ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 5, pp. 345–350. © Pleiades Publishing, Ltd., 2016.

Syntheses and Crystal Structures of Copper(II) and Nickel(II) Complexes Derived from 2-Bromo-4-Chloro-6-[(2-Methylaminoethylimino)methyl]phenol[1]

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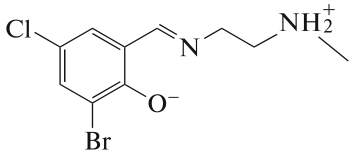
Received June 6, 2015

Abstract—A new centrosymmetric mononuclear copper(II) complex $[Cu(L)_2](ClO_4)_2$ (**I**) and a new centrosymmetric mononuclear nickel(II) complex $[Ni(L)_2(MeOH)_2](ClO_4)_2$ (**II**), where L is the zwitterionic ligand 2-bromo-4-chloro-6-[(2-methylammonioethylimino)methyl]phenolate, have been prepared from the Schiff base 2-bromo-4-chloro-6-[(2-methylaminoethylimino)methyl]phenol with copper perchlorate and nickel perchlorate, respectively. The complexes were characterized by elemental analysis, infrared spectra, and single-cyrstal X-ray diffraction (CIF files CCDC nos. 1408054 (**I**) and 1407973 (**II**)). Complex **I** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 7.7736(4)$, $b = 21.608(1)$, $c = 8.5194(4)$ Å, $\beta = 93.907(2)°$, $V = 1427.7(1)$ Å^3, $Z = 2$, $R_1 = 0.0546$, and $wR_2 = 0.1531$. Complex **II** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 21.324(3)$, $b = 16.821(2)$, $c = 9.425(1)$ Å, $\beta = 90.114(2)°$, $V = 3380.5(7)$ Å^3, $Z = 4$, $R_1 = 0.0693$, and $wR_2 = 0.1627$. The Cu atom in **I** is in square planar coordination, and the Ni atom in **II** is in octahedral coordination.

DOI: 10.1134/S1070328416040059

INTRODUCTION

Schiff base complexes have been received considerable attention for their importance in the field of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [1–5]. Copper and nickel complexes with Schiff base ligands have been proved to possess interesting biological, catalytic, and magnetic properties [6–10]. During the search of literature, we found that a large number of complexes with Schiff bases derived from salicylaldehyde and its derivatives with versatile organic amines had been reported. Yet, to the best of our knowledge, only one complex derived from the Schiff base 2-bromo-4-chloro-6-[(2-methylaminoethylimino)methyl]phenol (L) has been reported [11]. As an extension of work on Schiff base complexes [12–14], we report in this paper the syntheses and crystal structures of two new copper(II) and nickel(II) complexes, $[CuL_2](ClO_4)_2$ (**I**) and $[NiL_2(MeOH)_2](ClO_4)_2$ (**II**), where L is the zwitterionic ligand 2-bromo-4-chloro-6-[(2-methylammonioethylimino)methyl]phenolate.



EXPERIMENTAL

Materials and measurements. Commercially available 3-bromo-5-chlorosalicylaldehyde and *N*-methylethane-1,2-diamine were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H, and N elemental analyses were performed with a Perkin-Elmer elemental analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. UV-Vis spectra were recorded on a Lambda 900 spectromether.

Synthesis of the Schiff base. 3-Bromo-5-chlorosalicylaldehyde (1.0 mmol, 0.235 g) and *N*-methyethane-1,2-diamine (1.0 mmol, 0.074 g) were dissolved in MeOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to

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give yellow solution. The solvent was evaporated to give yellow gummy product of the Schiff base.

For $C_{10}H_{12}N_2OClBr$

anal. calcd., %:	C, 41.2;	H, 4.2;	N, 9.6.
Found, %:	C, 41.0;	H, 4.1;	N, 9.7.

Synthesis of I. A methanolic solution (5 mL) of copper perchlorate (0.1 mmol, 37.0 mg) was added to a methanolic solution (10 mL) of the Schiff base (0.1 mmol, 29.2 mg) with stirring. The mixture was stirred for 30 min to give blue solution. The resulting solution was allowed to stand in air for a few days. Blue block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold methanol, and dried in a vacuum over anhydrous $CaCl_2$. The yield was 17.2 mg (41% on the basis of the Schiff base).

For $C_{20}H_{24}N_4O_{10}Cl_4Br_2Cu$

anal. calcd., %:	C, 28.41;	H, 2.86;	N, 6.63.
Found, %:	C, 28.23;	H, 2.97;	N, 6.77.

