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Syntheses, Characterization and Crystal Structures of $[Ni(L^a)_2]$ and $[Zn(L^b)(N_3)(Amp)]$[1]

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Abstract—A new centrosymmetric mononuclear nickel(II) complex, $[Ni(L^a)_2]$ (**I**), and a new mononuclear zinc(II) complex, $[Zn(L^b)(N_3)(AMP)]$ (**II**) (L^a = 2-iminomethyl-4-methylphenolate, L^b = 4-methyl-2-[(4-methylpyridin-2-ylimino)methyl]phenolate, AMP = 2-amino-4-methylpyridine), have been prepared and characterized by elemental analysis, IR and UV-Vis spectra, and single-cyrstal X-ray diffraction (CIF files CCDC nos. 1059023 (**I**) and 1059024 (**II**)). Complex **I** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 16.067(2), b = 5.7222(6), c = 7.9004(9) Å, β = 92.471(4)°, V = 725.7(1) Å^3, Z = 2, R_1 = 0.0298, and wR_2 = 0.0695. Complex **II** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions a = 7.649(1), b = 10.414(2), c = 13.903(3) Å, α = 106.896(2)°, β = 91.581(2)°, γ = 103.033(2)°, V = 1027.3(4) Å^3, Z = 2, R_1 = 0.0372, and wR_2 = 0.0823. The Ni atom in **I** is in a square planar coordination, and the Zn atom in **II** is in a tetrahedral coordination. Crystals of the complexes are stabilized by hydrogen bonds and π···π interactions.

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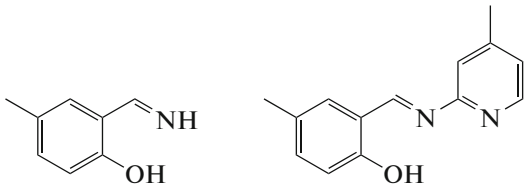
INTRODUCTION

Metal complexes with Schiff bases have been received considerable attention for their importance in the fields of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [1–5]. Nickel and zinc 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 great number of complexes with the tridentate Schiff bases derived from salicylaldehyde and its derivatives with various organic primary amines had been reported. Yet, to the best of our knowledge, no complexes have been reported for the Schiff bases 2-iminomethyl-4-methylphenol (HL^a) and 4-methyl-2-[(4-methylpyridin-2-ylimino)methyl]phenol (HL^b). As an extension of the work on the Schiff base complexes [11–13], we report in this paper the syntheses and crystal structures of two new nickel(II) and zinc(II) complexes, $[Ni(L^a)_2]$ (**I**) and $[Zn(L^b)(N_3)(AMP)]$ (**II**) (AMP = 2-amino-4-methylpyridine).

[1]The article is published in the original.



(HL^a) (HL^b)

EXPERIMENTAL

Materials and measurements. Commercially available 5-methylsalicylaldehyde and 2-amino-4-methylpyridine 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 Lambder 900 spectrometer.

Synthesis of $[Ni(L^a)_2]$ (I). 5-Methylsalicylaldehyde (0.1 mmol, 13.4 mg) and 2-amino-4-methylpyridine (0.2 mmol, 21.6 mg) were mixed in MeOH (10 mL). The mixture was stirred at room temperature for 10 min. Then, nickel nitrate hexahydrate (0.1 mmol,

29.1 mg) dissolved in MeOH (10 mL) was added with stirring. The mixture was stirred for 30 min to give a red solution. The resulting solution was allowed to stand in air for a few days. Red 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 EtOH and dried in a vacuum over anhydrous $CaCl_2$. The yield was 12.5 mg (38% based on Ni).

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

anal. alcd., %:	C, 58.77;	H, 4.93;	N, 8.57.
Found, %:	C, 58.56;	H, 5.07;	N, 8.68.

Synthesis of [Zn(L^b)(N_3)(AMP)] (II). 5-Methylsalicylaldehyde (0.1 mmol, 13.4 mg) and 2-amino-4-methylpyridine (0.2 mmol, 21.6 mg) were mixed in MeOH (10 mL). The mixture was stirred at room temperature for 10 min. Then, zinc nitrate hexahydrate (0.1 mmol, 29.7 mg) dissolved in MeOH (10 mL) and sodium azide (0.1 mmol, 6.5 mg) dissolved in distilled water (1 mL) were added with stirring. The mixture was stirred for 30 min to give a colorless solution. The resulting solution was allowed to stand in air for a few days. Colorless 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 EtOH and dried in a vacuum over anhydrous $CaCl_2$. The yield was 23.2 mg (53% based on Zn).

