

Synthesis and Crystal Structures of Ni(II)/(III) and Zn(II) Complexes with Schiff Base Ligands

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(Received September 27, 2013; Accepted October 26, 2013)

Key words: Ni(II)/(III), Zn(II), Schiff base, Crystal structure

Coordination polymers are of great interest due to their intriguing structural motifs and potential applications in optical, electronic, magnetic, and porous materials.¹⁻³ The most commonly used strategy for designing such materials relies on the utilization of multidentate N- or O-donor ligands which have the capacity to bridge between metal centers to form polymeric structures.⁴ The Schiff bases with N,O,S donor atoms are an useful source as they are readily available and easily form stable complexes with most transition metal ions.^{5,6} Schiff bases are also important intermediates in synthesis of some bioactive compounds⁷ and are potent anti-bacterial, anti-fungal, anticancer and antiviral compounds.⁸

In this work, the Schiff bases, Hapb and Hbpb, derived from 2-acetylpyridine or 2-benzoylpyridine and benzhydrazide were taken as trifunctional (N,N,O) monobasic ligand (Scheme 1). This ligand is of important because the π -delocalization of charge and the configurational flexibility of their molecular chain can give rise to a great variety of coordination modes. Although many metal-Schiff base complexes have been reported, the 1D, 2D, and 3D networks of coordination polymers linked through the bridging of ligands such as dicyanamide, $N(CN)_2^-$ as coligand have been little published.^{9,10} In the process of working to extend the dimensionality of the metal-Schiff base complexes using benzoic acid as a bridging ligand, we obtained three simple metal (II)/(III) complexes of acetylpy-

ridine/2-benzoyl pyridine based benzhydrazide ligand. Therefore, we report here the synthesis and crystal structures of the complexes.

EXPERIMENTAL

Chemicals and Measurements

All chemicals are commercially available and were used as received without further purification. Elemental analyses (CHN) were performed on a Vario EL EA-Elementar Analyzer.

Preparation of [Zn(bpb)]₂ (1)

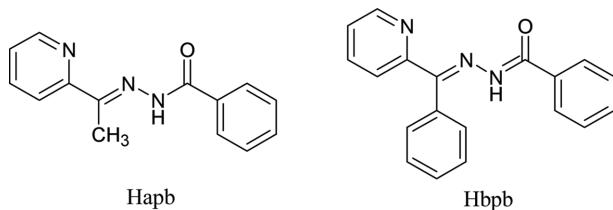
To a methanolic solution (30 mL) of Hbpb ligand (0.302 g, 1.0 mmol) was added Zn(ClO₄)₂·6H₂O (0.372 g, 1.0 mmol). To the resulting pale yellow solution was added a methanolic solution (3 mL) of benzoic acid (0.228 g, 1.0 mmol) and triethylamine (0.152 g, 1.5 mmol). The solution turned to yellow and was refluxed for 3 h to yield yellow solid. The yellow solid was isolated by filtration and air-dried. The yellow filtrate was kept at room temperature to give yellow block crystals in good quality for X-ray crystallography. Yield: 63% (0.419 g) based on Zn. Elemental Anal. Calcd. For C₃₈H₂₈N₆O₂Zn: C, 68.52; H, 4.24; N, 12.62. Found: C, 68.30; H, 4.57; N, 12.30%.

Preparation of [Ni(bpb)]₂ (2)

The compound was prepared similarly by the method described above for the preparation of **1**, with use of Ni(ClO₄)₂·6H₂O instead of Zn(ClO₄)₂·6H₂O. Yield 58% (0.382 g) based on Ni. Elemental Anal. Calcd. for C₃₈H₂₈N₆O₂Ni: C, 69.22; H, 4.28; N, 12.75. Found: C, 68.72; H, 4.52; N, 12.28%.

Preparation of [Ni(apb)]₂·ClO₄·CH₃OH (3)

The compound was prepared similarly by the method



Scheme 1. Chemical structures of Schiff bases and their abbreviations.