IR data (KBr; ν, cm^{-1}): 3195 w, 1626 s, 1446 s, 1324 w, 1212 w, 1084 s, 856 m, 808 w, 744 w, 622 w, 547 s.

Synthesis of II. A methanolic solution (5 mL) of nickel perchlorate (0.1 mmol, 36.6 mg) was added to a methanolic solution (10 mL) of the Schiff base (0.1 mmol, 29.2 mg) with stirring. The mixture was stirred for 30 min to give green solution. The resulting solution was allowed to stand in air for a few days. Green block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold methanol and dried in a vacuum over anhydrous $CaCl_2$. The yield was 21.3 mg (47% on the basis of the Schiff base).

For $C_{22}H_{32}N_4O_{12}Cl_4Br_2Ni$

anal. calcd., %:	C, 29.20;	H, 3.56;	N, 6.19.
Found, %:	C, 29.33;	H, 3.73;	N, 6.11.

IR data (KBr; ν, cm^{-1}): 3211 w, 1630 s, 1446 s, 1313 w, 1217 w, 1087 s, 856 m, 739 w, 622 w, 547 s, 473 w.

X-ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 area-detector with MoK_α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [15], and multi-scan absorption corrections were performed using the SADABS program [16]. The structures of the complexes were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL [17]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and constrained to ride on their parent atoms. Crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1408054 (**I**) and 1407973 (**II**)); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complexes **I** and **II** were readily prepared by the similar synthetic procedure:

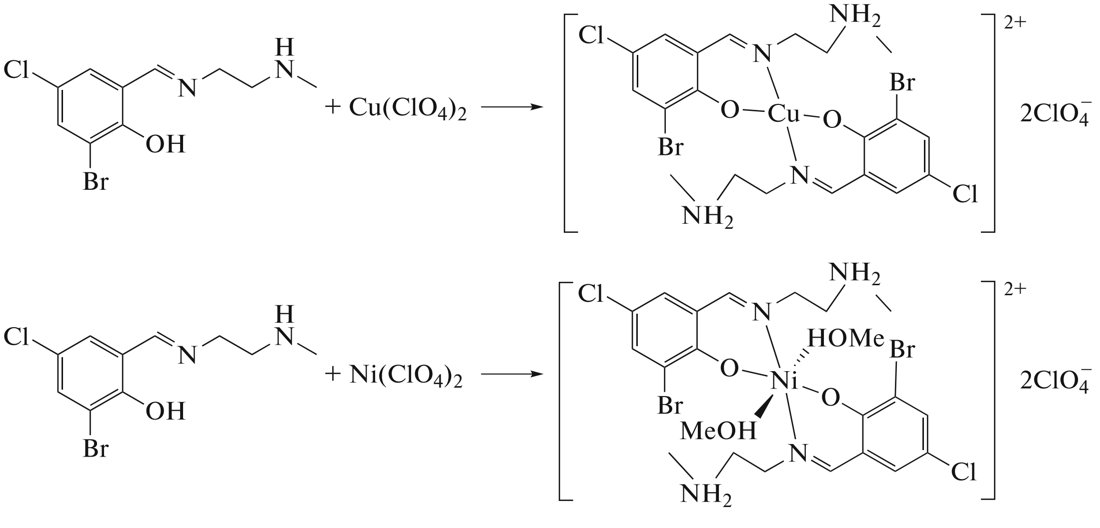

Table 1. Crystallographic data and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
Fw	845.6	904.8
Crystal shape/color	Block/blue	Block/green
Crystal size, mm	0.33 × 0.30 × 0.26	0.30 × 0.27 × 0.23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	7.7736(4)	21.324(3)
b, Å	21.6078(11)	16.821(2)
c, Å	8.5194(4)	9.4246(13)
β, deg	93.907(2)	90.114(2)
V, Å^3	1427.68(12)	3380.5(7)
Z	2	4
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	3.998	3.316
ρ_{calcd}, g cm^{-3}	1.967	1.778
$F(000)$	838	1816
$T_{\mathrm{min}}/T_{\mathrm{max}}$	0.3521/0.4229	0.4362/0.5160
Collected reflections/unique (R_{int})	13120/2661 (0.346)	29684/5989 (0.797)
Observed reflections ($I \geqslant 2\sigma(I)$)	2201	3587
Refinement parameters	188	413
Goodness of fit on F^2	1.048	1.030
R_1, wR_2 ($I \geqslant 2\sigma(I)$)*	0.0546, 0.1531	0.0693, 0.1627
R_1, wR_2 (all data)*	0.0677, 0.1628	0.1272, 0.1973
Large diff. peak and hole, e Å^{-3}	1.271, –1.255	1.071, –0.684

