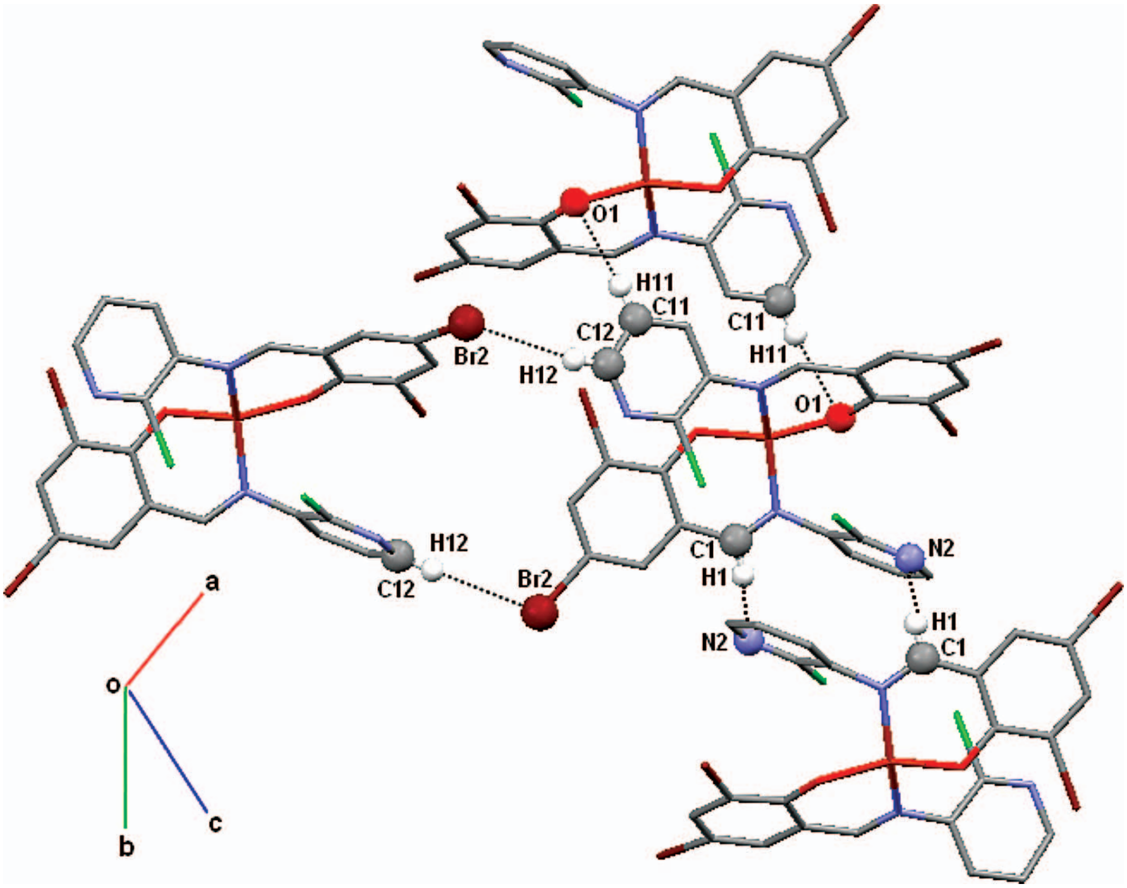


FIG. 5. The diagram showing intermolecular hydrogen bonds in complex **2.** (Figure is provided in color online.)

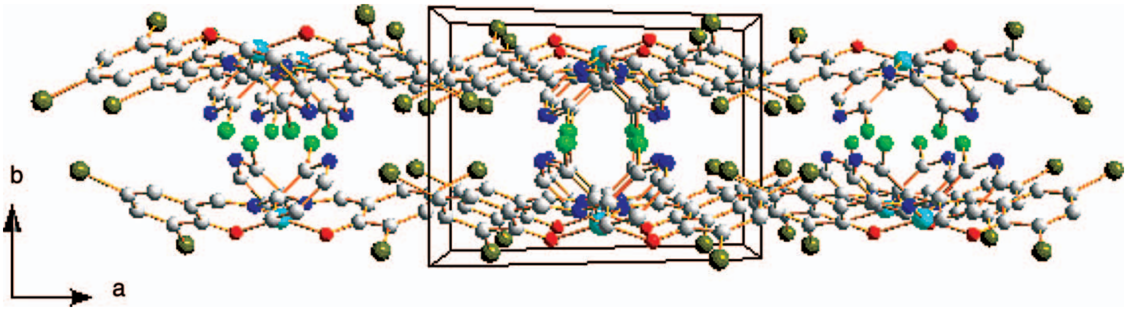


FIG. 6. The packing diagram along the *c*-axis for complex **2.** (Figure is provided in color online.)

