

Synthesis and Crystal Structures of Copper(II) Complexes Derived from 5-Methoxy-2-[(2-morpholin-4-ylethylimino)methyl]phenolate and (2-Morpholin-4-ylethyl)-(1-pyridin-2-ylethylidene)amine

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Abstract A pair of copper(II) complexes, $[\text{CuL}^1(\text{ONO}_2)(\text{OH}_2)]$ **1** and $[\text{CuBrL}^2\text{N}_3]$ **2**, where L^1 is 5-methoxy-2-[(2-morpholin-4-ylethylimino)methyl]phenolate, and L^2 is (2-morpholin-4-ylethyl)-(1-pyridin-2-ylethylidene)amine, have been synthesized and characterized by elemental analysis, IR spectra and single crystal X-ray diffraction. Complex **1** crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.496(2)$, $b = 19.113(3)$, $c = 8.586(2)$ Å, $\beta = 105.186(10)^\circ$. Complex **2** crystallizes in the monoclinic space group $C2/c$, with $a = 16.606(3)$, $b = 7.357(2)$, $c = 26.043(5)$ Å, $\beta = 94.996(2)^\circ$. The Cu atom in each complex is five-coordinate in a square pyramidal geometry.

Keywords Synthesis · Crystal structure · Schiff base · Copper

Introduction

Schiff bases derived from the condensation of aldehydes with organic amines are a kind of versatile ligands in coordination chemistry due to their easy synthesis and wide applications [1–6]. The biological and catalytic properties

of Schiff bases and their metal complexes have been widely investigated [7–11]. Recent research indicates that in the presence of metal ions, the phenolic-containing compounds are believed to damage the cytoplasmic membrane, and show potential antimicrobial activity [12, 13]. 5-Methoxy-2-[(2-morpholin-4-ylethylimino)methyl]phenolate (HL^1) and (2-morpholin-4-ylethyl)-(1-pyridin-2-ylethylidene)amine (L^2) (Scheme 1) are two new Schiff bases, the metal complexes with them have never been reported so far. In order to construct new Schiff base complexes and understand the coordination mode of the Schiff bases, in this article, two new copper(II) complexes, $[\text{CuL}^1(\text{ONO}_2)(\text{OH}_2)]$ **1** and $[\text{CuBrL}^2\text{N}_3]$ **2**, have been synthesized and characterized by elemental analysis, IR spectra and single crystal X-ray diffraction.

Experimental

Materials and Measurements

All chemicals were available commercially as AR grade and were used without further purification. C, H, and N elemental analyses were performed on a Vario-EL-III analyser. The IR spectra were recorded on a Perkin Elmer 2000 spectrophotometer with KBr pellets in the region 4000–400 cm^{-1} .

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

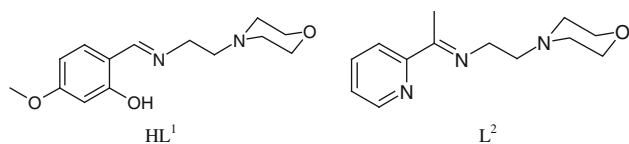
Synthesis of HL^1

4-Methoxysalicylaldehyde (1.0 mmol, 152.2 mg) and 2-morpholin-4-ylethylamine (1.0 mmol, 130.2 mg) were mixed in 50 mL methanol and then stirred and refluxed for

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Scheme 1 The Schiff bases HL¹ and L²

30 min. The solvent was removed by distillation to give yellow product. Yield: 97%.

Elemental analysis calcd. for C₁₄H₂₀N₂O₃ (%): C 63.6, H 7.6, N 10.6; Found: C 63.5, H 7.6, N 10.7.

Synthesis of L²

2-Acetylpyridine (1.0 mmol, 121.1 mg) and 2-morpholin-4-ylethylamine (1.0 mmol, 130.2 mg) were mixed in 50 mL methanol and then stirred and refluxed for 30 min. The solvent was removed by distillation to give yellow product. Yield: 99%.

Elemental analysis calcd. for C₁₃H₁₉N₃O (%): C 66.9, H 8.2, N 18.0; Found: C 67.1, H 8.3, N 17.8.