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

Table 2. Selected bond lengths (Å) and angles (deg) in structures **I** and **II***

Bond	d, Å	Bond	d, Å
		I	
Cu(1)–O(1)	1.907(4)	Cu(1)–N(1)	2.013(4)
		II	
Ni(1)–O(1)	2.015(5)	Ni(1)–N(1)	2.081(6)
Ni(1)–O(2)	2.120(5)	Ni(2)–O(3)	2.012(5)
Ni(2)–N(3)	2.082(6)	Ni(2)–O(4)	2.124(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
O(1)Cu(1)N(1)	91.44(17)		
		II	
O(1)Ni(1)O(2)	83.9(2)	N(1)Ni(1)O(2)	89.8(2)
N(3)Ni(2)O(4)	90.1(2)	O(3)Ni(2)N(3)	89.3(2)
O(1)Ni(1)N(1)	89.1(2)	O(3)Ni(2)O(4)	83.9(2)

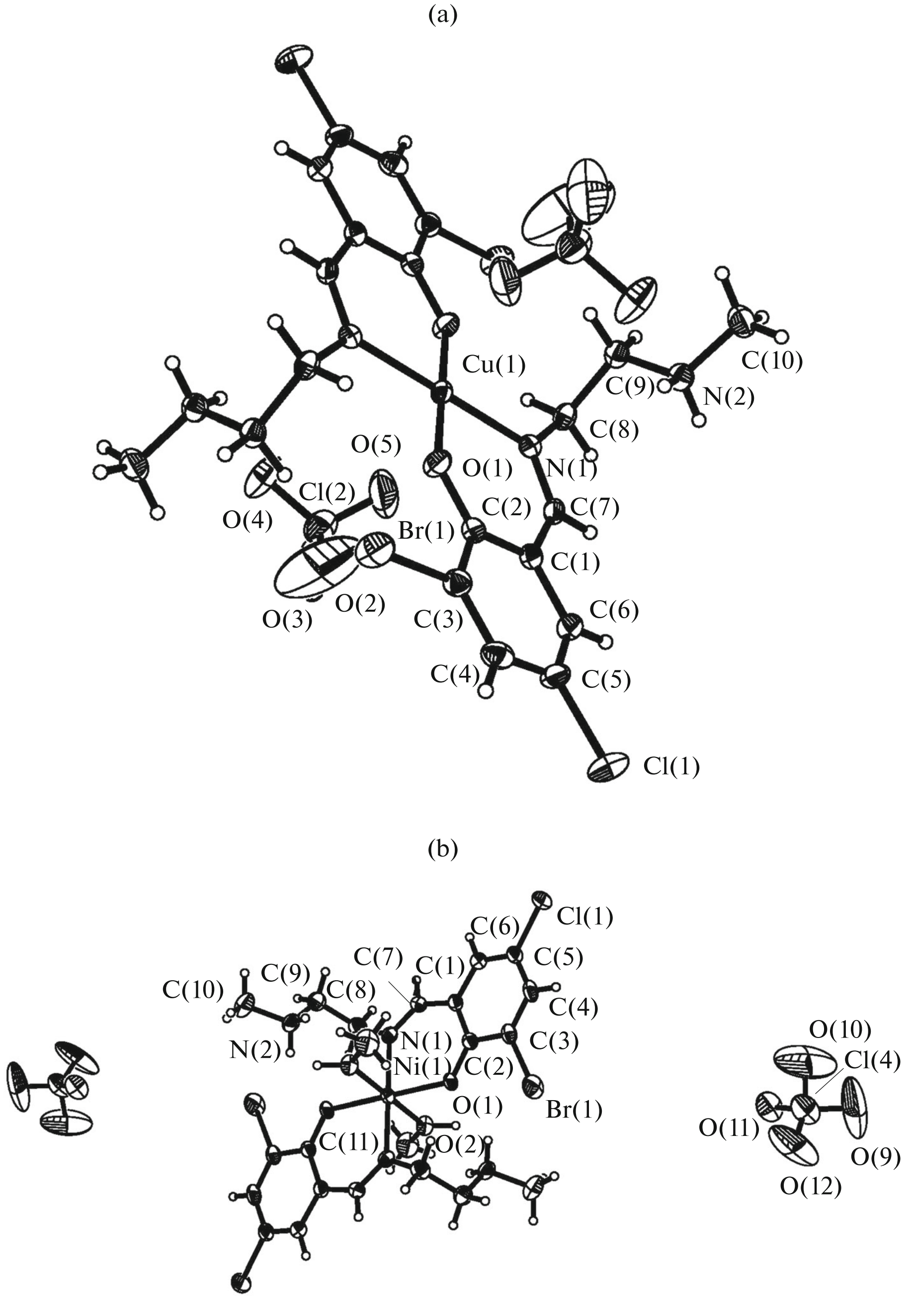

Fig. 1. Molecular structures of **I** (a) and **II** (b) at 30% probability displacement. Unlabeled atoms are at the symmetry positions: $1 - x$, $1 - y$, $1 - z$ for **I** and $-x$, $-y$, $1 - z$ for **II**.

The complexes are similar with a mononuclear complex cation and two perchlorate anions. The main difference lies in the central metal ions and their coordination geometries. In **I**, the Cu atom is in square planar geometry, while in **II**, the Ni atom is in octahedral geometry.

