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Synthesis, Characterization, and Crystal Structure of Three Coordination Polymers from 5-(Pyridin-2-ylmethyl)aminoisophthalic Acid

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Abstract. Three new complexes: [M(L)(H_2O)] [M = Zn (**1**), Co (**2**), Ni (**3**); H_2L = 5-(pyridin-2-ylmethyl)aminoisophthalic acid] were synthesized under hydrothermal conditions at 180 °C and were characterized by elemental analysis, FT-IR spectroscopy, single-crystal X-ray diffraction, and thermogravimetric analysis (TGA). The results of X-ray diffraction analysis reveal that complexes **1**–**3** are isostructural and crystallize in the monoclinic system with space group $P2_1/c$. Each of the complexes displays a (3,3')-connected two-dimensional (2D) wave-like network with ($4,8^2$) topology, within which five-membered uncoplanar N,N-chelated metallacycles are shaped. Delicate N–H···O and O–H···O hydrogen bonding interactions exist in complexes **1**–**3**. Adjacent 2D layers are linked by intermolecular interactions, resulting in the construction of extended metal-organic frameworks (MOFs) in complexes **1** and **2**.

1 Introduction

During the past few decades, the rational design, synthesis, and characterization of metal-organic frameworks (MOFs) with well-defined sizes, beautiful shapes, and chemical environments have attracted more and more attention, which is justified by their fascinating architectures and tremendous potential applications in heterogeneous catalysis, ion-recognition, nonlinear optics, and molecular adsorption.[1] Hitherto, a great number of open frameworks with abundant structural motifs and interesting properties were developed and discussed in some comprehensive reviews.[2] An effective strategy for the construction of such complexes is to select suitable organic ligands as building blocks that enable the control of structural motifs and functional properties.[3] Among popularly employed ligands, rigid or flexible N, O multidentate donor ligands are always regarded as excellent candidates for building the blocks of desirable frameworks.[4]

However, due to the complexity of self-assembly processes, it is impossible to regulate coordinating processes for most organic ligands and to predict the structure of the resultant complexes. Therefore, it is still a great challenge to rationally design and synthesize desired complexes. With this background in mind, recently we focused our attention on the design and synthesis of a carboxylic- and (2-pyridyl)-containing ligand: [H_2L = 5-(pyridin-2-ylmethyl)aminoisophthalic acid] to achieve new MOFs. One of the goals is to investigate the influence of the intrinsic features of the H_2L ligand on the structure and functional properties of the resultant complexes. Compared with other N or O donor ligands, the arene-cored ligand H_2L has several distinctive traits. In the first place, H_2L contains (pyridin-2-ylmethyl)amino groups. This type of N,N bidentate donor groups are always inclined to shape an N,N-chelated metallacycle, which could play a very important role in inducing a structural evolution and maintaining a specific coordinating configuration.[5] Secondly, as an aromatic dicarboxylate-containing ligand, on account of the fine coordinating performance of carboxylate groups,[6] H_2L could reliably act as a bridging rod. Thirdly, due to the presence of N–H groups as potential hydrogen-bonding groups, hydrogen bonding interactions may be available to extend the coordinating networks and direct overall 3D metal-organic frameworks (MOFs).[7] Thus, the structural prediction of resulting polymeric species may be possible to some extent. Because of the above considerations, we selected 5-(pyridin-2-ylmethyl)aminoisophthalic acid as organic ligand rather than (pyridin-3-ylmethyl)amino-containing or (pyridin-4-ylmethyl)amino-containing ones that could build higher-dimensional architectures and shape more complicated structural motifs.[8]

Herein, we describe the synthesis, characterization, and crystal structure of three complexes: {[Zn(L)(H_2O)] (**1**), [Co(L)(H_2O)] (**2**), and [Ni(L)(H_2O)] (**3**)} in order to explore the essence of coordinating behaviors of the H_2L ligand. As expected, the results of the X-ray crystallographic analysis revealed that the these complexes have similar architectures: a five-membered noncoplanar N,N-chelated metallacycle is generated via the (pyridin-2-ylmethyl)amino groups coordinating towards the M^{II} ions; the L^{2-} ligand unsurprisingly acts as