Table 1. Crystal data and structure refinement for complexes 1–3

Complex	1	2	3
Empirical formula	C ₃₈ H ₂₈ N ₆ O ₂ Zn	C ₃₈ H ₂₈ N ₆ O ₂ Ni	C ₂₉ H ₂₈ N ₆ O ₇ ClNi
Formula weight	666.03	659.37	666.73
T(K)	200(2)	200(2)	296(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n
<i>a</i> (Å)	10.6428(6)	10.7854(5)	8.648(2)
<i>b</i> (Å)	12.5122(7)	12.3971(5)	10.625(2)
<i>c</i> (Å)	12.9696(7)	12.6910(6)	33.376(6)
α (°)	66.234(1)	66.726(1)	
β (°)	83.802(1)	83.472(1)	96.438(4)
γ (°)	83.602(1)	82.652(1)	
<i>V</i> (Å ³)	1567.0(2)	1542.3(1)	3047.3(1)
<i>Z</i>	2	2	4
μ (mm ⁻¹)	0.829	0.675	0.780
<i>F</i> (000)	688	684	1380
θ (°)	1.72 to 28.29	1.80 to 28.30	1.23 to 28.31
Absorption correction	none	none	multi-scan T _{min} = 0.814, T _{max} = 0.901
Limiting indices	-14 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, -10 ≤ <i>l</i> ≤ 17	-14 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 10	-10 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 13, -44 ≤ <i>l</i> ≤ 39
Reflections collected	11790	11603	22130
Independent reflections	7684 [R(int) = 0.0464]	7545 [R(int) = 0.0459]	7523 [R(int) = 0.0642]
Observed reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	3588	4017	4094
Goodness-of-fit on <i>F</i> ²	0.890	1.092	1.103
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0523	0.0691	0.0520
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0690	0.1055	0.1154
<i>R</i> ₁	0.1332	0.1399	0.1208
<i>wR</i> ₂	0.1013	0.1706	0.1617
Largest peak and hole (eÅ ⁻³)	0.844 and -1.384	1.273 and -2.108	0.645 and -0.624

described above for the preparation of **1**, with use of Ni(ClO₄)₂·6H₂O and Hapb instead of Zn(ClO₄)₂·6H₂O and Hbpb ligand, respectively. Yield 65% (0.432 g) based on Ni. Elemental Anal. Calcd. for C₂₉H₂₈N₆O₇ClNi: C, 52.24; H, 4.23; N, 12.61. Found: C, 51.85; H, 4.48; N, 12.31%.

X-ray Structure Determination

Single crystals of **1–3** were obtained by the method described in the above procedures. Structural measurement for the complexes were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at the Korea Basic Science Institute. The structures were solved by direct method and refined on *F*² by full-matrix least-squares procedures using the SHELXTL programs.¹¹ All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with the ORTEP¹² or

DIAMOND program.¹³ The crystallographic data for complexes **1–3** are listed in Table 1.

RESULTS AND DISCUSSION

The complexes of **1–3** were prepared from the methanolic solution of M(ClO₄)₂·*x*H₂O (M = Ni, and Zn), Schiff base ligand, and benzilic acid. Our first aim in this work was to obtain the coordination polymers which metal centers are bridged by the benzilic acid as mixed ligand. However, the benzilic acid present in the initial reaction mixture was not found in the crystalline product. Unfortunately, attempts to obtain the product containing the benzilic acid and to improve yields by varying stoichiometry, temperature, and other reaction parameters proved to be generally unsuccessful.