Synthesis of [CuL¹(ONO₂)(OH₂)] (1)

A methanol solution (10 mL) of copper(II) nitrate trihydrate (0.1 mmol, 24.2 mg) was added to the methanol solution (10 mL) of HL¹ (0.1 mmol, 26.4 mg), and refluxed for 1 h. The resulting clear blue solution was allowed to evaporate slowly in air at room temperature for a week, affording deep blue single crystals which were collected by filtration, washed with methanol and dried in air. Yield: 54% (based on HL¹).

Elemental analysis calcd. for C₁₄H₂₁CuN₃O₇ (%): C 41.3, H 5.2, N 10.3; Found: C 40.9, H 5.4, N 10.5.

Synthesis of [CuBrL²N₃] (2)

A methanol solution (10 mL) of copper(II) bromide (0.1 mmol, 22.3 mg) was added to the methanol solution (10 mL) of L² (0.1 mmol, 23.3 mg) and sodium azide (0.1 mmol, 6.5 mg), and refluxed for 1 h. The resulting clear blue solution was allowed to evaporate slowly in air at room temperature for a few days, affording deep blue single crystals which were collected by filtration, washed with methanol and dried in air. Yield: 37% (based on L²).

Elemental analysis calcd. for C₁₃H₁₉BrCuN₆O (%): C 37.3, H 4.6, N 20.1; Found: C 37.5, H 4.6, N 19.9.

Crystal Structure Determination

The suitable single crystals of the complexes were mounted on glass fibers for data collection performed on a Bruker

SMART 1000 CCD area diffractometer equipped with a graphite-monochromatic MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. The unit cell dimensions were obtained with the least-squares refinements and the structures were solved by direct methods using SHELXTL-97 program [14]. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms on F^2 . The water H atoms in **1** are located in a difference Fourier map and refined isotropically, with O–H and H \cdots H distances restrained to 0.85(1) and 1.37(2) \AA , respectively. Other H atoms were placed in calculated positions and constrained to ride on their parent atoms. Multi-scan absorption correction was applied by using the SADABS program [15]. The crystallographic data and experimental details for structural analysis of the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3.

Table 1 Crystal data and structure refinement parameters

Complex	1	2
CCDC no.	776832	776833
Formula	C ₁₄ H ₂₁ CuN ₃ O ₇	C ₁₃ H ₁₉ BrCuN ₆ O
FW	406.88	418.79
Crystal shape/colour	Block/blue	Block/blue
Crystal size (mm ³)	0.20 × 0.18 × 0.18	0.27 × 0.23 × 0.23
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>C2/c</i>
<i>a</i> (\AA)	10.4962(17)	16.606(3)
<i>b</i> (\AA)	19.113(3)	7.3574(14)
<i>c</i> (\AA)	8.5865(15)	26.043(5)
β ($^\circ$)	105.186(10)	94.996(2)
<i>V</i> (\AA^3)	1662.4(5)	3169.8(10)
<i>Z</i>	4	8
λ (MoK α) (\AA)	0.71073	0.71073
τ (K)	298(2)	298(2)
μ (MoK α) (cm ⁻¹)	1.357	3.910
<i>T</i> _{min}	0.773	0.418
<i>T</i> _{max}	0.792	0.467
Measured reflections	9830	10639
Unique reflections	3599	3422
Observed reflections	2708	2661
Parameters/restraints	233/3	200/0
Goodness of fit on F^2	1.066	1.079
R_1, wR_2 [$I \geq 2\sigma(I)$] ^a	0.0382, 0.0817	0.0343, 0.0724
R_1, wR_2 (all data) ^a	0.0574, 0.0894	0.0520, 0.0791

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table 2 Selected bond lengths (Å) and bond angles (°)