For $C_{20}H_{21}N_7OZn$

anal. alcd., %:	C, 54.49;	H, 4.80;	N, 22.24.
Found, %:	C, 54.63;	H, 4.92;	N, 22.13.

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 SAINT [14], and multi-scan absorption corrections were performed using SADABS [15]. Structures of the complexes were solved by direct methods and refined against F^2 by full-matrix least-squares methods using SHELXTL [16]. All of the non-hydrogen atoms were refined anisotropically. The imino H atoms in **I** and the amino H atoms in **II** were located from difference Fourier maps and refined isotropically with N–H and H···H distances restrained to 0.90(1) and 1.45(2) Å, respectively. The remaining H atoms were placed in idealized 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. 1059023 (**I**) and 1059024 (**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 same synthetic procedure. It is interesting that for the preparation of **I**, the Schiff base ligand HL^b was transferred to HL^a in the presence of Ni^{2+} ion. We have used different nickel salts, including nickel acetate, nickel nitrate, nickel perchlorate, and nickel chloride, yet, the same complex with ligands L^a was formed. This phenomenon is in accordance with the literature that the presence of Ni^{2+} ion can dissociate the N–C bonds in Schiff base ligands [17]. As for complex **II**, the ligand didn't change in the presence of Zn^{2+} ion.

The molecular structure of complex **I** is shown in Fig. 1a. The compound is a centrosymmetric mononuclear nickel(II) complex with the Ni atom located at the inversion center. The Ni atom in the complex is coordinated by two phenolate O and two imine N atoms from two L^a ligands, forming a square planar geometry. The Ni–O and Ni–N bond lengths in the complex are comparable to the corresponding values observed in nickel(II) complexes with similar Schiff base ligands [18–20]. In the crystal structure of complex **I** (Fig. 1b), molecules are stacked by π···π interactions among Ni(1)–O(2)–C(2)–C(1)–C(8)–N(1) rings, with the distances between ring centroids of 4.41(3) Å.

The molecular structure of complex **II** is shown in Fig. 2a. The Zn atom is coordinated by one phenolate O and one imino N atoms of L^b, one pyridine N atom of 2-amino-4-methylpyridine, and one azido N atom, forming a tetrahedral coordination. Distortion of the tetrahedral coordination is revealed by bond lengths and angles related to the Zn atom. The bond lengths are ranging from 1.965(2) to 2.029(2) Å, and the bond angles are ranging from 93.19(7)° to 119.79(7)°. The coordinate bond lengths are within normal ranges and comparable to the corresponding values observed in other Schiff base zinc(II) complexes [21–23]. The azide ligand is nearly linear and shows bent coordination with the Zn atom (N(5)N(6)N(7) 176.1(3)°, Zn(1)N(5)N(6) 125.7(2)°). The dihedral angle between the C(1)–C(6) benzene ring and the C(9)–C(13)N(2) pyridine ring is 5.3(3)°. There forms N(4)–H(4*A*)···O(1) hydrogen bond between L^b and 2-amino-4-methylpyridine ligands (N(4)–H(4*A*) 0.89(1), H(4*A*)···O(1) 2.02(1), N(4)···O(1) 2.838(3) Å, N(4)–H(4*A*)···O(1) 153(3)°).

In the crystal structure of complex **II** (Fig. 2b), molecules are linked by N(4)–H(4*B*)···N(5) hydrogen bonds (N(4)–H(4*B*) 0.89(1), H(4*B*)···N(5)^i 2.16(1), N(4)···N(5)^i 3.042(3) Å, N(4)–H(4*B*)···N(5)^i 169(3)°; symmetry code: ^{i} $-1 + x, y, z$) to form 1D chains along the *x* axis direction.