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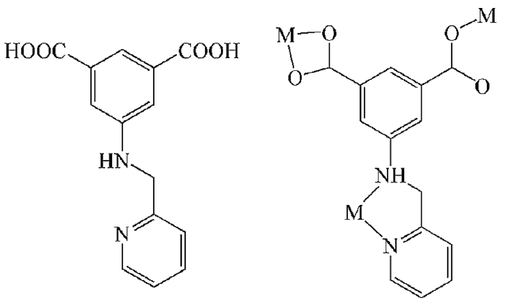
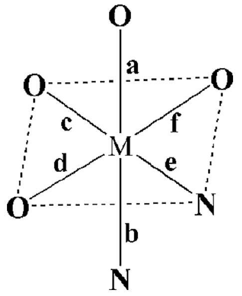
bridging rod, leading to the formation of a 2D wave-like network (Scheme 1); besides, delicate N–H···O and O–H···O hydrogen bonding interactions also exist in the three complexes, which superpose adjacent layers to construct the three-dimensional (3D) supramolecular structures in complexes **1** and **2**. Complexes **1**–**3** were characterized by elemental analysis, FT-IR spectroscopy, single-crystal X-ray diffraction, and thermogravimetric analysis (TGA).



Scheme 1. Molecular structure and coordination mode of the H_2L ligand in complexes **1**–**3**.



Scheme 2. Schematic representation of distorted octahedral coordination arrangements of [MN_2O_4] in complexes **1**–**3**.

2 Results and Discussion

2.1 Preparation

The hydrothermal reaction at 180 °C of stoichiometric amounts of $M(NO_3)_2\cdot 6H_2O$ [M = Zn (**1**), Co (**2**), and Ni (**3**)] with H_2L in the presence of NaOH provided single crystals of complexes **1**–**3** analyzed as [$M(L)(H_2O)$] by single-crystal X-ray diffraction analysis, which are stable in air.

2.2 Structural Description

Determination of the structures of complexes **1**–**3** by X-ray crystallography revealed that the molecular structures of the three complexes are similar. The three complexes crystallize in the monoclinic system with space group $P2_1/c$ (Table 3). Thus, only complex **1** is discussed in detail herein.

As shown in Figure 1(A), in the asymmetric unit of complex **1**, there are one Zn^{II} ion, one L^{2-} ligand, and one coordinated water molecule. Each Zn^{II} ion is six-coordinate by two nitrogen atoms from one L^{2-} ligand, one oxygen atom from the coordinated water molecule, and three oxygen atoms from two carboxylate groups of two different L^{2-} ligands to furnish a distorted octahedral coordination arrangement [ZnN_2O_4] [Figure 1(B)]. Two carboxylate groups of the L^{2-} ligand exhibit different coordination mode in complex **1**, one adopts a κ^2-O,O-chelating coordination mode [the value of angle subtended at Zn^{II} ion by them being 54.29(13)°], whereas the other carboxylate group shows a κ^1-O-monodentate coordination. The obvious difference in bond lengths [Zn1–O1 = 1.951(3) Å, Zn1–O2 = 2.675(4) Å, Zn1–O4(c) = 2.051(3) Å] is just the reflection of the overall molecular distortion. Two nitrogen atoms from the (pyridin-2-ylmethyl)amino group coordinate towards one Zn^{II} ion to generate a five-membered uncoplanar N,N-chelated metallacycle [Zn(1)–N1(b) = 2.382(5) Å, Zn(1)–N2(b) = 2.061(4) Å]: one nitrogen atom is located in the equatorial plane of the octahedral coordination arrangement; the other nitrogen atom occupies the apex [N1(b)–Zn1–N2(b) = 75.25(15)°]. The dihedral angle between the pyridyl ring of the flexible arm and the central benzene ring is about 79.02°. Selected bond lengths and angles are listed in Table 2.

