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Synthesis and Crystal Structures of Schiff Base Copper(II) Complexes $[Cu(L^1)(NCS)]$, $[CuBr(L^2)]$, and $[CuCl(L^3)]$[1]

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Abstract—A series of copper(II) complexes, $[Cu(L^1)(NCS)]$ (**I**), $[CuBr(L^2)]$ (**II**), and $[CuCl(L^3)]$ (**III**), where L^1, L^2, and L^3 are 2,4-dibromo-6-[(pyridin-2-ylmethylimino)methyl]phenolate, 4-chloro-2-[(pyridin-2-ylmethylimino)methyl]phenolate, and 1-[(pyridin-2-ylmethylimino)methyl]-naphthalen-2-ol, respectively, were prepared. The complexes were characterized by elemental analysis, IR spectra, and single crystal X-ray determination. The crystals of the three complexes crystalize in the monoclinic space group $P2_1/n$. For **I**, $a = 8.127(2)$, $b = 13.077(3)$, $c = 14.967(3)$ Å, $\beta = 91.975(2)°$, $V = 1589.8(6)$ Å^3, $Z = 4$. For **II**, $a = 7.736(2)$, $b = 10.613(2)$, $c = 16.199(3)$ Å, $\beta = 91.130(2)°$, $V = 1329.8(5)$ Å^3, $Z = 4$. For **III**, $a = 8.062(2)$, $b = 8.599(2)$, $c = 21.087(2)$ Å, $\beta = 100.338(2)°$, $V = 1438.1(4)$ Å^3, $Z = 4$. The Cu atom in each of the complexes is in square planar geometry.

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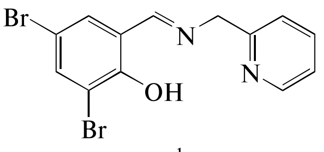
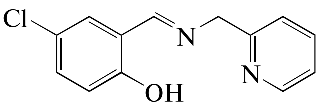
INTRODUCTION

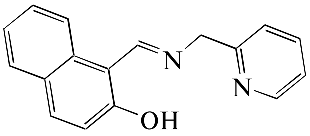
Transition metal complexes with Schiff bases are considered to be among the most important stereochemical models in coordination chemistry due to their preparative accessibility and structural variety [1–3]. The halide and pseudohalide anions are widely used co-ligands for the construction of complexes with Schiff bases [4–7]. In the present paper, a series of three new mononuclear copper(II) complexes, $[CuL^1(NCS)]$ (**I**), $[CuBrL^2]$ (**II**), and $[CuClL^3]$ (**III**), where L^1, L^2, and L^3 are 2,4-dibromo-6-[(pyridin-2-ylmethylimino)methyl]phenolate (HL^1), 4-chloro-2-[(pyridin-2-ylmethylimino)methyl]phenolate (HL^2), and 1-[(pyridin-2-ylmethylimino)methyl]-naphthalen-2-ol (HL^3), respectively, were prepared and characterized.



(HL^1)



(HL^2)



(HL^3)

EXPERIMENTAL

Materials and methods. 3,5-Dibromosalicylaldehyde, 5-chlorosalicylaldehyde, 2-hydroxy-1-naphthaldehyde, and 2-aminomethylpyridine were purchased from Alfa Aesar. All other chemicals and solvents were of analytical grade and used as obtained. The Schiff bases were prepared according to the literature method [8]. Microanalyses of the Schiff bases and the copper complexes were performed with a Vario EL III CHNOS elemental analyzer. The infrared spectra were recorded as KBr pellets with an FTS-40 spectrophotometer.

Synthesis of I. A stirred solution of HL^1 (0.370 g, 1 mmol) and ammonium thiocyanate (0.076 g, 1 mmol) in absolute methanol (20 mL) was mixed with copper perchlorate (0.389 g, 1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h and then cooled to room temperature, yielding a blue solution. The solution was stand still at ambient temperature to slow evaporation of the solvent, yielding deep blue crystals of **I**. The yield was 0.323 g (66%).