The middle and sharp band at 3307 cm^{-1} for **I** is assigned to the N–H streching vibration of the CH=NH group. The weak and sharp bands at 3291 and 3147 cm^{-1} for **II** are assigned to the N–H strech-

Table 1. Crystallographic and experimental data for the complexes **I** and **II**

Parameter	Value	
	I	**II**
Fw	327.0	440.8
Crystal shape/color	Block/red	Block/colorless
Crystal size, mm	0.17 × 0.15 × 0.15	0.32 × 0.30 × 0.29
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	16.067(2)	7.649(1)
b, Å	5.7222(6)	10.414(2)
c, Å	7.9004(9)	13.903(3)
α, deg	90	106.896(2)
β, deg	92.471(4)	91.581(2)
γ, deg	90	103.033(2)
V, Å^3	725.7(1)	1027.3(4)
Z	2	2
μ(MoK_α), mm^{-1}	1.342	1.221
ρ_{calcd}, g cm^{-3}	1.497	1.425
F(000)	340	456
T_{min}, T_{max}	0.8040, 0.8241	0.6960, 0.7184
Reflections measured	6299	10875
Unique reflections	1300	4685
Observed reflections ($I \geqslant 2\sigma(I)$)	1055	3865
Parameters	101	270
Restraints	1	3
Goodness of fit on F^2	1.078	1.045
R_1, wR_2 ($I \geqslant 2\sigma(I)$)*	0.0298, 0.0695	0.0372, 0.0823
R_1, wR_2 (all data)*	0.0427, 0.0745	0.0520, 0.0893
Largest diff. peak and hole, *e* Å^{-3}	0.226 and –0.227	0.376 and –0.264

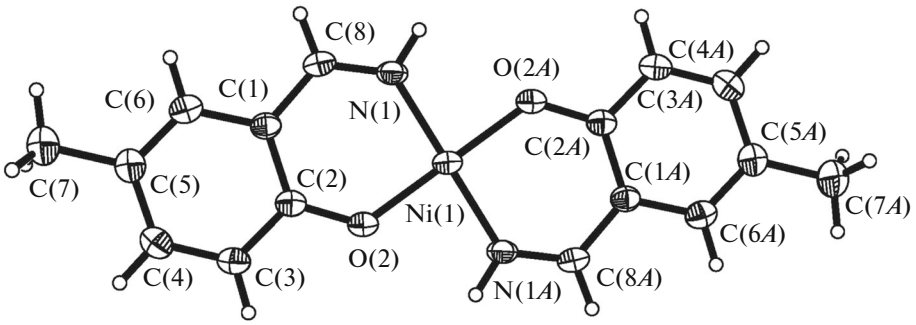
* $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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

Bond	*d*, Å	Bond	*d*, Å
		I	
Ni(1)–O(1)	1.837(2)	Ni(1)–N(1)	1.847(2)
		II	
Zn(1)–O(1)	1.965(2)	Zn(1)–N(1)	2.004(2)
Zn(1)–N(3)	2.029(2)	Zn(1)–N(5)	1.968(2)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Ni(1)N(1)	94.11(8)	O(1)Ni(1)N(1*A*)	85.89(8)
		II	
O(1)Zn(1)N(5)	112.44(8)	O(1)Zn(1)N(1)	93.19(7)
N(1)Zn(1)N(5)	114.20(8)	O(1)Zn(1)N(3)	105.18(7)
N(5)Zn(1)N(3)	110.33(8)	N(1)Zn(1)N(3)	119.79(7)

* Symmetry code for *A*: $2 - x$, $2 - y$, $1 - z$

(a)



(b)

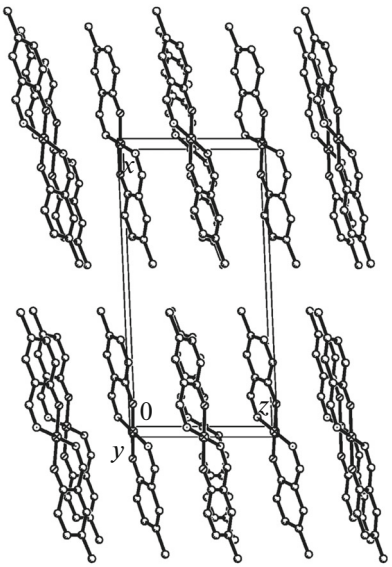


Fig. 1. Molecular structure of **I** at 30% probability displacement (atoms labeled with the suffix *A* are at the symmetry position $2 - x$, $2 - y$, $1 - z$) (a); molecular packing structure of **I**, viewed along the *y* axis (b).