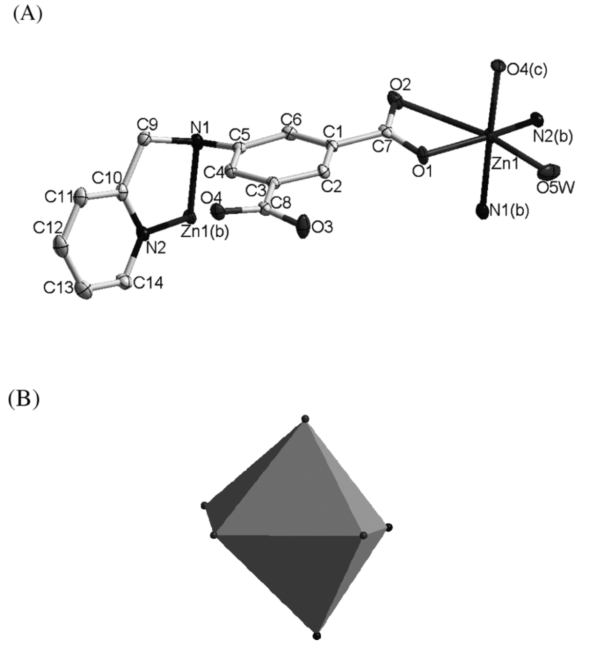


Figure 1. (A) Coordination arrangement of the Zn^{II} ion in complex **1** with 30 % probability displacement ellipsoids. Hydrogen atoms were omitted for clarity. Symmetry transformations: b: $-x$, $1-y$, $-z$; c: x, $0.5-y$, $0.5+z$. (B) Polyhedral representation of [ZnN_2O_4].

As described above, each L^{2-} ligand bridges three different Zn^{II} ions and every Zn^{II} ion is coordinated by three different L^{2-} ligands. This kind of connection extend the coordination and makes complex **1** a neutral infinite 2D wave-like network [Figure 2(B)]. Both Zn^{II} ion and L^{2-} ligand can be considered as three-connected nodes in a ratio of 1:1 in complex **1**. Therefore, complex **1** exhibits a (3,3')-connected 2D network with a ($4,8^2$) topology [Figure 2(C)]. Within the 2D layer, two L^{2-}

Table 1. Varying extent of distorted octahedral coordination arrangements of [MN_2O_4].

Complex	a /Å	b /Å	c /Å	d /Å	e /Å	f /Å	$S^{a)}$ /Å
Zn^{II}	2.051(3)	2.382(5)	1.951(3)	2.024(4)	2.061(4)	2.675(4)	1.018(3)
Co^{II}	2.065(2)	2.306(1)	2.010(2)	2.406(2)	2.087(2)	2.076(2)	0.626(1)
Ni^{II}	2.015(1)	2.024(2)	2.284(1)	2.044(2)	2.147(2)	2.052(2)	–0.326(2)

a) $S = (b - a) + (d - c) + (f - e)$.

Table 2. Selected bond lengths /Å and angles /° for complexes **1**–**3**.

