TWO NEW SCHIFF BASE NI^{II} AND CU^{II} COMPLEXES: SYNTHESIS AND STRUCTURES

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ABSTRACT

Schiff base ligands 2-bromo-4-chloro-6-[(2-piperidin-1-ylethylimino)methyl]phenol (BCP) and 2,4-dibromo-6-[(2-morpholin-4-ylethylimino)methyl]phenol (DBP) and their nickel(II) and copper(II) complexes $[\text{Ni}(\text{BCP})_2(\text{CH}_3\text{OH})_2] \cdot 2\text{NO}_3$ (**1**) and $[\text{Cu}(\text{DBP})_2]$ (**2**), have been prepared and characterized by elemental analyses, IR, and single crystal X-ray crystallographic determination. The crystal of (**1**) is orthorhombic: space group *Pbcn*, $a = 23.894(1)$, $b = 8.244(2)$, $c = 19.900(2)$ Å, $V = 3919.9(10)$ Å³, $Z = 4$. The crystal of (**2**) is monoclinic: space group *P2₁/c*, $a = 7.072(2)$, $b = 15.426(3)$, $c = 14.214(3)$ Å, $\beta = 96.718(2)^\circ$, $V = 1540.0(7)$ Å³, $Z = 2$. The Schiff bases coordinate to the metal atoms through the phenolate O and imine N atoms. The Ni atom in (**1**) is in an octahedral coordination, and the Cu atom in (**2**) is in a square planar coordination.

Keywords: Schiff base; nickel complex; copper complex; crystal structure.

INTRODUCTION

Schiff bases have been widely used as versatile ligands in coordination chemistry.¹⁻³ In recent years, metal complexes of Schiff bases have attracted considerable attention due to their remarkable biological activity, such as antifungal, antibacterial, and antitumor.⁴⁻⁶ It has been shown that the Schiff base complexes derived from salicylaldehyde and its derivatives with primary amines, bearing the N₂O, N₂S, NO₂, or NSO donor sets, have interesting biological activity.⁶⁻⁸ Recent research indicates that the halide-substituent groups in aromatic rings of Schiff bases or aroylhydrazones can remarkably increase the antimicrobial activity.⁹ As a continuation of our work on the synthesis and structures of Schiff base complexes,¹⁰ in the present paper, the preparation and characterization of new nickel(II) and copper(II) complexes, $[\text{Ni}(\text{BCP})_2(\text{CH}_3\text{OH})_2] \cdot 2\text{NO}_3$ (**1**) and $[\text{Cu}(\text{DBP})_2]$ (**2**), derived from the Schiff base ligands 2-bromo-4-chloro-6-[(2-piperidin-1-ylethylimino)methyl]phenol (BCP) and 2,4-dibromo-6-[(2-morpholin-4-ylethylimino)methyl]phenol (DBP, Chart 1), are reported.

EXPERIMENTAL

Materials and Methods: All organic chemicals were purchased from Fluka. The metal salts and solvents with analytical grade were obtained commercially. The Schiff bases were prepared according to the literature method.¹⁰ Elemental (C, H, and N) analyses were made on a Perkin Elmer Model 240B automatic analyzer. Nickel and copper analyses were carried out by EDTA titration. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

Synthesis of $[\text{Ni}(\text{BCP})_2(\text{CH}_3\text{OH})_2] \cdot 2\text{NO}_3$ (1**):** The Schiff base BCP (0.345 g, 1.0 mmol) were dissolved in methanol (30 ml), to which was added with stirring a methanol solution (15 ml) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.145 g, 0.5 mmol). The mixture was stirred for 1 h at ambient temperature to give a green solution. Green block-shaped single crystals suitable for X-ray diffraction were formed by slow evaporation of the solution in air for about a week. The yield was 53% (based on BCP). Analysis: Calcd. (%) for $\text{C}_{30}\text{H}_{44}\text{Br}_2\text{Cl}_2\text{N}_6\text{NiO}_{10}$: C 38.4, H 4.7, N 9.0, Ni 6.3. Found (%): C 38.3, H 4.8, N 8.9, Ni 6.5. IR spectra (ν , cm⁻¹): 3413 m, 3025 w, 2950 w, 2860 w, 1621 v.s., 1508 s, 1567 s, 1385 s, 1326 m, 1309 m, 1210 m, 1148 m, 1028 w, 869 m, 740 m, 464 w.

