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Synthesis, Characterization, and X-ray Crystal Structures of Copper(II) and Nickel(II) Complexes with Schiff Base[1]

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Abstract—New copper(II) complexes, $[Cu_2L^1L^2] \cdot ClO_4$ (**I**) and $[Ni(L^3)_2]$ (**II**), where L^1 is the mono-anionic form of 2-[1-(2-emthylaminoethylimino)ethyl]phenol, L^2 is the dianionic form of N,N'-ethylene-bis(2-hydroxyacetophenonylideneimine), L^3 is the mono-anionic form of 2-(1-iminoethyl)phenol, were prepared and characterized using elemental analysis, FT-IR spectroscopy, and X-ray single-crystal diffraction. In complex **I**, the Cu(1) atom is coordinated by the NNO tridentate ligand L^1 and the two phenolate O atoms of L^2, forming a square pyramidal geometry. The Cu(2) atom in complex **I** is coordinated by the NNOO tetradenate ligand L^2, forming a square planar geometry. The Ni atom in complex **II** is coordinated by two phenolate O and two imine N atoms from two ligands L^3, forming a square planar geometry. In the crystal structure of **I**, the perchlorate anions are linked to the dinuclear copper(II) complex cations through intermolecular N–H···O hydrogen bonds. In the crystal structure of **II**, the mononuclear nickel complex molecules are linked through intermolecular N–H···O hydrogen bonds, forming a trimer.

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INTRODUCTION

Schiff bases are a kind of versatile ligands in coordination chemistry. The compounds containing strong donor sites, such as phenoxo oxygen and imine nitrogen atoms have attracted much attention in catalysis and biological application for their special coordination ability with transition metal atoms [1–4]. In particular, copper and nickel complexes with Schiff base ligands have received considerable interest in the fields of medicinal chemistry for their antibacterial, antitumor and antifungal activities [5–8]. Recently, we have reported a few Schiff base complexes [9]. As an extension of the work on such complexes, in this paper, a new dinuclear copper(II) complex $[Cu_2L^1L^2] \cdot ClO_4$ (**I**) and a new mononuclear nickel(II) complex $[Ni(L^3)_2]$ (**II**), where L^1 is the mono-anionic form of 2-[1-(2-methylaminoethylimino)ethyl]phenol, L^2 is the dianionic form of N,N'-ethylene-*bis*(2-hydroxyacetophenonylideneimine), L^3 is the mono-aninic form of 2-(1-iminoethyl)phenol, were prepared and structurally characterized.

EXPERIMENTAL

Materials and physical measurements. 2-Acetylphenol, ethane-1,2-diamine, and N-methylethane-1,2-diamine were purchased from Lancaster Chemical Company Inc. Copper perchlorate was prepared by the reaction of $Cu_2(OH)_2CO_3$ with perchloric acid in distilled water. Nickel acetate was purchased from Sinpeuo Fine Chemical Company Inc. and used as received. All other chemicals were of AR grade. Elemental analyses for C, H, and N were performed using a PerkinElmer 240C elemental analyzer. Infrared spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Molar conductance measurements were performed in a DDS-11A conductivity meter.

Synthesis of complex I. 2-Acetylphenol (0.136 g, 1 mmol), *N*-methylethane-1,2-diamine (0.037 g, 0.5 mmol), and ethane-1,2-diamine (0.030 g, 0.5 mmol) were mixed in methanol (20 mL). The mixture was stirred at ambient temperature for 30 min. To the above mixture was added dropwise a methanolic solution (10 mL) of copper perchlorate (0.388 mg, 1 mmol) with stirring. The final mixture was further stirred at ambient temperature for 30 min to give a blue solution. The blue single crystals of **I** suitable for X-ray analysis were obtained several days later. The yield was 51%.

For $C_{29}H_{33}N_4O_7ClCu_2$

anal. calcd., %:	C, 48.91;	H, 4.67;	N, 7.87.
Found, %:	C, 48.73;	H, 4.75;	N, 7.96.

Selected IR data (KBr; ν, cm^{-1}): 3344 w, sh; 1604 s, 1553 m, 1474 m, 1439 s, 1305 s, 1236 s, 1106–1066 v.s, 858 m, 769 m, 624 w, 588 w, 523 w, 439 w.