1			
Zn(1)–O(1)	1.951(3)	Zn(1)–O(2)	2.675(4)
Zn(1)–N(1)#1	2.382(5)	Zn(1)–N(2)#1	2.061(4)
Zn(1)–O(5W)	2.024(4)	Zn(1)–O(4)#2	2.051(3)
O(4)#2–Zn(1)–N(2)#1	97.75(15)	O(4)#2–Zn(1)–O(2)	85.79(13)
O(5W)–Zn(1)–O(4)#2	95.05(16)	O(1)–Zn(1)–O(4)#2	96.48(15)
O(1)–Zn(1)–N(1)#1	88.65(15)	N(1)#1–Zn(1)–O(2)	92.51(13)
N(2)#1–Zn(1)–N(1)#1	75.25(15)	O(5W)–Zn(1)–N(1)#1	88.75(16)
O(1)–Zn(1)–O(2)	54.29(13)	N(2)#1–Zn(1)–O(2)	103.79(14)
O(1)–Zn(1)–O(5W)	109.30(18)	O(5W)–Zn(1)–N(2)#1	92.47(19)
O(4)#2–Zn(1)–N(1)#1	172.20(14)		
2			
Co(1)–O(1)	2.0102(16)	Co(1)–O(2)	2.4069(19)
Co(1)–N(1)#3	2.3066(19)	Co(1)–N(2)#3	2.0878(19)
Co(1)–O(4)#4	2.0654(15)	Co(1)–O(5W)	2.0760(19)
O(4)#4–Co(1)–O(1)	96.38(7)	O(4)#4–Co(1)–O(5W)	92.82(7)
O(4)#4–Co(1)–N(2)#3	97.65(7)	O(4)#4–Co(1)–O(2)	87.47(6)
O(1)–Co(1)–N(1)#3	89.39(7)	O(5W)–Co(1)–N(1)#3	87.07(7)
N(2)#3–Co(1)–N(1)#3	76.42(7)	N(1)#3–Co(1)–O(2)	94.35(6)
O(1)–Co(1)–O(2)	59.07(6)	O(1)–Co(1)–O(5W)	104.23(8)
O(5W)–Co(1)–N(2)#3	88.34(8)	N(2)#3–Co(1)–O(2)	108.32(7)
O(4)#4–Co(1)–N(1)#3	174.07(7)		
3			
Ni(1)–O(1)	2.0158(17)	Ni(1)–N(2)#5	2.024(2)
Ni(1)–O(4)#6	2.0437(15)	Ni(1)–O(5W)	2.0518(16)
Ni(1)–N(1)#5	2.147(2)	Ni(1)–O(3)#6	2.2843(16)
O(1)–Ni(1)–O(4)#6	87.19(7)	O(1)–Ni(1)–O(5W)	92.89(7)
O(1)–Ni(1)–N(1)#5	93.41(8)	O(1)–Ni(1)–O(3)#6	91.27(7)
N(2)#5–Ni(1)–O(3)#6	92.56(7)	N(2)#5–Ni(1)–O(4)#6	91.87(7)
N(2)#5–Ni(1)–O(5W)	88.78(7)	N(2)#5–Ni(1)–N(1)#5	81.64(8)
O(4)#6–Ni(1)–O(3)#6	60.51(6)	O(5W)–Ni(1)–O(3)#6	110.76(6)
O(5W)–Ni(1)–N(1)#5	99.85(7)	O(4)#6–Ni(1)–N(1)#5	88.87(7)
O(1)–Ni(1)–N(2)#5	174.99(8)		

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $1 - y$, $-z$; #2: x, $1/2 - y$, $-1/2 + z$; #3: $2 - x$, $-y$, $2 - z$; #4: x, $1/2 - y$, $1/2 + z$; #5: $-x$, $1 - y$, $1 - z$; #6: $-x$, $-1/2 + y$, $1/2 - z$.

ligands doubly connect two different Zn^{II} ions to form a secondary building unit (SBU) [$Zn_2(L)_2(H_2O)_2$] [Figure 2(A)].

Delicate N–H···O and O–H···O hydrogen bonding interactions exist in complex **1**. There are two kinds of intermolecular hydrogen bonding: (1) the hydrogen bonding (N1–H1N···O2) between the hydrogen atom (H1N) from a (pyridin-2-ylmethyl)amino group and the oxygen atom (O2) of the carboxylate unit (O1C7O2); (2) the hydrogen bonding (O5W–H5WB···O4) between the hydrogen atom (H5WB) of the coordinated water molecules and the oxygen atom (O4) from carboxylate (O3C8O4) [Figure 3(A); Table S1, Supporting Information]. More significantly, this system of intermolecular strong hydrogen bonding superposes adjacent layers to construct a three-dimensional framework [Figure 3(B)].

Although the three complexes are isostructural, there is still a little difference among them: (1) the tortuosity of five-membered uncoplanar N,N-chelated metallacycles in each complex is different, which is the reflection of varying degrees of the molecular distortion. The detailed torsion angles are listed in Table S2 (Supporting Information); (2) despite showing the same coordination arrangement [MN_2O_4] (Scheme 2, Table 1), the six coordinating atoms array in different spatial order. For example, in complexes **1** and **2**, the nitrogen atom of amino group (–NH–) is located at the axial position of the octahedral polyhedron, and the nitrogen atom from the pyridyl ring is located in the equatorial plane. However, the case is just reverse for complex **3**. The molecular structures of **2** and **3** are presented in Figure S1 and S2 (Supporting Information).