The molecular structure of complex **I** is shown in Fig. 1a. The compound is a centrosymmetric mononuclear copper(II) complex. There are two perchlorate counteranions in the compound. The Cu atom in the complex cation is coordinated by two phenolate O and two imine N atoms from two Schiff base ligands, forming a square planar geometry. The Cu–O and Cu–N bond lengths in complex **I** are comparable to the corresponding values observed in other Schiff base copper(II) complexes [18, 19]. In the crystal structure of complex **I**, molecules are linked through intermolecular N–H···O (N(2)–H(2*B*) 0.90, H(2*B*)···O(3)^i 1.97, N(2)···O(3)^i 2.821(8) Å, N(2)–H(2*B*)···O(3)^i

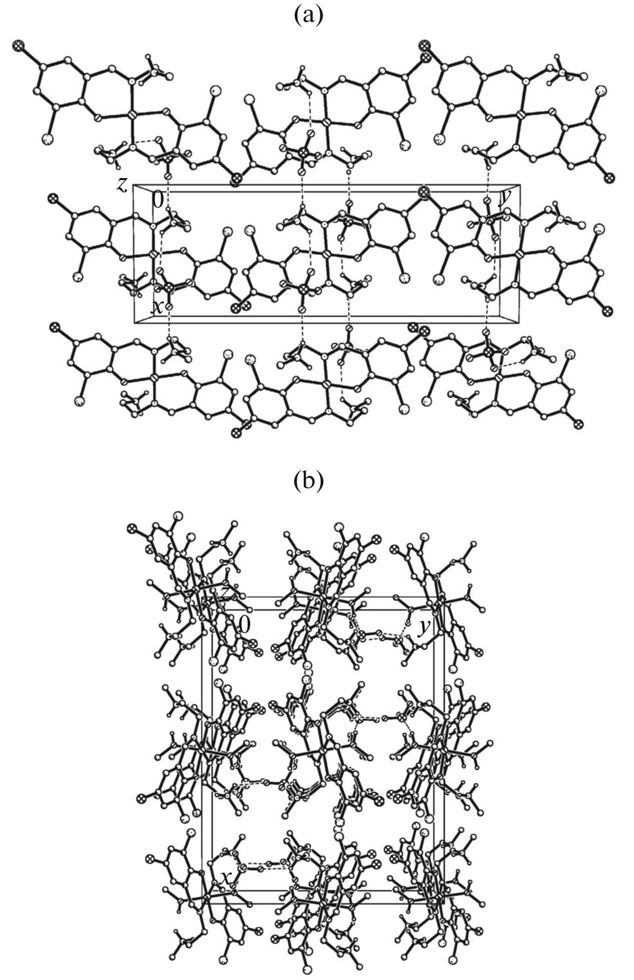

Fig. 2. Molecular packing structures of **I** (a) and **II** (b), viewed along the *z* axis. Hydrogen bonds are shown as dashed lines.