Synthesis of complex II. 2-Acetylphenol (0.136 g, 1 mmol) and a few drops of ammonia water were mixed in methanol (20 mL). The mixture was stirred at

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Table 1. Crystallographic data and details of refinements for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	712.1	327.0
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions:		
a, Å	10.434(1)	9.096(2)
b, Å	11.355(1)	11.351(2)
c, Å	13.079(1)	11.790(2)
α, deg	101.306(2)	100.947(2)
β, deg	97.326(2)	93.050(2)
γ, deg	97.885(2)	109.682(2)
V, Å^3	1486.0(1)	1116.3(3)
Z	2	3
ρ_{calcd}, g cm^{-3}	1.591	1.459
F(000)	732	510
μ(MoK_α), mm^{-1}	1.574	1.308
θ Range, deg	1.6–27.0	2.3–27.0
Index ranges h, k, l	$-13 \leq h \leq 13$, $-14 \leq k \leq 9$, $-16 \leq l \leq 16$	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-15 \leq l \leq 14$
Collected reflections	8538	9245
Independent reflections (R_{int})	6150 (0.0246)	4768 (0.0268)
Observed reflections ($I > 2\sigma(I)$)	3856	3545
Parameter	395	298
R_1 ($I > 2\sigma(I)$)	0.0473	0.0388
wR_2 ($I > 2\sigma(I)$)	0.1089	0.0845
Goodness-of-fit on F^2	1.011	1.029
Largest diff. peak and hole, e Å^{-3}	0.766 and –0.631	0.488 and –0.306

ambient temperature for 30 min. To the above mixture was added dropwise a methanolic solution (10 mL) of nickel nitrate (0.291 g, 1 mmol) with stirring. The final mixture was further stirred at ambient temperature for 30 min to give a red solution. The red single crystals of **II** suitable for X-ray analysis were obtained several days later. The yield was 36%.

For $C_{16}H_{16}N_2O_2Ni$

anal. calcd., %:	C, 58.77;	H, 4.93;	N, 8.57.
Found, %:	C, 58.95;	H, 5.01;	N, 8.46.

Selected IR data (KBr; ν, cm^{-1}): 3320 m, sh; 1604 s, 1534 m, 1472 w, 1437 s, 1406 w, 1335 s, 1276 s, 1254 w, 1219 m, 1155 w, 1133 m, 1033 w, 989 w, 874 m, 847 w, 830 w, 771 w, 746 m, 591 w, 508 w, 457 m.

X-ray structure determination. The crystal and instrumental parameters used in the unit cell determination and data collection are summarized in Table 1. Diffraction measurements were made 298(2) K on a Bruker SMART APEX II X-ray diffractometer using graphite-monochromated MoK_α radiation using ω scan mode. Unit-cell dimensions were determined and refined in the $2.61° < \theta < 27.00°$ range for **I** and in the $2.33° < \theta < 27.00°$ range for **II**. The program SMART [10] was used for data collection, indexing reflection and determination of lattice parameters, SAINT [10] for integration of the reflection intensity and scaling and SADABS [11] for absorption correction. The structures were solved by the direct method using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [12, 13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The amino hydrogen atoms in both complexes were located from difference Fourier maps and refined isotropically with N–H distances restrained to 0.90(1) Å and with $U_{\rm iso}$(H) values set to 0.08 Å^2. The remaining hydrogen atoms were included in their idealized positions and refined isotropically. Selected bond distances and angles for complexes are list in Table 2. Hydrogen bonding geometries are given in Table 3. Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 853812 (**I**) and 853813 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac. uk).

RESULTS AND DISCUSSION

The copper complex was prepared by reaction of 2-acetylphenol, N-methylethane-1,2-diamine, ethane-1,2-diamine, and copper perchlorate in methanol at ambient condition. The nickel complex was prepared by reaction of 2-acetylphenol, ammonia water, and nickel nitrate in methanol at ambient condition. The structures of the complexes were characterized by elemental analysis, IR spectra, and single crystal X-ray diffraction. The molar conductivity measurements of the complexes in DMSO at the concentration of 10^{-3} mol/L suggest that the copper complex is a 1 : 1 electrolyte, and the nickel complex is a non-electrolyte, with the conductance values of 173.5 Ω^{-1} cm^2 mol^{-1} for **I** and 19.0 Ω^{-1} cm^2 mol^{-1} for **II**, respectively [14].

The molecular structure of the dinuclear complex **I** is shown in Fig. 1a. The Cu···Cu separation is 3.166(1) Å. The Cu(1) atom is in a distorted square pyramidal coordination, with the NNO donor atoms of L^1 and one phenolate O atom of L^2, defining the basal plane, and with the other phenolate O atom of L^2 occupying the apical position. The distortion of the square pyramidal coordination can be observed from the bond angles between the apical and basal donor atoms, ranging from 70.6(1)° to 113.6(1)°. The Cu(2) atom is in a square planar coordination, with two phenolate O and two imine N atoms of L^2. The bond lengths related to the Cu atoms are comparable with those observed in other Schiff base copper complexes with similar coordination [15, 16]. In the crystal structure of the complex, the perchlorate anions are linked to the dinuclear complex cations through intermolecular N–H···O hydrogen bonds, as shown in Fig. 2a.