Table 3. Crystallographic data and structure refinement details for complexes **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{14}H_{12}N_2O_5Zn$	$C_{14}H_{12}CoN_2O_5$	$C_{14}H_{12}N_2NiO_5$
Formula weight	353.63	347.19	346.97
Temperature /K	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a /Å	5.5356(7)	5.4613(7)	8.9619(6)
b /Å	14.4821(19)	14.681(2)	12.0053(8)
c /Å	16.449(2)	16.443(2)	14.7534(7)
β /°	93.329(2)	92.457(2)	123.762(3)
V /Å^3	1316.4(3)	1317.1(3)	1319.62(14)
Z, D_{calc} /Mg·m^{-3}	4, 1.784	4, 1.751	4, 1.746
Absorption coefficient	1.511	1.330	1.497
$F(000)$	720	708	712
θ range /°	1.87–25.01	1.86–28.00	2.37–26.95
Reflections collected / unique	6453/2310 (R_{int} = 0.0213)	8138/3125 (R_{int} = 0.0379)	8114/3143 (R_{int} = 0.0381)
Data / restraints / parameters	2310/0/193	3125/0/199	3143/0/193
GOF on F^2	1.353	1.029	1.004
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0581 / 0.1168	0.0365 / 0.0784	0.0337 / 0.0812
R_1 / wR_2 [all data]	0.0595 / 0.1173	0.0484 / 0.0814	0.0450 / 0.0842

2.3 Thermogravimetric Analyses

Thermogravimetric analyses (TGA) of complexes **1**–**3** were recorded in a nitrogen atmosphere with a heating rate of 10 °C·min^{-1} in order to study their thermal stability. The three complexes were heated from 20 to 680 °C. The TGA curves of compounds **1**–**3** exhibit similar thermal behaviors (Figure 4). The first step (224–253 °C for **1**, 205–247 °C for **2**, and 206–249 °C for **3**) corresponds to the release of one coordinated water molecule and the observed weight losses of 5.36 % for **1**, 4.90 % for **2**, and 5.48 % for **3** are very close to the calculated value (5.09 %, 5.18 %, and 5.19 % for **1**, **2**, and **3**, respectively). The second step occurs at 383 °C for **1**, 375 °C for **2**, and 347 °C for **3** and is associated with the combustion of the L^{2-} ligands. The continuous decomposition of complexes **1** and **2** does not end above 680 °C, so the final residuals are not characterized. But in the TGA curve of complex **3**, the second step terminates at 471 °C with a total weight loss of 78.3 %, which is in agreement with the total weight loss calculated for the decomposition of complex **3** leading to the formation of NiO (78.5 %) as final residuals.

3 Conclusion

The arene-cored ligand H_2L, which has several distinctive properties, was synthesized. Three new 2D complexes from the H_2L ligand were synthesized and characterized by elemental analysis, FT-IR spectroscopy, single-crystal X-ray diffraction, and thermogravimetric analysis. N–H···O and O–H···O hydrogen bonding interactions exist in complexes **1**–**3**. Adjacent 2D layers are linked by intermolecular interactions, which results in the construction of extended metal-organic frameworks (MOFs) in complexes **1** and **2**.

4 Experimental Section

4.1 Materials and Characterization

All commercially available chemicals and solvents were of reagent grade and used as received without further purification. The H_2L ligand was readily prepared according to the literature.[9] Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 240C Elemental analyzer. Analysis of thermal stability was carried out with a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C·min^{-1}. FT-IR spectra were recorded in the range of 400–4000cm^{-1} with a Bruker Vector22 FT-IR spectrophotometer using KBr pellets.