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for complexes **I**–**III**

Parameter	Value		
	I	**II**	**III**
Formula weight	490.7	389.1	360.3
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Crystal size, mm	0.17 × 0.15 × 0.15	0.18 × 0.17 × 0.17	0.22 × 0.21 × 0.18
a, Å	8.127(2)	7.736(2)	8.062(2)
b, Å	13.077(3)	10.613(2)	8.599(2)
c, Å	14.967(3)	16.199(3)	21.087(2)
β, deg	91.975(2)	91.130(2)	100.338(2)
V, Å	1589.8(6)	1329.8(5)	1438.1(4)
Z	4	4	4
ρ_{calcd}, g cm^{-3}	2.050	1.944	1.664
μ, mm^{-1}	6.534	4.838	1.706
F(000)	948	764	732
θ Range, deg	2.72–26.00	2.29–26.00	2.56–26.00
Index ranges	$-10 \le h \le 10$,	$-9 \le h \le 9$,	$-9 \le h \le 9$,
	$-16 \le k \le 14$,	$-13 \le k \le 13$,	$-10 \le k \le 10$,
	$-18 \le l \le 18$	$-19 \le l \le 19$	$-26 \le l \le 25$
Measured reflections	11563	9675	10429
Independent reflections (R_{int})	3108(0.0572)	2606(0.0493)	2824
Observed reflections ($I > 2\sigma(I)$)	1820	1860	2183(0.0460)
Parameters	199	172	199
Absorption correction	Multiscan	Multiscan	Multiscan
GOOF on F^2	0.992	1.053	1.050
$R(I \ge 2\sigma(I))$	$R_1 = 0.0404$,	$R_1 = 0.0474$,	$R_1 = 0.0378$,
	$wR_2 = 0.0689$	$wR_2 = 0.1147$	$wR_2 = 0.0861$
R (all data)	$R_1 = 0.962$,	$R_1 = 0.0732$,	$R_1 = 0.0555$,
	$wR_2 = 0.0829$	$wR_2 = 0.1261$	$wR_2 = 0.0958$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.488/–0.425	0.863/–0.701	0.457/–0.324

Selected IR data (KBr; ν_{max}, cm^{-1}): 1606 (C=N), 2083 (NCS).

For $C_{14}H_9N_3OSBr_2Cu$

anal. calcd., %:	C, 34.3;	H, 1.8;	N, 8.6.
Found, %:	C, 34.2;	H, 1.9;	N, 8.5.

Synthesis of II. A stirred solution of HL^2 (0.247 g, 1 mmol) in absolute methanol (20 mL) was mixed with copper bromide (0.223 g, 1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h and then cooled to room temperature, yielding a blue solution. The solution was stand still at ambient temperature to slow evaporation of the solvent, yielding deep blue crystals of **II**. The yield was 0.210 g (54%).

Selected IR data (KBr; ν_{max}, cm^{-1}): 1604 (C=N).

For $C_{13}H_{10}N_2OClBrCu$

anal. calcd., %:	C, 40.1;	H, 2.6;	N, 7.2.
Found, %:	C, 39.9;	H, 2.6;	N, 7.3.

Synthesis of III. A stirred solution of HL^3 (0.262 g, 1 mmol) in absolute methanol (20 mL) was mixed with copper chloride (0.170 g, 1 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h and then cooled to room temperature, yielding a blue solution. The solution was stand still at ambient temperature to slow evaporation of the solvent, yielding deep blue crystals of **III**. The yield was 0.187 g (52%).

Selected IR data (KBr; ν_{max}, cm^{-1}): 1601 (C=N).

For $C_{17}H_{13}N_2OClCu$

anal. calcd, %:	C, 56.7;	H,3.6;	N, 7.8.
Found, %:	C, 56.5;	H,3.7;	N, 7.7.

X-ray structure determination. Data were collected on a Bruker SMART 1000 CCD area diffractometer using a graphite monochromator and MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The data were corrected with the SADABS programs and refined on F^2 with the Siemens SHELXL software [9, 10]. The structures were solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the last cycles of refinement. Crystal data and details of the data collection and refinement are listed in Table 1. Selected coordination bond lengths and angles are listed in Table 2.