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

Bond	*d*, Å	Bond	*d*, Å
		I	
Cu(1)–O(1)	1.868(3)	Cu(1)–O(2)	2.293(3)
Cu(1)–O(3)	2.061(3)	Cu(1)–N(1)	1.963(3)
Cu(1)–N(2)	1.997(4)	Cu(2)–O(2)	1.882(3)
Cu(2)–O(3)	1.900(3)	Cu(2)–N(3)	1.921(4)
Cu(2)–N(4)	1.928(4)		
		II	
Ni(1)–O(3)	1.816(2)	Ni(1)–N(3)	1.849(2)
Ni(2)–O(1)	1.822(2)	Ni(2)–O(2)	1.823(2)
Ni(2)–N(1)	1.846(2)	Ni(2)–N(2)	1.843(2)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Cu(1)N(1)	93.0(1)	O(1)Cu(1)N(2)	172.4(2)
N(1)Cu(1)N(2)	85.8(1)	O(1)Cu(1)O(3)	91.5(1)
N(1)Cu(1)O(3)	173.1(1)	N(2)Cu(1)O(3)	89.0(1)
O(1)Cu(1)O(2)	100.2(1)	N(1)Cu(1)O(2)	113.6(1)
N(2)Cu(1)O(2)	87.2(1)	O(3)Cu(1)O(2)	70.6(1)
O(2)Cu(2)O(3)	83.6(1)	O(2)Cu(2)N(3)	94.0(1)
O(3)Cu(2)N(3)	175.9(1)	O(2)Cu(2)N(4)	176.9(2)
O(3)Cu(2)N(4)	93.3(1)	N(3)Cu(2)N(4)	89.0(2)
		II	
O(1)Ni(2)O(2)	178.7(1)	O(1)Ni(2)N(2)	87.0(1)
O(2)Ni(2)N(2)	93.4(1)	O(1)Ni(2)N(1)	92.6(1)
O(2)Ni(2)N(1)	87.0(1)	N(2)Ni(2)N(1)	178.1(1)
O(3)Ni(1)N(3)	93.5(1)		

Table 3. Hydrogen bonding geometry for complexes **I** and **II***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
N(2)–H(2)···O(7)$^{\rm i}$	0.90(1)	2.51(4)	3.273(7)	144(5)
N(2)–H(2)···O(6)$^{\rm i}$	0.90(1)	2.26(3)	3.081(5)	152(5)
		II		
N(3)–H(3*A*)···O(1)$^{\rm ii}$	0.90(1)	2.17(2)	3.045(3)	169(3)
N(2)–H(2)···O(3)	0.90(1)	2.25(2)	3.140(3)	174(3)

* Symmetry codes: $^{\rm i}$ $x, -1 + y, z$; $^{\rm ii}$ $1 - x, 1 - y, 1 - z$.