Description of the Structures

The molecular structure of complex **1** consists of one

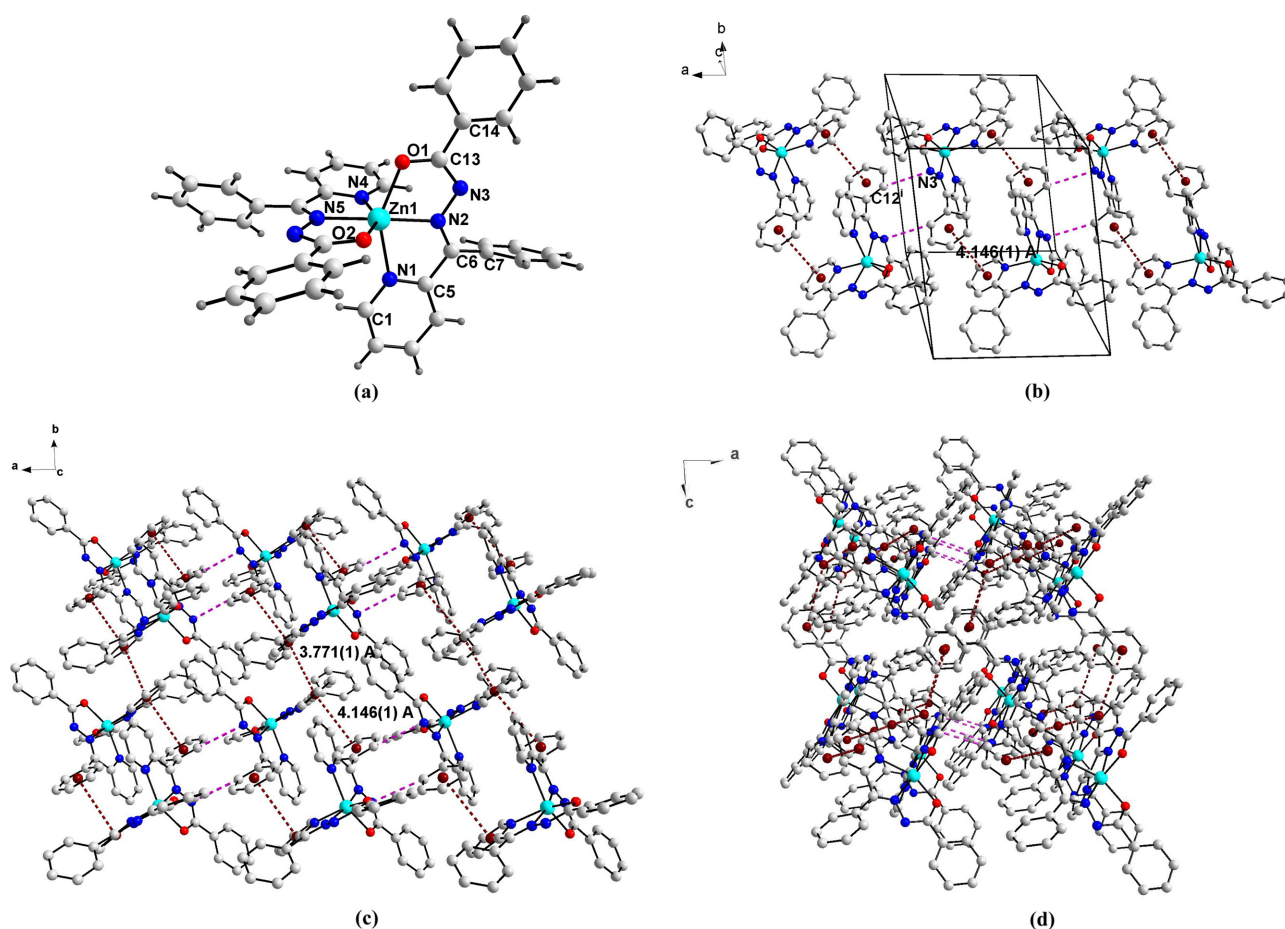


Figure 1. (a) Molecular structure of complex **1** with atomic labeling. (b) The 1D chain formed by H-bond and π - π interactions in **1** along the a -axis. Geometric details describing the H-bond operating in the crystal structure: C12¹-H12¹...N3 = 2.46 Å with angle at H12 = 139.4° for symmetry operation $i: 2-x, 1-y, 1-z$. (c) The 2D layer framework of complex **1** formed by H-bond and π - π interactions. (d) Packing diagram of complex **1**. The hydrogen bonds and π - π interactions have been shown as dashed and dotted lines, respectively. All H-atoms in (b)–(d) have been omitted for clarity.

