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## Syntheses and crystal structures of three pillared complexes based on H<sub>2</sub>AIP and triazole-bipyridine ligands

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Three pillared polymeric complexes, {[Ni<sub>2</sub>(AIP)<sub>2</sub>(4,4'-bpt)(H<sub>2</sub>O)<sub>2</sub>·4H<sub>2</sub>O}<sub>n</sub> (**1**), {[Co(AIP)(3,3'-bpt)·H<sub>2</sub>O]<sub>n</sub> (**2**), and {[Ni(AIP)(3,3'-bpt)·H<sub>2</sub>O]<sub>n</sub> (**3**) (H<sub>2</sub>AIP = 5-aminoisophthalic, 4,4'-bpt = 1H-3,5-bis(4-pyridyl)-1,2,4-triazole and 3,3'-bpt = 1H-3,5-bis(3-pyridyl)-1,2,4-triazole), have been hydrothermally synthesized and characterized by X-ray diffraction analysis. Both **1** and **3** have 2-D (6,3) honeycomb layers, which are further interlinked by bent pillared triazole-bipyridine ligands to form a bilayer structure. The structures can be simplified to a (3,4)- and (3,5)-connected geometrical topology, respectively. Compound **2** has a Co-AIP layer structure in which the layers are pillared by 3,3'-bpt spacers to form the 3-D CsCl net.

*Keywords:* Coordination polymer; Pillar structure; Polycarboxylate

### 1. Introduction

Coordination polymers have attracted attention for fascinating topologies and potential applications in gas adsorption, catalysis, magnetism, photoluminescence, and medicine [1–5]. Generally, the diversity of framework structures in such materials depends on selection of the metal centers, organic spacers, and reaction pathways. Ligands with carboxylate and pyridines are crucial and have been widely explored [6].

Metal-organic frameworks (MOFs) have been obtained by mixed ligands, such as polycarboxylates combined with triazole-bipyridine or thiadiazole-bipyridine [7]. In this paper, we select triazole-bipyridine with 5-aminoisophthalic acid (H<sub>2</sub>AIP) to construct MOFs. The ligands were chosen based on the following considerations. First, 5-aminoisophthalic acid (H<sub>2</sub>AIP) containing two carboxylic groups may be completely or partially deprotonated, resulting in rich coordination modes to Co(II)/Ni(II). The amino group can also act as a hydrogen-bond acceptor/donor to form hydrogen bonds with adjacent units to form stable frameworks. Second, 1H-3,5-bis(4-pyridyl)-1,2,4-triazole and 1H-3,5-bis(3-pyridyl)-1,2,4-triazole have several interesting characteristics: (a) the triazole-bipyridine ligands have

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more coordination modes than 4,4'-bipyridine-like ligands due to their two more potential N-donors; (b) conformational geometries favor a synergistic effect with auxiliary ligand [8]. Accordingly, we have chosen the H<sub>2</sub>AIP and bpt ligands to construct pillared complexes [9].

Herein, we report the syntheses and crystal structures of three Co(II)/Ni(II) coordination polymers, {[Ni<sub>2</sub>(AIP)<sub>2</sub>(4,4'-bpt)(H<sub>2</sub>O)<sub>2</sub>·4H<sub>2</sub>O]<sub>n</sub> (**1**), {[Co(AIP)(3,3'-bpt)]·H<sub>2</sub>O]<sub>n</sub> (**2**), and {[Ni(AIP)(3,3'-bpt)]·H<sub>2</sub>O]<sub>n</sub> (**3**), in which **1** and **2** are 2-D pillared layer structures with (3,4)- and (3,5)-connected geometrical topologies, respectively, and **3** can be described as a body-centered cubic formation with the Schläfli symbol of 4<sup>2</sup>6<sup>4</sup>.