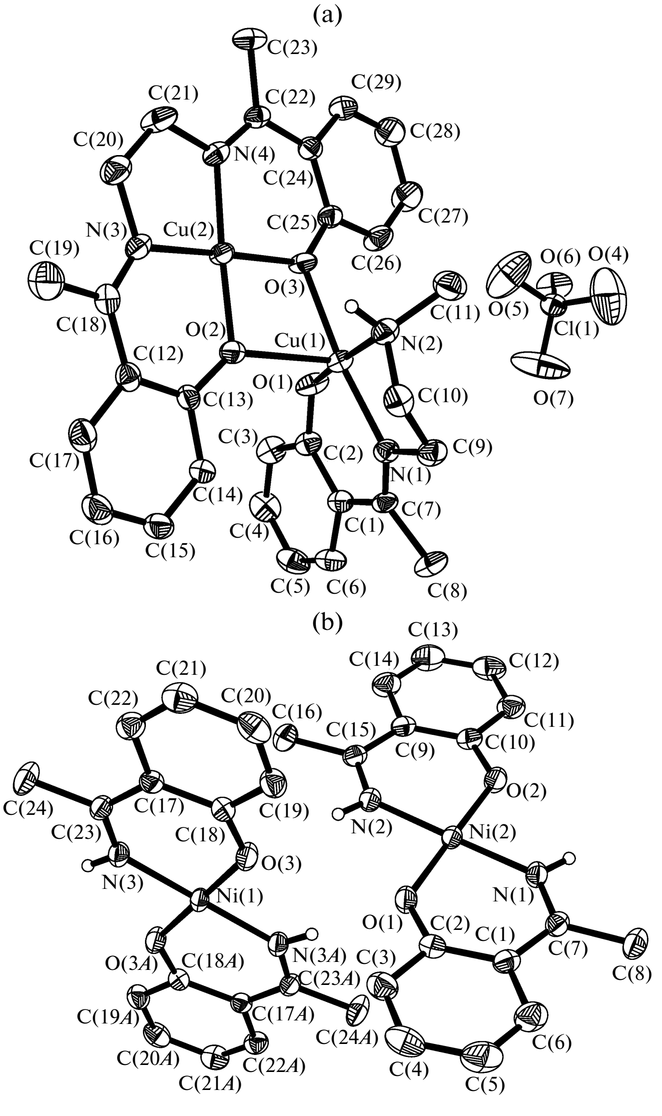

Fig. 1. ORTEP view of **I** (a) and **II** (b) with 30% thermal ellipsoids and with atom numbering scheme.

The molecular structure of the mononuclear complex **II** is shown in Fig. 1b. The asymmetric unit of complex **II** contains three independent molecules linked together by four intermolecular N–H···O hydrogen bonds (Fig. 2b). The Ni atom is coordinated by two phenolate O and two imine N atoms from two L^3, forming a square planar coordination. The adjacent molecules are nearly perpendicular to each other, with the dihedral angle of 87.4(2)°. The bond lengths related to the Ni atoms are comparable with those observed in other Schiff base nickel complexes with square planar coordination [17, 18].

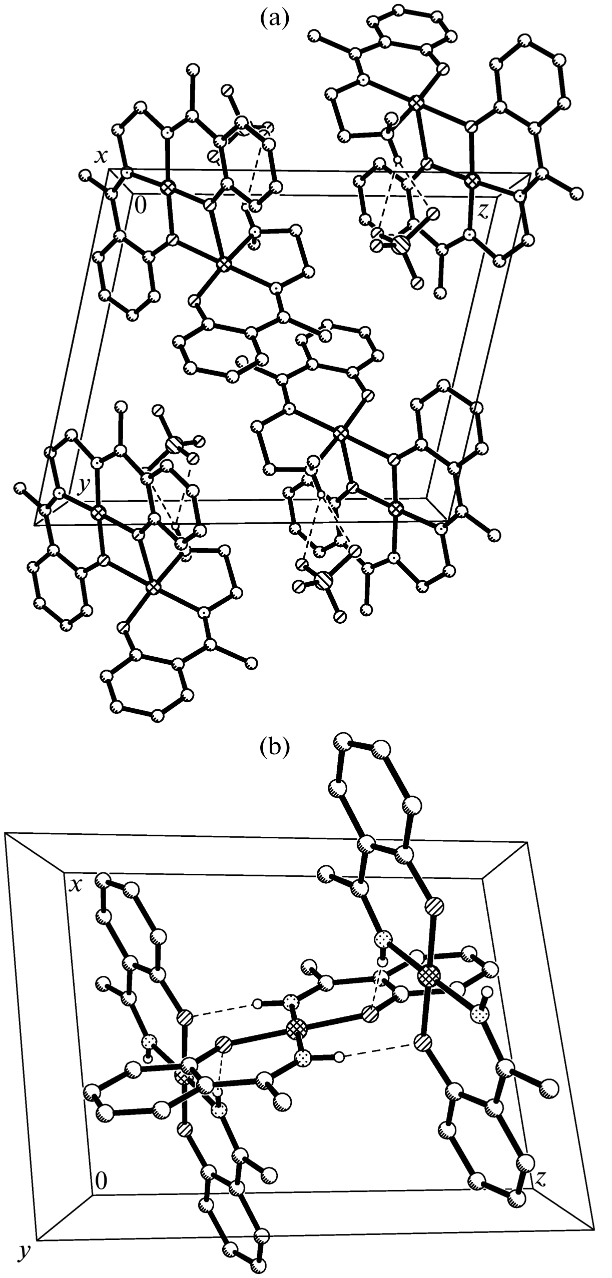

Fig. 2. Molecular packing structure of **I** (a) and **II** (b). Hydrogen bonds are drawn as dashed lines.

In the present paper, a new dinuclear copper(II) complex and a new mononuclear nickel(II) complex with bi-, tri-, and tetra-dentate Schiff bases have been prepared and structurally characterized. The Schiff bases coordinate to the metal atoms through all the donor atoms.

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