Zn(II) ion and two coordinated bpb^- ligands (Fig. 1(a)). Zn(II) ion center is six-coordinated by four nitrogen atoms (N1, N2, N4, N5) and two oxygen atoms (O1, O2) from two bpb^- ligands. The Zn–N bond lengths are slightly longer than the Zn–O distances. The basal plane (N2N4N5O2) is nearly planar (mean deviation 0.053(3) Å) and the Zn1 is displaced by 0.041(1) from the plane toward O1. The structural data are listed in Table 2 and are in agreement with those of the Zn(II) complexes which exhibit the similar geometry.^{14,15} Three planes [N1C1–C5, C7–C12 and C14–C19] in bpb^- are nearly planar with the largest deviations of atoms from the mean planes: C1; 0.005(4), C9; –0.003(5), and C17; 0.003(4) Å, respectively. The dihedral angles between two phenyl rings (C7–C12 and C14–C19) and between two planes N1C1–C5 and C14–C19 are 71.97 (13) and 18.39(11)°, respectively.

The principal feature of the crystal packing is the formation of a three-dimensional network by C–H...N and π ... π contacts. Two monomeric molecules in the unit cell are linked by π ... π stacking between pyridine and phenyl rings of neighboring molecules with inter-ring distance of 4.146 (1) Å. The unit cell is further extended by intermolecular H-bonds (C12–H12...N3) to give 1D chain network along a -axis (Fig. 1(b)). This chains also constructs 2D plane (ab -plane) by the π ... π stacking between adjacent pyridine rings (centroid-to-centroid distance of 3.771(1) Å) (Fig. 1(c)). The 3D supramolecular structure is formed by inter-layer face-to-face π ... π stacking (4.352(1) Å) between phenyl rings of adjacent 2D layers along c -axis. The packing diagram is shown in Fig. 1(d).

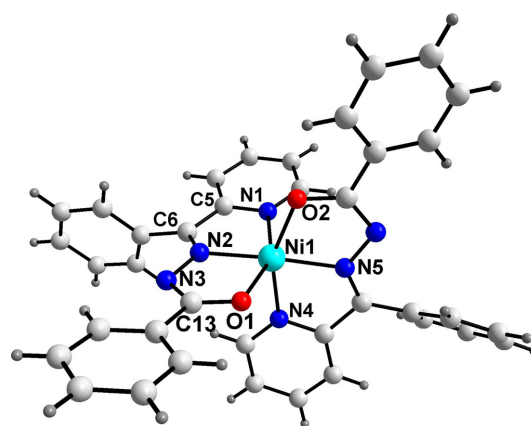
The complex **2** has basically the same structure of **1** (Fig. 2). Nickel(III) ion exhibits a distorted octahedral

Table 2. Selected bond lengths (Å) and angles (°) for complexes 1–3

Complex 1			
Zn1–O2	2.056(2)	Zn1–O1	2.104(3)
Zn1–N5	2.076(3)	Zn1–N2	2.082(3)
Zn1–N4	2.210(3)	Zn1–N1	2.213(3)
O1–C13	1.271(4)	N3–C13	1.367(4)
O2–Zn1–N5	75.8(1)	O2–Zn1–N2	116.1(1)
N5–Zn1–N2	166.9(1)	O2–Zn1–N4	150.3(1)
N5–Zn1–N4	74.5(1)	N2–Zn1–N4	93.7(1)
N2–Zn1–N1	74.3(1)	O1–Zn1–N1	148.9(1)
Complex 2			
Ni1–O2	2.063(3)	Ni1–O1	2.082(3)
Ni1–N5	2.003(4)	Ni1–N2	2.002(4)
Ni1–N4	2.098(4)	Ni1–N1	2.122(4)
O1–C13	1.277(6)	N3–C13	1.348(6)
N2–Ni1–N5	172.7(2)	N2–Ni1–O2	109.6(2)
N5–Ni1–O2	77.1(2)	N2–Ni1–O1	76.8(2)
N2–Ni1–N4	95.1(2)	N5–Ni1–N4	78.3(2)
O2–Ni1–N4	155.2(2)	O1–Ni1–N1	154.8(2)
Complex 3			
Ni1–N2	1.983(3)	Ni1–N5	2.016(3)
Ni1–O1	2.072(2)	Ni1–N1	2.090(3)
Ni1–N4	2.109(3)	Ni1–O2	2.153(2)
N3–C8	1.331(4)	C8–O1	1.287(4)
N2–Ni1–N5	174.7(1)	O1–Ni1–N1	154.6(1)
N2–Ni1–N4	99.2(1)	N5–Ni1–N4	76.6(1)
N2–Ni1–O2	108.4(1)	N5–Ni1–O2	76.0(1)
N4–Ni1–O2	152.3(1)		