1			
Cu1–O1	1.9082(17)	Cu1–N1	1.928(2)
Cu1–O7	2.0010(19)	Cu1–N2	2.065(2)
Cu1–O4	2.355(2)		
O1–Cu1–N1	93.41(8)	O1–Cu1–O7	88.01(7)
N1–Cu1–O7	171.95(8)	O1–Cu1–N2	172.84(8)
N1–Cu1–N2	85.02(9)	O7–Cu1–N2	92.59(8)
O1–Cu1–O4	94.53(8)	N1–Cu1–O4	104.70(8)
O7–Cu1–O4	83.06(7)	N2–Cu1–O4	92.63(8)
2			
Cu1–N1	2.058(3)	Cu1–N2	1.966(2)
Cu1–N3	2.093(2)	Cu1–N4	1.968(3)
Cu1–Br1	2.6506(6)		
N2–Cu1–N4	164.79(11)	N2–Cu1–N1	78.59(10)
N4–Cu1–N1	94.76(11)	N2–Cu1–N3	81.55(10)
N4–Cu1–N3	99.58(11)	N1–Cu1–N3	152.35(10)
N2–Cu1–Br1	95.76(7)	N4–Cu1–Br1	99.07(8)
N1–Cu1–Br1	102.66(7)	N3–Cu1–Br1	98.29(7)

Table 3 Hydrogen-bond geometry (Å, °)

D–H...A	D–H	H...A	D...A	D–H...A
1				
O7–H7A...O1 ^a	0.845(10)	1.902(15)	2.717(3)	161(3)
O7–H7B...O6 ^a	0.843(10)	2.22(2)	2.969(4)	148(3)
O7–H7B...O4 ^a	0.843(10)	2.36(2)	3.026(3)	136(3)
O7–H7B...N3 ^a	0.843(10)	2.65(2)	3.394(3)	149(3)
2				
C4–H4...Br1 ^b	0.93	2.83	3.722(3)	162(3)
C8–H8B...Br1 ^c	0.97	2.91	3.790(3)	151(3)
C10–H10B...O1 ^d	0.97	2.51	3.358(3)	145(3)
C13–H13A...N5	0.97	2.58	3.258(3)	127(3)

Symmetry transformations used to generate equivalent atoms

^a $-x, -y, 2 - z$

^b $1/2 - x, 1/2 - y, -z$

^c $x, -1 + y, z$

^d $-x, y, 1/2 - z$

Results and Discussion

The two new Schiff bases have been synthesized by condensation reaction of 4-methoxysalicylaldehyde/2-acetylpyridine and 2-morpholin-4-ylethylamine in methanol (Scheme 2); the two copper complexes were easily prepared by using 1:1 ratio of Schiff base ligand and metal salts.

IR Spectra

The Schiff base HL¹ and the complex **1** show weak and broad band at about 3,400 cm⁻¹ corresponding to the

$\nu(-OH)$ of the phenolic group and the water molecule. The strong and sharp bands at 1,645 for HL¹ and 1,641 for L² are assigned to the $\nu(C=N)$, which are shifted to lower frequencies in the spectra of the complexes, 1,617 cm⁻¹ for **1** and 1,613 cm⁻¹ for **2**. For **1**, the bands indicative of the nitrate group are at 1,450 and 1,317 cm⁻¹. For **2**, the intense band indicative of the azide group is at 2,064 cm⁻¹. The spectra of the complexes also show some new bands in the 470–430 cm⁻¹ regions, which reflect the formation of Cu–O and Cu–N bonds [16, 17].

Structure Description of **1**

The molecular structure of complex **1** is shown in Fig. 1. The Cu atom in the complex is five-coordinated by the phenolate O, imine N, and amine N atoms of L¹ and by two O atoms, respectively from a nitrate anion and a water molecule, forming a square pyramidal geometry. All the bond lengths and angles are comparable to those observed in other copper(II) complexes with square pyramidal coordination [18–20]. The coordination around the Cu atom displays somewhat distortion. The Cu atom deviates from the least-squares plane defined by the four basal donor atoms by 0.128(2) Å. The N1–Cu1–N2 bond angle is deviate from the value for an ideal square pyramidal geometry by 5.0(1)°, which is caused by the strain created by the five-membered chelate ring Cu1–N1–C8–C9–N2.

In the crystal structure, molecules are linked through intermolecular O–H...O hydrogen bonds among the nitrate anions, water molecules and the phenolate O atoms, forming dimers, as shown by Fig. 2.