## 2. Experimental

### 2.1. Materials and physical measurements

With the exception of 3,3'-bpt and 4,4'-bpt, which were prepared according to literature procedure [10], all reagents and solvents for synthesis and analysis were commercially available and used as received. Elemental analyzes were performed on a CE-440 (Leemanlabs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer. TG-DTA tests were performed on a Perkin-Elmer thermal analyzer from room temperature to 1000 °C under N<sub>2</sub> at a heating rate of 5 °C min<sup>-1</sup>.

### 2.2. Synthesis of {[Ni<sub>2</sub>(AIP)<sub>2</sub>(4,4'-bpt)(H<sub>2</sub>O)<sub>2</sub>·4H<sub>2</sub>O]<sub>n</sub> (**1**)

A mixture containing NiCl<sub>2</sub>·6H<sub>2</sub>O (118 mg, 0.5 mM), 4,4'-bpt (112 mg, 0.5 mM), H<sub>2</sub>AIP (90.5 mg, 0.5 mM), NaOH (20 mg, 0.5 mM), water (10 mL), and ethanol (5 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 140 °C for three days and then cooled to room temperature at 5 °C/h. Pale green block crystals of **1** were obtained, separated, washed with distilled water, and dried in air. Yield: 57% (based on Ni(II)). Elemental analysis for C<sub>28</sub>H<sub>31</sub>N<sub>7</sub>Ni<sub>2</sub>O<sub>14</sub>: Calcd: C, 41.69; H, 2.85; N, 12.16. Found: C, 41.60; H, 2.91; N, 12.21. IR (KBr, cm<sup>-1</sup>): 3423s, 3269m, 3259w, 1621m, 1563m, 1519m, 1384s, 1078w, 727s.

### 2.3. Synthesis of {[Co(AIP)(3,3'-bpt)]·H<sub>2</sub>O]<sub>n</sub> (**2**)

A mixture containing CoCl<sub>2</sub>·6H<sub>2</sub>O (118 mg, 0.5 mM), 4,4'-bpt (112 mg, 0.5 mM), H<sub>2</sub>AIP (90.5 mg, 0.5 mM), NaOH (20 mg, 0.5 mM), water (10 mL), and ethanol (5 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 140 °C for three days and then cooled to room temperature at 5 °C/h. The resulting mixture was washed with water and dried in air to give light red block X-ray quality crystals of **2** in 5% yield (based on Co(II)). Anal. Calcd for C<sub>20</sub>H<sub>16</sub>CoN<sub>6</sub>O<sub>5</sub>: C, 50.07; H, 2.92; N, 17.52. Found: C, 50.04; H, 2.89; N, 17.58. IR (KBr, cm<sup>-1</sup>): 3386s, 3275m, 1624m, 1570s, 1532m, 1062w, 842w, 770m, 705m.

### 2.4. Synthesis of {[Ni(AIP)(3,3'-bpt)]·H<sub>2</sub>O]<sub>n</sub> (**3**)

A mixture containing NiCl<sub>2</sub>·6H<sub>2</sub>O (118 mg, 0.5 mM), 4,4'-bpt (112 mg, 0.5 mM), H<sub>2</sub>AIP (90.5 mg, 0.5 mM), NaOH (20 mg, 0.5 mM), water (10 mL), and ethanol (5 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 140 °C for three

days, cooled to room temperature at 5 °C/h, and green block-like crystals of **3** were obtained, washed with distilled water and dried in air. Yield: 63% (based on Ni(II)). Anal. Calcd for  $C_{20}H_{16}NiN_6O_5$ : C, 50.09; H, 2.95; N, 17.68. Found: C, 50.01; H, 2.97; N, 17.70. IR (KBr,  $cm^{-1}$ ): 3428 m, 3280 m, 1613 m, 1566s, 1356s, 1105 m, 965w, 778 m, 729 m.