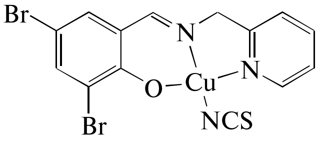
Supplementary material for structures **I**, **II**, and **III** has been deposited with the Cambridge Crystallographic Data Centre (nos. 860406 (**I**), 860407 (**II**), and 860408 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I–III**

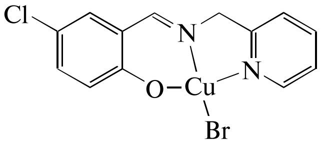
Bond	*d*, Å	Bond	*d*, Å
	I		
Cu(1)–O(1)	1.887(4)	Cu(1)–N(1)	1.924(4)
Cu(1)–N(2)	1.986(4)	Cu(1)–N(3)	1.927(5)
	II		
Cu(1)–O(1)	1.905(4)	Cu(1)–N(1)	1.962(4)
Cu(1)–N(2)	2.009(4)	Cu(1)–Br(1)	2.4095(10)
	III		
Cu(1)–O(1)	1.886(2)	Cu(1)–N(1)	1.943(2)
Cu(1)–N(2)	2.000(3)	Cu(1)–Cl(1)	2.2317(11)
Angle	ω, deg	Angle	ω, deg
	I		
O(1)Cu(1)N(1)	92.89(16)	O(1)Cu(1)N(3)	88.29(17)
N(1)Cu(1)N(3)	171.19(18)	O(1)Cu(1)N(2)	175.04(17)
N(1)Cu(1)N(2)	82.76(18)	N(3)Cu(1)N(2)	96.37(19)
	II		
O(1)Cu(1)N(1)	91.93(17)	O(1)Cu(1)N(2)	174.01(17)
N(1)Cu(1)N(2)	82.59(18)	O(1)Cu(1)Br(1)	89.51(11)
N(1)Cu(1)Br(1)	178.17(13)	N(2)Cu(1)Br(1)	95.93(13)
	III		
O(1)Cu(1)N(1)	91.58(9)	O(1)Cu(1)N(2)	173.65(10)
N(1)Cu(1)N(2)	82.95(10)	O(1)Cu(1)Cl(1)	89.78(7)
N(1)Cu(1)Cl(1)	176.93(8)	N(2)Cu(1)Cl(1)	95.83(8)

RESULTS AND DISCUSSION

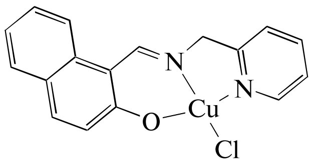
The overview of the three complexes is given below:



(I)



(II)



(III)

The complexes were readily prepared by the reaction of equimolar quantities of the Schiff base ligands with copper salts in absolute methanol. For the preparation of **I**, ammonium thiocyanate was added. The Schiff base ligands coordinate to the Cu atoms through all the thee donor atoms. Even though the Cl, Br and NCS groups readily bridge different metal atoms, forming versatile polymeric structures, in this work, they act as simple terminal ligands.

The crystal structures of **I**, **II**, and **III** with atom numbering scheme are shown in Fig. 1. The comounds are mononuclear copper(II) complexes. The Cu atom in each complex is coordinated by the Schiff base ligand and one terminal secondary ligand, viz. NCS for **I**, Br for **II**, and Cl for **III**. The Schiff base ligand coordinates to the Cu atom through the phenolate oxygen, imine nitrogen, and pyridine nitrogen atoms, forming a five- and a six-membered chelate rings. The Cu atom is in a square planar coordination sphere. The displacement of the Cu atom from the least-squares plane defined by the four donor atoms is 0.0564 Å for **I**, 0.0316 Å for **II**, and 0.0008 Å for **III**, indicating the well planarity of the square planar coordination. The bond lengths and angles in the three complexes are comparable to each other and within normal values [11–13]. The *cis* coordinate