Structure Description of **2**

The molecular structure of complex **2** is shown in Fig. 3. The Cu atom in the complex is five-coordinated by the three N atoms of L², and by one Br atom and one N atom of an azide group, forming a square pyramidal geometry. All the bond lengths and angles are comparable to those observed in **1** and other copper(II) complexes with square pyramidal coordination [21–23]. The coordination around the Cu atom displays somewhat distortion. The Cu atom deviates from the least-squares plane defined by the four basal donor atoms by 0.318(2) Å. The N1–Cu1–N2 and N2–Cu1–N3 bond angles are deviate from the values for an ideal square pyramidal geometry by 11.4(1) and 8.4(1)°, respectively, which are caused by the strain created by the five-membered chelate rings Cu1–N1–C5–C6–N2 and Cu1–N2–C8–C9–N3.

In the crystal structure, molecules are linked through intermolecular C–H...Br and C–H...O hydrogen bonds, forming a three-dimensional network, as shown by Fig. 4.

Scheme 2 a Synthesis of HL¹.
b Synthesis of L². c Synthesis of
1. d Synthesis of 2

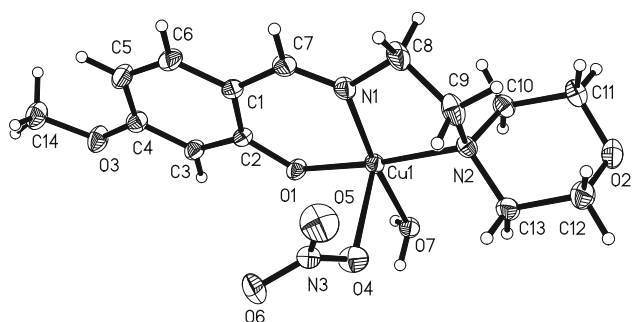
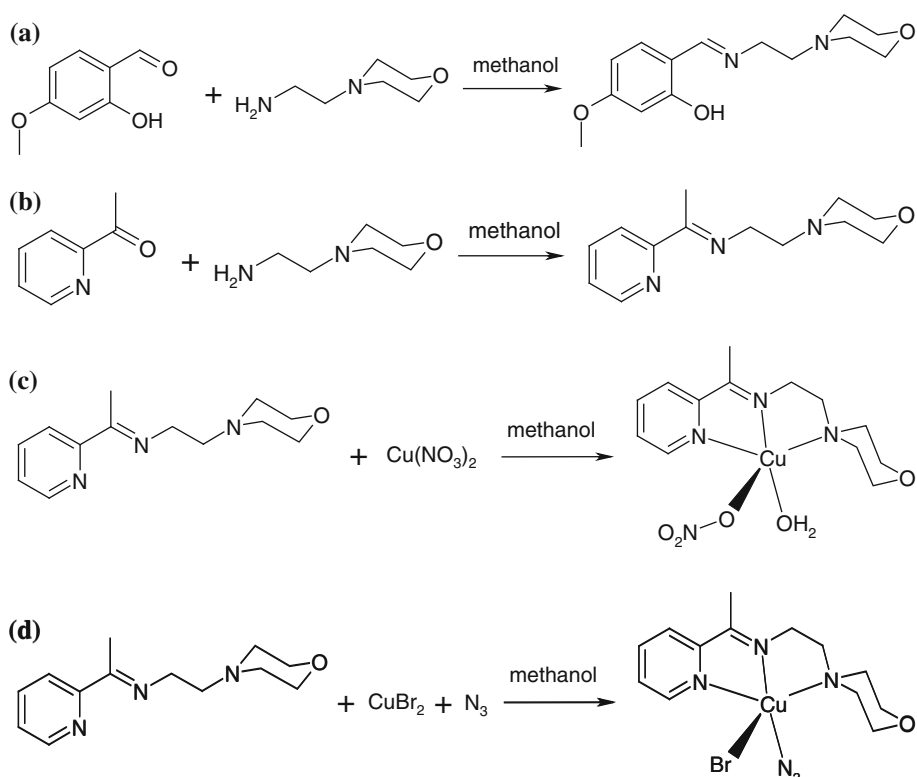


Fig. 1 The molecule of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level

In both complexes, the conformation of the morpholine rings is chair. The square pyramidal coordination of the Cu atoms can be proved by the τ parameter, an index of the degree of trigonality [24]. The τ values calculated for the complexes **1** and **2** are 0.015 and 0.207, respectively.