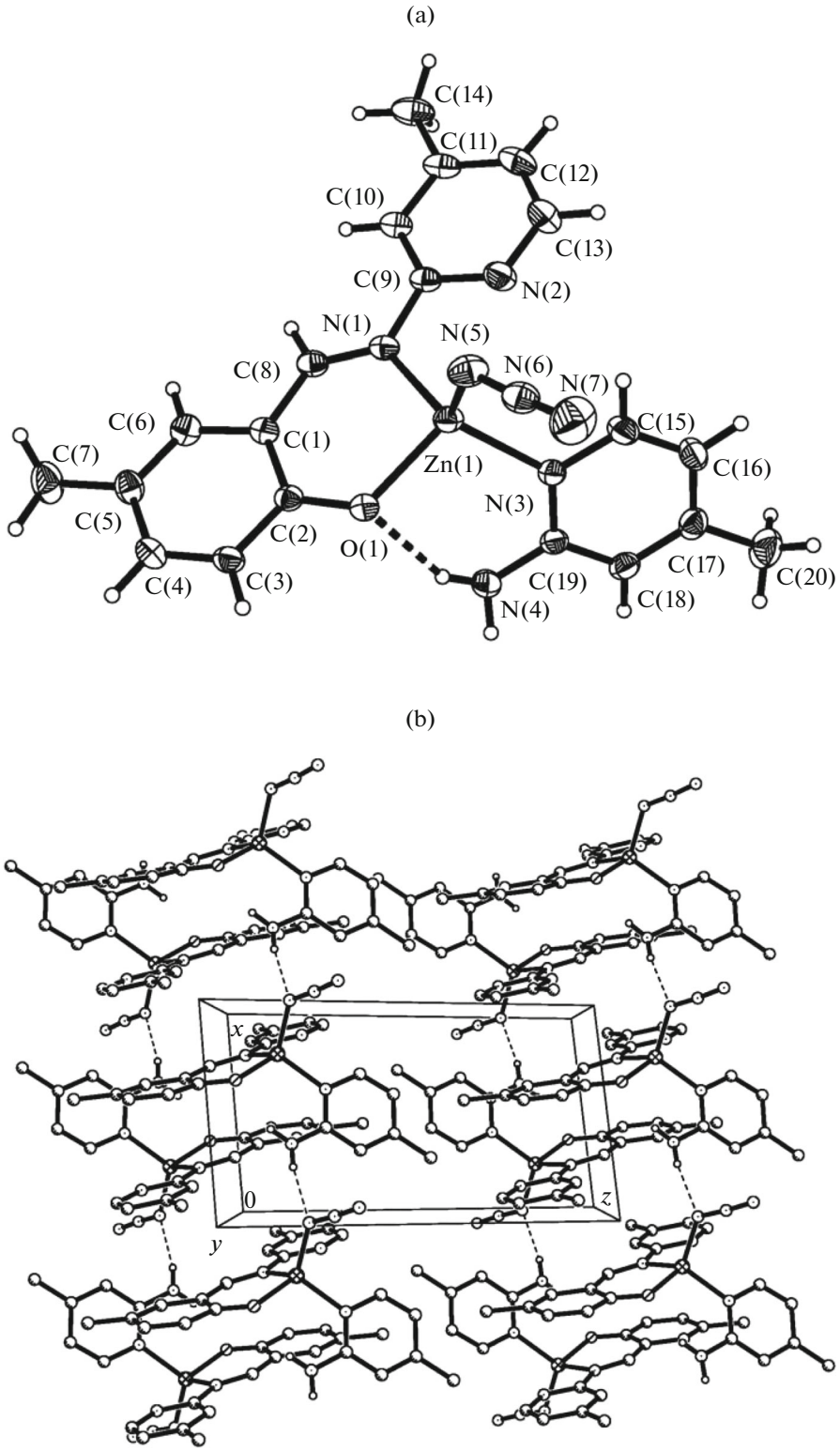


Fig. 2. Molecular structure of **II** at 30% probability displacement (hydrogen bond is shown as a dashed line) (a); molecular packing structure of **II**, viewed along the *y* axis. Hydrogen bonds are shown as dashed lines (b).

ing vibration of the NH_2 group. The strong absorption bands at 1621 cm^{-1} for **I** and 1612 cm^{-1} for **II** are assigned to the azomethine groups, ν(C=N). The phenolate ν(Ar–O) in the complexes exhibit middle bands at 1212 cm^{-1} for **I** and **II**. The intense band at 2073 cm^{-1} for **II** is assigned to the stretching vibrations of the azide ligands. The weak bands located at the low numbers may be assigned to the ν(M–O) and ν(M–N).

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