Synthesis of $[\text{Cu}(\text{DBP})_2]$ (2**):** The Schiff base DBP (0.392 g, 1.0 mmol) were dissolved in methanol (30 ml), to which was added with stirring a methanol solution (15 ml) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.121 g, 0.5 mmol). The mixture was stirred for 1 h at ambient temperature to give a blue solution. Blue block-shaped single crystals suitable for X-ray diffraction were formed by slow evaporation of the solution in air for about a week. The yield was 62% (based on DBP). Analysis: Calcd. (%) for $\text{C}_{26}\text{H}_{30}\text{Br}_2\text{CuN}_4\text{O}_4$: C 36.9, H 3.6, N 6.6, Cu 7.5. Found (%): C 36.7, H 3.6, N 6.5, Cu 7.7. IR spectra (ν , cm⁻¹): 3015 w, 2935 w, 2837 w, 1616 v.s., 1450 s, 1395 s, 1161 w, 1120 w, 858 w, 782 w, 713 w, 589 w, 533 w, 445 w.

Chart 1: The benzohydrazone ligands

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X-ray Crystal Determination: Data were collected from selected crystals mounted on glass fibers. The data for the two complexes were processed with SAINT¹¹ and corrected for absorption using SADABS.¹² Semiempirical absorption corrections were applied with ψ scans.¹³ The structures were solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters.¹⁴ The H atoms attached to O and N in (**1**) were located from a difference Fourier map and refined isotropically, with O–H and N–H distances restrained to 0.85(1) and 0.90(1) Å, respectively. The other hydrogen atoms were placed at the calculated positions. Idealized H atoms were refined with isotropic displacement parameters set to 1.2 (1.5 for methyl groups) times the equivalent isotropic U values of the parent carbon atoms. The crystallographic data for the complexes are listed in Table 1.

Table 1 Crystal and structure refinement data for the complexes

	(1)	(2)
Habit, colour	Block, green	Block, blue
Formula weight	938.1	845.7
Temperature, K	298(2)	298(2)
Crystal size, mm	0.27 × 0.27 × 0.23	0.12 × 0.08 × 0.07
Radiation, λ , Å	MoK $_{\alpha}$ (0.71073)	MoK $_{\alpha}$ (0.71073)
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>P2₁/c</i>
Unit cell dimensions:		
<i>a</i> , Å	23.894(1)	7.072(2)
<i>b</i> , Å	8.244(2)	15.426(3)
<i>c</i> , Å	19.900(2)	14.214(3)
β , deg		96.718(2)
<i>V</i> , Å ³	3919.9(10)	1540.0(7)
<i>Z</i>	4	2
ρ_{calcd} , mg cm ⁻³	1.590	1.824
<i>F</i> (000)	1912	830
Absorption coefficient, mm ⁻¹	2.729	5.936
θ range for data collection, deg	1.70-27.50	1.96-26.49
Index ranges	$-31 \leq h \leq 31$, $-10 \leq k \leq 10$, $-25 \leq l \leq 25$	$-8 \leq h \leq 8$, $-18 \leq k \leq 19$, $-17 \leq l \leq 17$
Reflections collected	31652	11664
Independent reflections	4500	3126
Data ($I > 2\sigma(I)$)/parameters	2656/237	1763/178
Restraints	2	0
Final <i>R</i> indices ($I > 2\sigma(I)$)	0.0507	0.0544
<i>R</i> indices (all data)	0.1115	0.1145
Goodness-of-fit	1.011	1.021
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$, $e \text{ Å}^{-3}$	0.704, -0.338	1.002, -0.874

RESULTS AND DISCUSSION

The nickel and copper complexes were readily synthesized by the reaction of the Schiff bases and metal nitrate at ambient temperature. The complexes are very stable at room temperature in the solid state and are soluble in common organic solvents, such as methanol, ethanol, chloroform, and acetonitrile. The results of elemental analyses are in accord with the composition suggested for the complexes.

IR Spectra: In the IR spectra of both complexes, the strong bands observed at 1621 cm⁻¹ for (1) and 1616 cm⁻¹ for (2) are assigned to the azomethine group vibration. The broad band centered at 3413 cm⁻¹ in the spectrum of (1) is attributed to the stretching vibration of the phenol groups of the methanol ligands, however, it is absent in (2). The characteristic bands indicative of the nitrate anions in (1) are located at 1385 and 869 cm⁻¹.