Supplementary Material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 776832 and 776833. Copies of this data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by

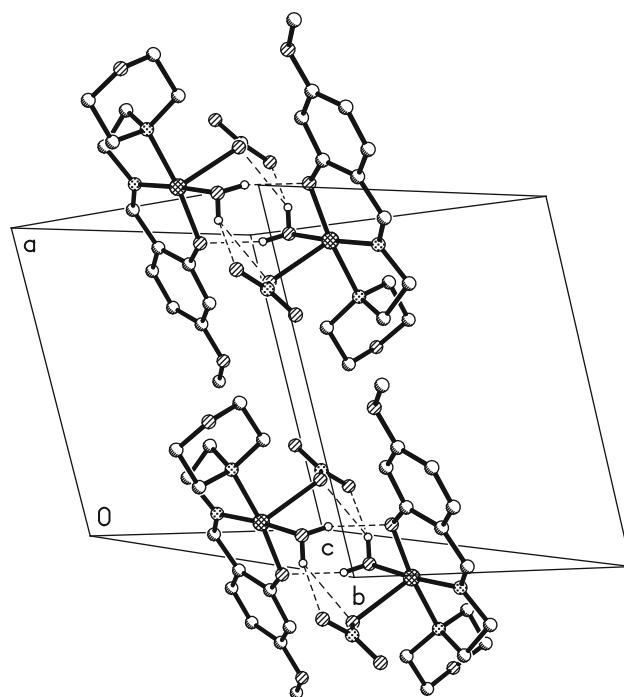


Fig. 2 The molecular packing of **1**. Intermolecular hydrogen bonds are shown as dashed lines

emailing data_request@ccdc.cam.ac.uk, or by contacting. The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

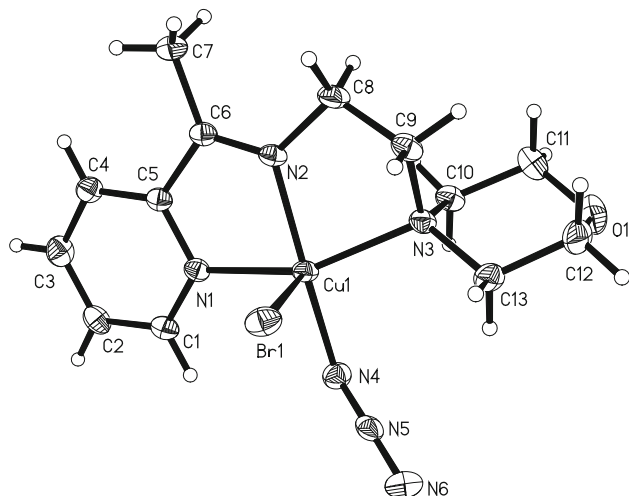


Fig. 3 The molecule of **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity

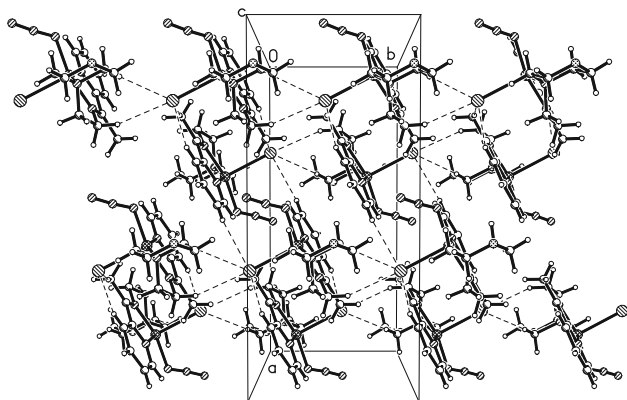


Fig. 4 The molecular packing of **2**, viewed along the *c* axis. Intermolecular hydrogen bonds are shown as *dashed lines*

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