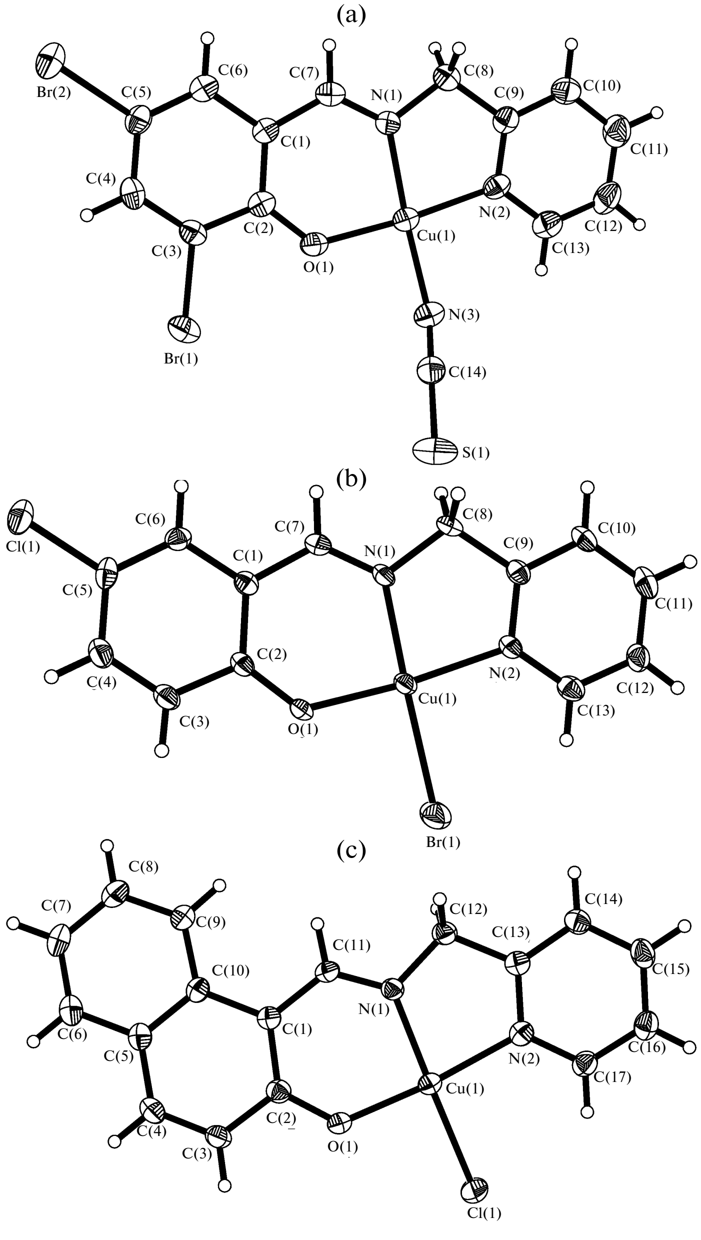


Fig. 1. ORTEP plots (30% probability level) and the numbering scheme for complexes **I** (a), **II** (b), and **III** (c).

bond angles are in the range 82.8(2)°–96.4(2)° for **I**, 82.6(2)°–95.9(1)° for **II**, and 83.0(1)°–95.8(1)° for **III**, and the *trans* bond angles are in the range 171.2(2)°–175.0(2)° for **I**, 174.0(2)°–178.2(1)° for **II**, and 173.6(1)°–176.9(1)° for **III**. In both complexes, the Schiff base ligands are approximately coplanar, with the dihedral angles between the benzene ring and the pyridine ring of 0.1(2)° for **I**, 3.7(2)° for **II**, and 6.8(2)° for **III**.

In the crystal structure of complexes **I**–**III** (Fig. 2), the molecules are stacked together by weak $\pi\cdots\pi$ interactions (Table 3) among the molecules.