158°; N(2)–H(2*A*) 0.90, H(2*A*)···O(4)^{ii} 2.32, N(2)···O(4)^{ii} 2.989(8) Å, N(2)–H(2*A*)···O(4)^{ii} 131°; N(2)–H(2*A*) 0.90, H(2*A*)···O(4)^{iii} 2.20, N(2)···O(4)^{iii} 2.936(8) Å, N(2)–H(2*A*)···O(4)^{iii} 139°; symmetry codes: ^{i} $-x$, $3/2 + y$, $3/2 - z$; ^{ii} $1 - x$, $3/2 + y$, $3/2 - z$; ^{iii} x, y, $1 + z$) hydrogen bonds, forming chains running along the *x* axis direction, as shown in Fig. 2a.

The molecular structure of complex **II** is shown in Fig. 1b. The compound is a centrosymmetric mononuclear nickel(II) complex. There are two perchlorate counteranions in the asymmetric unit of the compound. The Ni atom in the complex cation is coordinated by two phenolate O and two imine N atoms from two Schiff base ligands, and two methanol O atoms, forming an octahedral geometry. The Ni–O and Ni–N bond lengths in complex **II** are comparable to the corresponding values observed in other Schiff base nickel(II) complexes [20, 21]. In the crystal structure of complex **II**, molecules are linked through intermolecular N–H···O (N(4)–H(4*B*) 0.90, H(4*B*)···O(4)^{ii} 2.32, N(4)···O(4)^{ii} 3.020(9) Å, N(4)–H(4*B*)···O(4)^{ii} 135°; N(4)–H(4*A*) 0.90, H(4*A*)···O(3)^{ii} 2.03, N(4)···O(3)^{ii} 2.807(9) Å, N(4)–H(4*A*)···O(3)^{ii} 144°; N(4)–H(4*A*) 0.90, H(4*A*)···Br(2)^{ii} 2.80, N(4)···Br(2)^{ii} 3.494(8) Å, N(4)–H(4*A*)···Br(2)^{ii} 135°; O(4)–H(4*C*) 0.93, H(4*C*)···N(4)^{ii} 2.51, O(4)···N(4)^{ii} 3.020(9) Å, O(4)–H(4*C*)···N(4)^{ii} 115°; O(4)–H(4*C*) 0.93, H(4*C*)···O(11)^{iv} 2.26, O(4)···O(11)^{iv} 2.755(9) Å, O(4)–H(4*C*)···O(11)^{iv} 113°; symmetry code: ^{iv} $1 - x$, $-y$, $-z$) hydrogen bonds, forming dimmers, as shown in Fig. 2b.

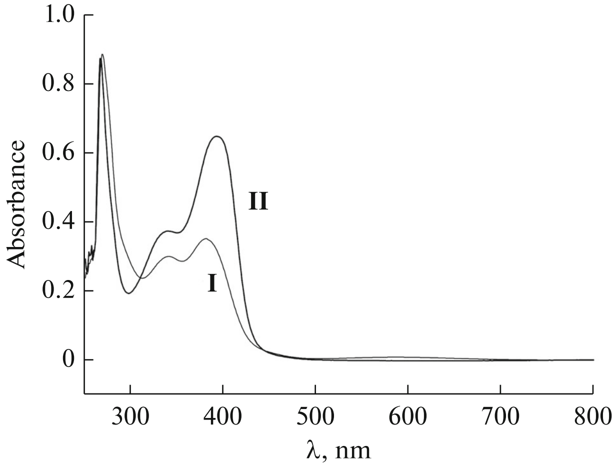

Fig. 3. UV-Vis spectra of complexes **I** and **II**.

IR spectra of the two complexes are very similar. The weak and sharp bands at 3195 cm^{-1} for **I** and 3211 cm^{-1} for **II** are assigned to the N–H streching vibration. The strong absorption bands at 1626 cm^{-1} for **I** and 1630 cm^{-1} for **II** are assigned to the azomethine groups, ν(C=N). The phenolate ν(Ar–O) in the complexes exhibit weak bands at 1212 cm^{-1} for **I** and 1217 cm^{-1} for **II**. The intense bands centered at about 1085 cm^{-1} for the complexes are assigned to the stretching vibrations of the perchlorate anions. The weak bands located at the low numbers may be assigned to the ν(M–O) and ν(M–N).

UV-Vis spectra of the two complexes recorded in acetonitrile are very similar (Fig. 3). The bands centered at about 340 nm are attributed to the azomethine chromophore π–π* transition. The bands at higher energies (340 nm) are associated with the benzene π–π* transition [22]. The bands centered at 383 nm for **I** and 394 nm for **II** may assigned to LMCT.

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