environments with the *cis*- and *trans*-L–Ni–L angles in the range of 76.8(2)–109.6(2)° and 154.8(2)–172.7(2)°, respectively (Table 2), compared to the complex 1 (*cis*- and *trans*-L–Zn–L angles in the range of 74.3(1)–116.1(1)° and 148.9(1)–166.9(1)°, respectively). The deviation from the ideal values for the octahedral structure is relatively small and more close to the octahedral compared to the complex 1. The average bond distances of Ni–N and Ni–O are 2.056(4) and 2.073(3) Å, respectively. The distances are slightly shorter than the distances (Zn–N = 2.145(3) and Zn–O = 2.080(3) Å) of complex 1. Most notably, the distance of Ni–N is smaller than Ni–O bond distances, contrast to the complex 1.

Complex 2 is also consolidated into a three-dimensional network by a C–H···N (C8ⁱ–H8···N3ⁱⁱ = 2.52 Å and C8ⁱ···N3ⁱⁱ = 3.28(1) Å with angle at H8 = 141° for symmetry operation i: x, 1+y, –1+z; ii: 2–x, 2–y, –z) and π ··· π interactions. Two monomeric molecules in the unit cell are linked by π ··· π stacking between pyridine and phenyl rings of neighboring molecules with inter-ring distance of 4.157(1)

**Figure 2.** Molecular structure of complex 2 with atomic labeling.

Å and intermolecular H-bonds (C8ⁱ–H8···N3ⁱⁱ) to give 1D chain network along *a*-axis as shown in complex 1. The chains constructs 2D framework by the π ··· π stacking between adjacent pyridine rings (centroid-to-centroid distance of 3.815(1) Å) and finally, 3D network is accomplished by inter-layer face-to-face π ··· π stacking (4.400(1) Å) between phenyl rings of adjacent 2D layers along *c*-axis.

While, complex 3 consists of one Ni(III) ion, two coordinated apb ligands, one perchlorate ion, and one solvent methanol molecule, respectively (Fig. 3(a)). Here, the oxidation state of nickel is +3 in contrast to Ni(II) of starting material. This oxidation to Ni(III) can be assumed that the starting Ni(II) salt undergoes aerial oxidation in the presence of the Schiff base ligand in methanolic solution during preparation of the complex.^{16–18}

The structure of complex 3 is similar to those of the complexes 1 and 2 with bpb[–] ligand. Two planes of apb[–] ligand, N4C15–C19 and C23–C28, are nearly plane with rms = 0.003(4), and 0.006(5) Å, respectively. The dihedral angle between them is 15.1(1)°. While, the dihedral angle between two pyridine planes (N1C1–C5 and N4C15–C19) of two apb[–] ligands is 89.9(1)°. The distances and bond angles are listed in Table 2. The structural data are similar to those of the Mn(II) and Zn(II) complexes with apb ligand, respectively.¹⁴

As shown in Fig. 3(b), the monomeric units construct 2D network by π ··· π stacking between pyridine and phenyl rings with inter-ring distance of 3.639(1) (*a*-axis) and 4.114(1) Å (*b*-axis), respectively. In contrast to complexes 1 and 2, there is not intermolecular H-bonding which construct 3D net work. For all complexes, the relatively short C13–N3 (for 1 and 2) and C8–N3 (for 3) bond distances (normal single bond is 1.52 Å),¹⁹ coupled with the length-