## 2.5. X-ray crystallography

X-ray single-crystal diffraction data for **1–3** were collected with a Bruker SMART CCD instrument by using graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were collected at 293(2) K, and there was no evidence of crystal decay during data collection. A semiempirical absorption correction was applied using SADABS, and the program SAINT was used for integration of the diffraction profiles [11]. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on all  $F^2$  data with SHELXL-97 [12]. The non-hydrogen atoms were refined anisotropically. Hydrogens of water were located in a difference Fourier map and refined isotropically in the final refinement cycles. Other hydrogens were placed in calculated positions and refined by using a riding model. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Crystal data and details of the structure are summarized in table 1. Selected bond lengths and angles are listed in table 2 (chart 1).

## 2.6. Synthetic conditions and discussion

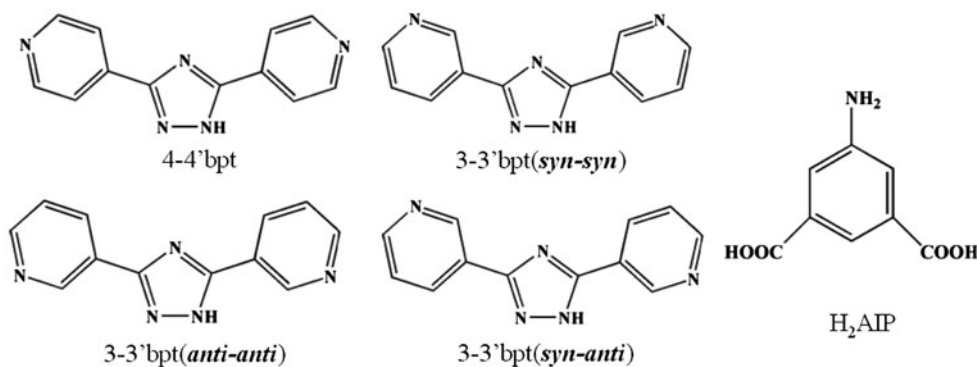
Because of the low solubility of the ligands used and the difficulty to grow crystals of coordination polymers, a hydrothermal technique was used. For **1**, we tried to optimize the employed ratio of  $H_2AIP$ , metal salts and 4,4'-bpt, such as 0.5 : 1 : 1, 1 : 1 : 1, 1.5 : 1 : 1, 2 : 1 : 1, 1 : 0.5 : 1, 1 : 1.5 : 1, 1 : 2 : 1, 1 : 1 : 0.25, 1 : 1 : 0.5, 1 : 1 : 0.75, 1 : 1 : 1.25, 1 : 1 : 1.5, 1 : 1 : 2, however, white silk-like solid (4,4'-bpt, difficult to clean) always wrapped around the as-synthesized crystals of **1** in above strategies. It seems that there is no direct relation

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

Complex	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$C_{28}H_{31}N_7Ni_2O_{14}$	$C_{20}H_{16}CoN_6O_5$	$C_{20}H_{16}Ni_6NiO_5$
Formula weight ( $M$ )	805.97	479.32	479.08
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pccn$	$P2_1/c$	$P2_1/c$
$a$ (Å)	24.922(5)	12.407(3)	16.606(3)
$b$ (Å)	7.6730(15)	11.909(2)	7.781(16)
$c$ (Å)	15.780(3)	17.656(6)	16.037(3)
$\beta$ (°)	90.00	126.26(2)	113.48(3)
$V$ (Å <sup>3</sup> )	3017.6(10)	2103.6(11)	1900.6(8)
$Z$	4	4	4
$D_c$ (Mg m <sup>-3</sup> )	1.774	1.513	1.674
$F(000)$	1660.0	980.0	984.0
Refns. collected/unique	16,996/2816	10,954/3698	10,195/3351
	[ $R(\text{int}) = 0.073$ ]	[ $R(\text{int}) = 0.154$ ]	[ $R(\text{int}) = 0.087$ ]
Goodness of fit on $F^2$	1.078	1.042	1.00
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0690$ ; $\omega R_2 = 0.1375$	$R_1 = 0.1328$ ; $\omega R_2 = 0.2418$	$R_1 = 0.0964$ ; $\omega R_2 = 0.1683$
$R$ indices (all data)	$R_1 = 0.0851$ ; $\omega R_2 = 0.1455$	$R_1 = 0.2078$ ; $\omega R_2 = 0.2823$	$R_1 = 0.1347$ ; $\omega R_2 = 0.1852$

Table 2. Selected distances (Å) and angles (°) for 1–3.