4.2 Syntheses

4.2.1 Synthesis of H_2L[9]

Triethylamine (6 mL) was added to a stirred mixture of 5-aminoisophthalic acid (2.90 g, 16.0 mmol), 4-pyridinecarboxaldehyde (1.80 g, 16.8 mmol), and dry methanol (100 mL). After 10 h, the mixture became limpid, and an excess of $NaBH_4$ (4 equiv.) was slowly added at 4 °C. After 10 h at 4 °C, the solvent was concentrated in vacuo. The residue was dissolved in water (100 mL) and acidified with AcOH to pH 5–6. After filtration, the product was obtained as a pale-yellowish solid (3.83 g, 87.9 %). Physical data: M.p. 162 °C. Elemental analysis: $C_{14}H_{12}N_2O_4$ (272.08): C 61.52 (calcd. 61.76); H 4.68 (4.44); N 10.58 (10.29) %. **^{1}H NMR** (500 MHz, [D$_6$]DMSO, 25 °C): δ = 13.19–12.64 (br., s, 2 H, -COOH), 8.54 [d, ^3J(H,H) = 4.57 Hz, 1 H, pyridine ring]; 7.73–7.76 (m, 1 H pyridine ring); 7.69 (s, 1 H, benzene ring); 7.37 (s, 2 H, benzene ring); 7.34 (s, 1 H, pyridine ring); 7.25–7.27 (m, 1 H, pyridine ring); 6.94–6.96 [t, ^3J(H,H) = 5.5 Hz, 1 H, –NH–]; 4.44 [d, ^3J(H,H) = 4.9 Hz, 2 H, -CH$_2$-]. **ESI-MS** (methanol) m/z: 272.08 (calcd. for $C_{14}H_{12}N_2O_4$, 272.03).

*4.2.2 Synthesis of [Zn(L)(H_2O)] (**1**)*

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (29.7 mg, 0.100 mmol), H_2L (27.2 mg, 0.100 mmol), and NaOH (8.00 mg, 0.200 mmol) in water (12 mL) was stirred for 10 min in air. Subsequently, the mixture was transferred to a 16 mL Teflon lined stainless steel container and heated at 180 °C for 3 days. After the mixture was cooled to room temperature, complex **1** was isolated from the mixture in colorless block crystalline form by filtration and washed with water and ethanol several times with a yield of 23.3 mg (0.0659 mmol, 65.9 % based on the H_2L ligand). Analytical data: $C_{14}H_{12}N_2O_5Zn$ (353.6): C 47.16 (calcd. 47.51); H 3.66 (3.39);