Crystal Structure Description of the Complexes: The molecular structure of complex (1) is shown in Fig. 1. Selected bond distances and angles are listed in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) for the complexes.

(1)			
Bond lengths			
Ni1–O1	1.9782	Ni1–N1	2.0713
Ni1–O5	2.1473		
Bond angles			
O1–Ni1–O1 <i>A</i>	170.62	O1–Ni1–N1	88.81
O1–Ni1–N1 <i>A</i>	97.81	N1–Ni1–N1 <i>A</i>	91.62
O1–Ni1–O5 <i>A</i>	88.71	N1–Ni1–O5 <i>A</i>	89.81
O1–Ni1–O5	84.61	O1–Ni1–O5 <i>A</i>	88.71
N1–Ni1–O5	173.41	O5–Ni1–O5 <i>A</i>	89.62
(2)			
Bond lengths			
Cu1–O1	1.9084	Cu1–N1	1.9935
Bond angles			
O1–Cu1–O1 <i>B</i>	180	O1–Cu1–N1 <i>B</i>	88.82
O1–Cu1–N1	91.212	N1–Cu1–N1 <i>B</i>	180

*Symmetry codes: (*A*): 1 – *x*, *y*, 1/2 – *z*; (*B*): – *x*, 1 – *y*, 1 – *z*.

Figure 1 Perspective view of (1) with 30% probability thermal ellipsoids. Hydrogen bonds are shown as dashed lines.

The complex possesses a crystallographic two-fold rotation axis symmetry, and consists of a mononuclear nickel(II) complex cation and two nitrate anions. The nitrate anions are linked to the complex cations through intermolecular N—H $\cdots$ O and O—H $\cdots$ O hydrogen bonds. The Ni atom is six-coordinated by two phenolate O and two imine N atoms from two Schiff bases, and by two O atoms from two methanol molecules, forming an octahedral geometry. The bond lengths related to the Ni atom are within normal ranges and are similar to the corresponding distances observed in other Schiff base nickel(II) complexes.^{15,16} The distortion of the octahedral geometry can be observed from the coordinate bond angles. The three *trans* angles in the coordination are 170.6(2), 173.4(2), and 173.4(2)°, and the other angles are ranging from 84.6(2) to 97.8(2)°. As expected, the piperidine rings adopt chair conformation.

The molecular packing diagram is shown in Fig. 2. The nickel complex cations are linked by nitrate anions through intermolecular O—H $\cdots$ O and C—H $\cdots$ O hydrogen bonds (Table 3), forming a 3D network.

Figure 2 Molecular packing of (1), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

The molecular structure of complex (2) is shown in Fig. 3. Selected bond distances and angles are listed in Table 2.

The complex is a centrosymmetric mononuclear copper(II) complex. The Cu atom, lying on the inversion center, is coordinated by two imine N and two phenolate O atoms from two DBP ligands, forming a square planar geometry. The Schiff base ligand acts as a bidentate ligand, forming a six-membered chelate ring with the Cu atom. The bond distances subtended at the Cu atom are comparable to those observed in the similar copper(II) complexes with Schiff bases.^{17,18} The morpholine rings adopt well-shaped chair conformation.

The molecular packing diagram is shown in Fig. 4. The crystal structure of (2) is stabilized by intermolecular C—H $\cdots$ O and C—H $\cdots$ Br hydrogen bonds (Table 3).

Figure 3 Perspective view of (2) with 30% probability thermal ellipsoids.

Figure 4 Molecular packing of (2), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

Table 3 Geometric parameters of hydrogen bond for complex (1)*

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
N2–H2···O4	0.90(1)	2.61(3)	3.424(8)	152(4)
N2–H2···O2	0.90(1)	2.06(3)	2.877(5)	151(5)
O5–H5···O3 ^{#1}	0.85(1)	2.42(3)	3.129(7)	142(5)
O5–H5···O2 ^{#1}	0.85(1)	2.36(3)	3.130(6)	150(4)

*Symmetry code: ^{#1} 1 – x, –1 + y, 1/2 – z.**Supplementary material**

CCDC-763156 (1) and 884165 (2) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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