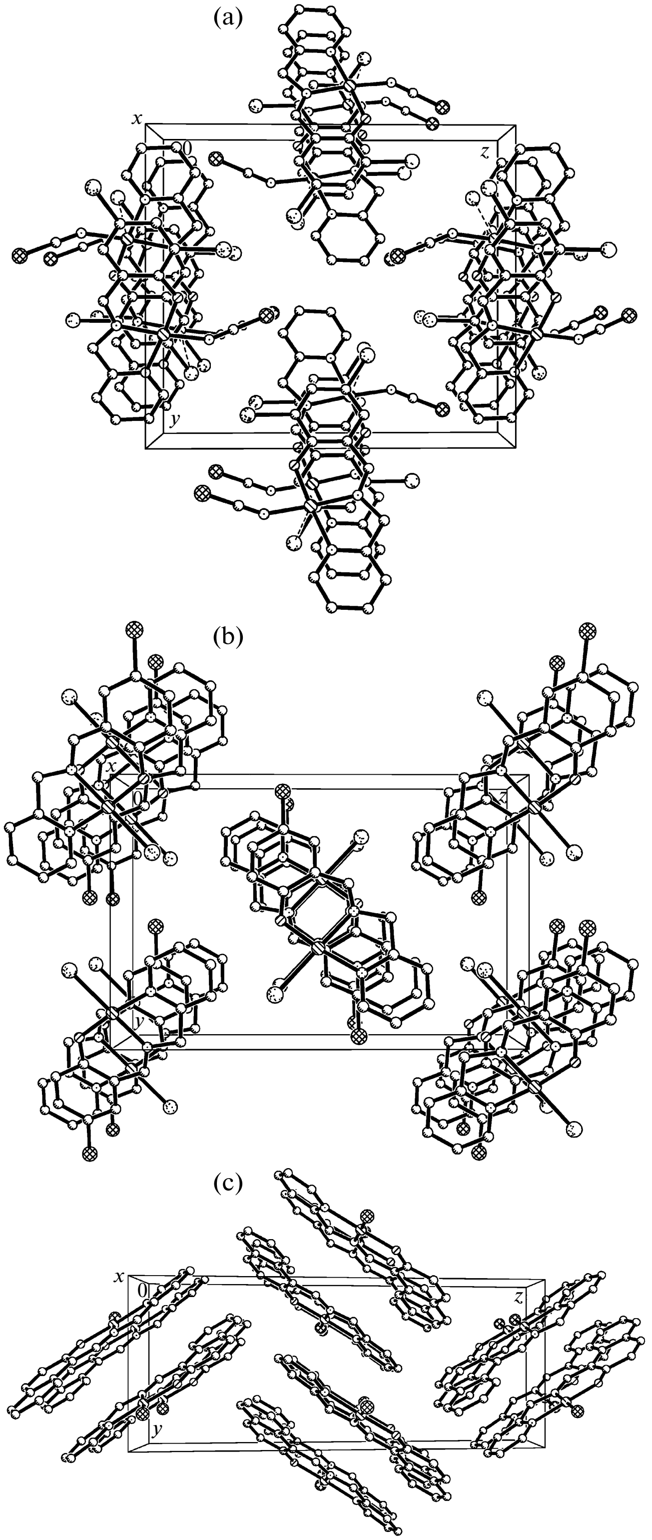


Fig. 2. Molecular packing diagram for **I** (a), **II** (b), and **III** (c) viewed along the *x* axis.

The weak bands in the region 3320–3410 cm^{-1} of the free Schiff base ligands are assigned to the ν(O–H) vibrations, which are absent in the spectra of the com-

Table 3. $\pi\cdots\pi$ interactions for complexes **I–III***

$Cg(I)\cdots Cg(J)$	Distance between ring centroids, Å	Dihedral angle, deg	Perpendicular distance of $Cg(I)$ on $Cg(J)$, Å	Perpendicular distance of $Cg(J)$ on $Cg(I)$, Å
		I		
$Cg(1)\cdots Cg(2)^{\mathrm{i}}$	3.831	1.06	3.372	3.349
$Cg(1)\cdots Cg(4)^{\mathrm{ii}}$	4.927	1.66	3.246	3.330
$Cg(1)\cdots Cg(4)^{\mathrm{i}}$	3.642	1.66	3.398	3.400
$Cg(2)\cdots Cg(2)^{\mathrm{i}}$	3.486	0.00	3.358	3.358
$Cg(2)\cdots Cg(4)^{\mathrm{i}}$	4.754	1.40	3.360	3.365
$Cg(3)\cdots Cg(3)^{\mathrm{iii}}$	4.753	0.03	4.005	4.005
$Cg(3)\cdots Cg(4)^{\mathrm{i}}$	4.754	0.06	3.425	3.427
$Cg(4)\cdots Cg(2)^{\mathrm{ii}}$	3.541	1.40	3.280	3.284
$Cg(4)\cdots Cg(4)^{\mathrm{ii}}$	3.503	0.00	3.286	3.286
		II		
$Cg(5)\cdots Cg(5)^{\mathrm{iii}}$	4.290	0.00	3.254	3.254
$Cg(5)\cdots Cg(6)^{\mathrm{iii}}$	3.480	3.78	3.217	3.296
$Cg(5)\cdots Cg(6)^{\mathrm{iv}}$	4.960	3.78	3.323	3.405
$Cg(5)\cdots Cg(8)^{\mathrm{iii}}$	4.442	5.14	3.216	3.361
$Cg(5)\cdots Cg(8)^{\mathrm{iv}}$	3.532	5.14	3.342	3.340
$Cg(6)\cdots Cg(6)^{\mathrm{iii}}$	4.266	0.00	3.233	3.233
$Cg(6)\cdots Cg(6)^{\mathrm{iv}}$	3.574	0.00	3.308	3.308
$Cg(6)\cdots Cg(7)^{\mathrm{iii}}$	4.069	3.37	3.238	3.327
$Cg(6)\cdots Cg(8)^{\mathrm{iv}}$	3.561	1.81	3.277	3.309
$Cg(7)\cdots Cg(8)^{\mathrm{iii}}$	3.567	3.71	3.297	3.373
$Cg(7)\cdots Cg(8)^{\mathrm{iv}}$	4.741	3.71	3.261	3.398
		III		
$Cg(9)\cdots Cg(9)^{\mathrm{v}}$	4.632	0.00	3.358	3.358
$Cg(9)\cdots Cg(9)^{\mathrm{vi}}$	4.022	0.00	3.448	3.448
$Cg(9)\cdots Cg(10)^{\mathrm{v}}$	3.602	3.29	3.431	3.431
$Cg(9)\cdots Cg(11)^{\mathrm{vi}}$	3.401	4.48	3.399	3.388
$Cg(9)\cdots Cg(12)^{\mathrm{v}}$	3.981	3.30	3.428	3.494
$Cg(9)\cdots Cg(13)^{\mathrm{v}}$	4.746	1.84	3.442	3.410
$Cg(10)\cdots Cg(10)^{\mathrm{v}}$	4.100	0.00	3.376	3.376
$Cg(10)\cdots Cg(11)^{\mathrm{v}}$	4.735	7.73	3.387	3.587
$Cg(10)\cdots Cg(11)^{\mathrm{vi}}$	3.983	7.73	3.174	3.421
$Cg(11)\cdots Cg(11)^{\mathrm{vi}}$	4.184	0.02	3.443	3.443
$Cg(11)\cdots Cg(12)^{\mathrm{v}}$	3.724	7.51	3.498	3.574
$Cg(11)\cdots Cg(13)^{\mathrm{v}}$	3.721	6.08	3.503	3.430