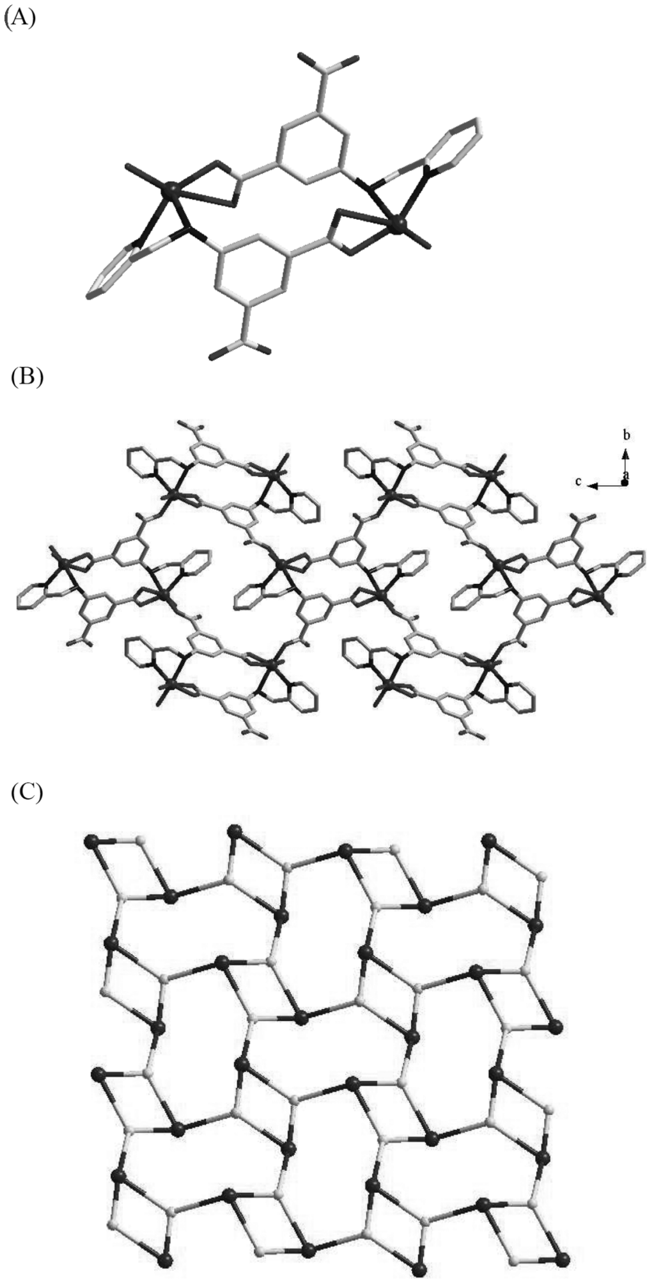


Figure 2. (A) Two L^{2-} ligands doubly bridge two different Zn^{II} ions to form a secondary building unit (SBU) $[Zn_2(L)_2(H_2O)_2]$ in complex **1**. (B) View of the 2D wave-like networks of complex **1**. (C) Schematic representation of the 2D net topology $(4,8^2)$ of complex **1**.

N 7.56 (7.92) %. **IR** (KBr): $\tilde{\nu}$ = 3407 (br., m), 3260 (m), 1574 (s), 1498(m), 1417 (s), 1351 (s), 1086 (w), 958 (w), 891 (w), 773 (m), 726 (m), 593 (w) cm^{-1}.

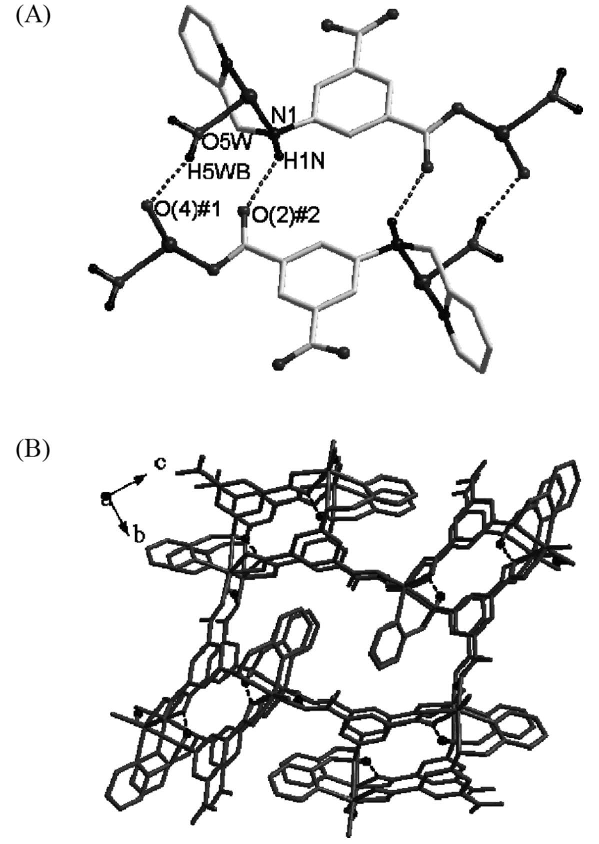


Figure 3. (A) Hydrogen bonding interactions existing in complex **1**. Symmetry transformations: #1 = –1 + *x*, 0.5 + *y*, 0.5 – *z*; #2 = 1 – *x*, 1 – *y*, –*z*. (B) View of the three-dimensional supramolecular framework of complex **1** constructed by hydrogen bonding interactions.