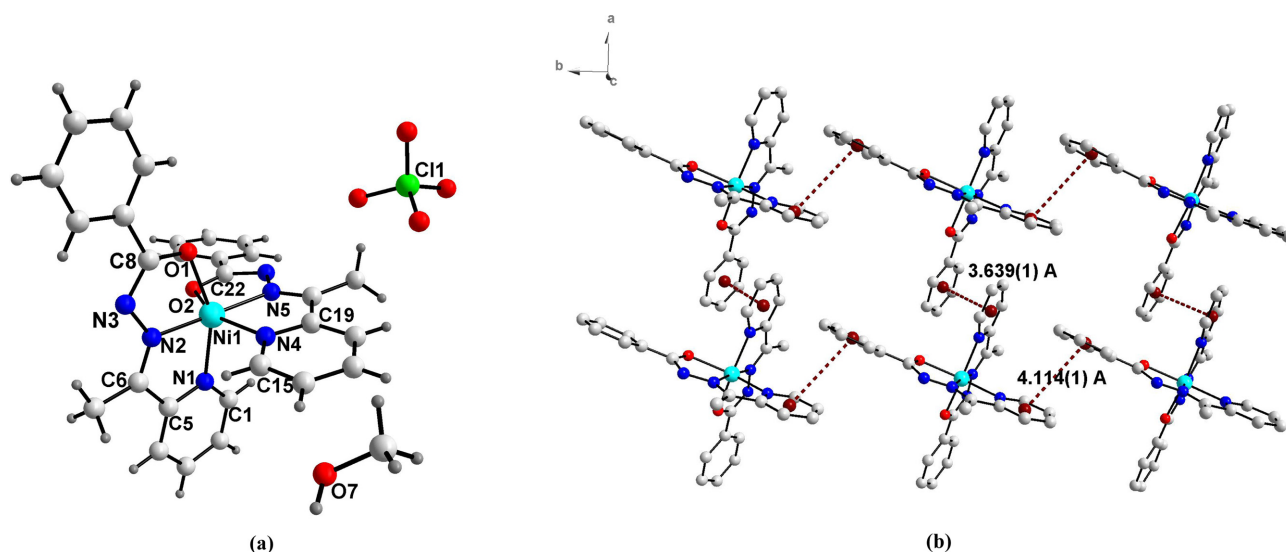


Figure 3. (a) Molecular structure of complex **3** with atomic labeling. (b) 2D layer in complex **3**. All H atoms, CH₃OH, and ClO₄⁻ have been omitted for clarity.

ened C13–O1 (for **1** and **2**) and C8–O1 (for **3**) distances which is typical of ketonic linkage (1.23 Å)^{20,21} indicate that the ligands act as enol form.

In conclusion, by the reactions of Ni(II)/Zn(II) ions and Schiff base ligands, three new metal(II)/(III) complexes, [Zn(bpb)₂] (**1**), [Ni(bpb)₂] (**2**), and [Ni(apb)₂]-ClO₄·CH₃OH (**3**), have been synthesized. In each complex, metal ion is six-coordinated with N4O2 donors. The Schiff base is coordinated to metal(II)/(III) ions as a trifunctional ligand. The structures are further extended into supramolecular framework by hydrogen bonds and π ... π stacking interactions. Unfortunately, it has failed to obtain the polymeric complexes of Schiff base through benzoic acid in this work. The development of synthetic routes to the systems containing Schiff base is still required for the rational design and synthesis.

Acknowledgments. This work was supported by the 2012 Research Fund of Catholic University of Daegu. The author also acknowledges the Korea Basic Science Institute for providing the crystal structure results.

Supporting Information. Crystallographic data in CIF format have been deposited with the Cambridge Structural Database CCDC 927522 (for **1**), 927523 (for **2**), and 927521 (for **3**), respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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