* For **I**: *Cg*(1), *Cg*(2), *Cg*(3), and *Cg*(4) are the centroids of Cu(1)–N(1)–C(8)–C(9)–N(2), Cu(1)–O(1)–C(2)–C(1)–C(7)–N(1), N(2)–C(9)–C(10)–C(11)–C(12)–C(13), and C(1)–C(2)–C(3)–C(4)–C(5)–C(6). For **II**: *Cg*(5), *Cg*(6), *Cg*(7), and *Cg*(8) are the centroids of Cu(1)–N(1)–C(8)–C(9)–N(2), Cu(1)–O(1)–C(2)–C(1)–C(7)–N(1), N(2)–C(9)–C(10)–C(11)–C(12)–C(13), and C(1)–C(2)–C(3)–C(4)–C(5)–C(6). For **III**: *Cg*(9), *Cg*(10), *Cg*(11), *Cg*(12), and *Cg*(13) are the centroids of Cu(1)–N(1)–C(12)–C(13)–N(2), Cu(1)–O(1)–C(2)–C(1)–C(11)–N(1), N(2)–C(13)–C(14)–C(15)–C(16)–C(17), C(1)–C(2)–C(3)–C(4)–C(5)–C(10), and C(5)–C(6)–C(7)–C(8)–C(9)–C(10). Symmetry codes: $^{\mathrm{i}}\ 1-x, -y, 1-z$; $^{\mathrm{ii}}\ -x, -y, 1-z$; $^{\mathrm{iii}}\ 1-x, 1-y, 1-z$; $^{\mathrm{iv}}\ 2-x, 1-y, 1-z$; $^{\mathrm{v}}\ 2-x, 1-y, -z$; $^{\mathrm{vi}}\ 2-x, 2-y, -z$.

plexes. The strong bands at 1606 cm^{-1} in the spectrum of **I**, 1604 cm^{-1} in the spectrum of **II**, and 1601 cm^{-1} in the spectrum of **III** are assigned to the azomethine groups, which are shift to lower frequencies when compared with the free Schiff base ligands. The bands indicative of the Cu–O and Cu–N bonds are in the range 400–600 cm^{-1}. The intense band indicative of the thiocyanate ligand in **I** is observed at 2083 cm^{-1}.

Three new structurally similar mononuclear copper(II) complexes with tridentate Schiff bases were prepared. The complexes were characterized by IR spectroscopy and single crystal X-ray diffraction. The Schiff base ligands coordinate to the Cu atoms through the phenolate oxygen, the imine nitogen, and the pyridine nitrogen atoms.

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