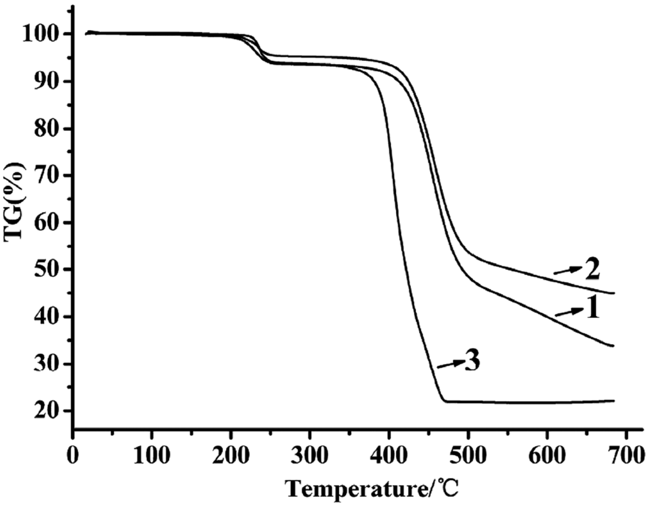


Figure 4. TGA curves of complexes **1**–**3**.

4.2.3 Synthesis of [Co(L)(H₂O)] (2)

Complex **2** was synthesized by the same procedure as for the preparation of complex **1**, except that $Co(NO_3)_2{\cdot}6H_2O$ (29.1 mg, 0.100 mmol) was used instead of $Zn(NO_3)_2{\cdot}6H_2O$ as the starting material. A few red block single crystals and some red powders of complex **2** were isolated by filtration and washed with water and ethanol several times with a yield of 20.1 mg (0.0579 mmol, 57.9 % based on the H_2L ligand). Analytical data: $C_{14}H_{12}CoN_2O_5$ (347.2): C 48.02 (calcd. 48.39); H 3.79 (3.46); N 7.98 (8.36) %. **IR** (KBr): $\tilde{\nu}$ = 3421 (br., m), 3260 (m), 1602 (m), 1555 (s), 1448(m), 1417 (s), 1356 (s), 1161 (w), 1105 (w), 773 (m), 721 (m), 602 (w) cm^{-1}.

4.2.4 Synthesis of [Ni(L)(H_2O)] (3)

Complex **3** was also synthesized by the same procedure as for the preparation of complex **1**, except that $Ni(NO_3)_2{\cdot}6H_2O$ (29.1 mg, 0.100 mmol) was used instead of $Zn(NO_3)_2{\cdot}6H_2O$ as the starting material. Green block crystals of complex **3** were obtained by filtration and washed with water and ethanol several times with a yield of 16.6 mg (0.0478 mmol, 47.8 % based on the H_2L ligand). Analytical data: $C_{14}H_{12}N_2NiO_5$ (346.9): C 48.78 (calcd. 48.42); H 3.44 (3.46); N 8.36 (8.07) %. **IR** (KBr): $\tilde{\nu}$ = 3317 (br., m), 1607 (m), 1536 (s), 1488 (m), 1441 (s), 1422 (s), 1403 (s), 1370 (s), 1285 (m), 1048 (m), 915 (m), 773 (m), 721 (m), 678 (m) cm^{-1}.

4.3 X-ray Crystallography Study

The crystallographic data collections for complexes **1**–**3** were carried out with a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated (Mo-K_α) radiation (λ = 0.71073 Å) at 293(2) K using the ω-scan technique. The diffraction data were integrated by using the SAINT program, which was also used for the intensity corrections for the Lorentz and polarization effects. Multiscan absorption correction was applied using the SADABS program. The structures of complexes **1**–**3** were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.[10] Hydrogen atoms except the ones in the (–NH–) of the (pyridin-2-ylmethyl)amino group and the coordinated water molecules in complexes **1**–**3** were added geometrically and allowed to ride on its parent atom. The hydrogen atoms in (–NH–) of the (pyridin-2-ylmethyl)amino group and the coordinated water molecules in complexes **1**–**3** were located from Fourier map directly. The contribution of these hydrogen atoms was included in the structure factor calculations. The crystallographic details and selected bond lengths and bond angles are provided in Table 2 and Table 3, respectively.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-811705 (for **2**), CCDC-811706 (for **3**), and CCDC-811707 (for **1**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): Figure S1 and S2 describe the molecular structures of complexes **2** and **3**, respectively. Table S1 reveals hydrogen bonding geometries of complexes **1**–**2**; Table S2 contains the detailed torsion angles of the five-membered uncoplanar metallacycle in complexes **1**–**3**.

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