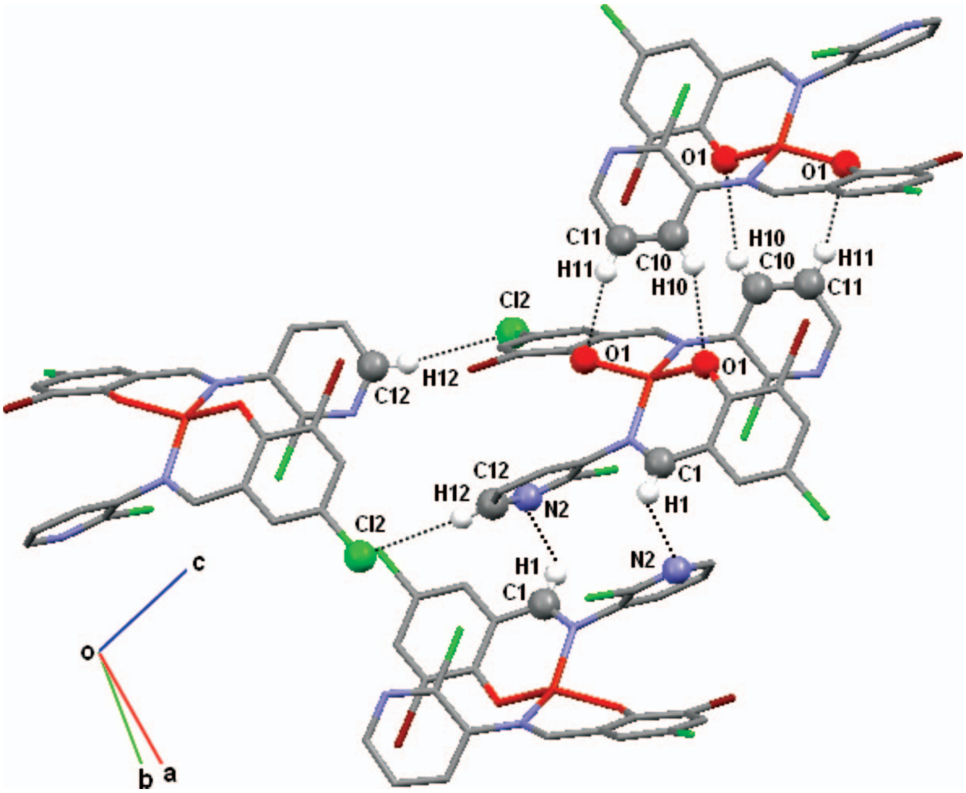


FIG. 7. The diagram showing intermolecular hydrogen bonds in complex **3.** (Figure is provided in color online.)

(Table 5) also linked adjacent four complex **3** molecule units into a tetra-polymeric structure. Similar to complexes **1** and **2**, two pairs of C12–H12· · ·Br2 and C1–H1· · ·N2 hydrogen bonds can be described as graph motifs of $R_2^2(26)$ and $R_2^2(12)$. Meanwhile, intermolecular C10–H10· · ·O1 and C11–H11· · ·O1 hydrogen bonding interactions between aromatic carbon and phenolic oxygen produce a seven membered ring with a graph-motif of $R_2^2(7)$. The packing diagram of complex **3** also shows an infinite regular network structure along the *b* axis, and form a centrosymmetric rectangle-like large cave structure via carbon, oxygen, bromine, and copper atoms along the *c* axis of the unit cell, as shown in Figure 8.

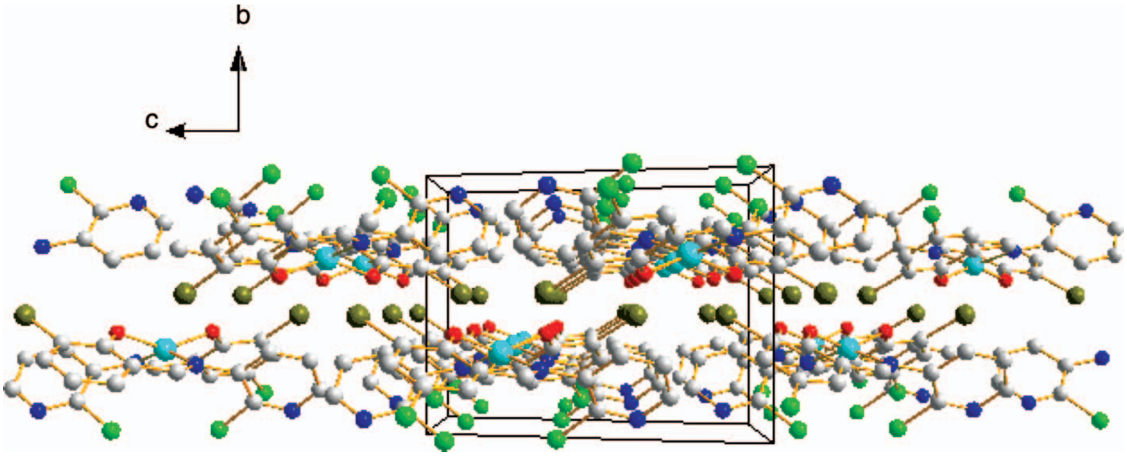


FIG. 8. The packing diagram along the *c*-axis for complex **3.** (Figure is provided in color online.)

CONCLUSION

In a summary, a series of new three copper complexes, bearing a 2:1 ligand:metal stoichiometry, have been synthesized from respective ligands, 2,4-dichloro-6-[(2-chloro-3-pyridyl)iminomethyl]phenol (HL^1), 2,4-dibromo-6-[(2-chloro-3-pyridyl)iminomethyl]phenol (HL^2) and 2-bromo-4-chloro-6-[(2-chloro-3-pyridyl)iminomethyl]phenol (HL^3), by the reactions with $Cu(OAc)_2 \cdot H_2O$ in moderate to high yields. It is interesting that each copper metal in three complexes is tetracoordinated by two Schiff base ligands and the distance of Cu–N is longer than that of Cu–O. Besides, there exist many hydrogen bonds that link adjacent molecules into polymeric structure showing many cavities. However, the substituted groups on the aromatic ring or pyridyl ring could play a small impact on the coordination geometries.

SUPPLEMENTARY MATERIALS

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, No. CCDC 757716, 757715 and 757714 for complexes **1**, **2**, and **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Telephone: (44) 01223 762910; Fax: +44-1223-3360 33; E-mail: deposit@ccdc.cam.ac.uk). These data can be also obtained free of charge at www.ccdc.cam. ac.uk/conts/retrieving.htm

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