<b>1</b> (symmetry codes: A $x, -y + 5/2, z + 1/2$ ; B $x, -y + 3/2, z + 1/2$ )			
Ni1–O1A	2.074(4)	Ni1–O3	1.997(4)
Ni1–O2A	2.196(4)	Ni1–O5	2.157(5)
Ni1–N1	2.051(5)	Ni1–N4B	2.120(5)
O3–Ni1–N1	101.43(17)	O1A–Ni1–O5	87.30(17)
O3–Ni1–O1A	100.36(15)	N4B–Ni1–O5	174.53(18)
N1–Ni1–O1A	156.37(17)	O3–Ni1–O2A	161.44(15)
O3–Ni1–N4B	94.77(18)	N1–Ni1–O2A	96.04(16)
N1–Ni1–N4B	97.05(18)	O1A–Ni1–O2A	61.44(14)
O1C–Ni1–N4B	90.12(17)	N4B–Ni1–O2A	89.21(17)
O3–Ni1–O5	80.97(17)	O5–Ni1–O2A	93.79(17)
N1–Ni1–O5	87.19(18)		
<b>2</b> (symmetry codes: A $-x + 1, y + 1/2, -z + 1/2$ ; B $x, -y + 1/2, z + 1/2$ ; C $x-1, -y + 3/2, z-1/2$ )			
Co1–O4A	1.986(8)	Co1–N1	2.155(9)
Co1–O3B	2.009(7)	Co1–O2	2.161(7)
Co1–N5C	2.140(9)	Co1–O1	2.218(7)
O4A–Co1–O3B	117.0(3)	N5C–Co1–O2	91.1(3)
O4A–Co1–N5C	87.6(3)	N1–Co1–O2	90.0(3)
O3A–Co1–N5C	93.3(3)	O4A–Co1–O1	97.7(3)
O4A–Co1–N1	89.3(4)	O3B–Co1–O1	145.3(3)
O3B–Co1–N1	92.0(3)	N5C–Co1–O1	86.1(3)
N5C–Co1–N1	174.7(3)	N1–Co1–O1	90.0(3)
O4A–Co1–O2	157.3(3)	O2–Co1–O1	59.7(3)
O3B–Co1–O2	85.7(3)		
<b>3</b> (symmetry codes: A $x, -y + 5/2, z + 1/2$ ; B $x, -y + 3/2, z + 1/2$ ; C $-x, y + 1/2, -z + 1/2$ )			
Ni1–O1	2.048(5)	Ni1–N6B	2.167(6)
Ni1–N1	2.093(7)	Ni1–N5C	2.189(7)
Ni1–O4A	2.107(5)	Ni1–O3A	2.233(5)
O1–Ni1–N1	104.9(2)	O4A–Ni1–N5C	92.1(2)
O1–Ni1–O4A	95.4(2)	N6B–Ni1–N5C	175.9(2)
N1–Ni1–O4A	158.8(2)	O1–Ni1–O3A	156.6(2)
O1–Ni1–N6B	92.5(2)	N1–Ni1–O3A	98.4(2)
N1–Ni1–N6B	93.1(2)	O4A–Ni1–O3A	61.15(19)
O4A–Ni1–N6B	92.0(2)	N6B–Ni1–O3A	89.0(2)
O1–Ni1–N5C	87.8(2)	N5C–Ni1–O3A	92.3(2)
N1–Ni1–N5C	82.8(3)	O4A–Ni1–N5C	92.1(2)

Chart 1. The ligands used in this work: positional isomeric bridging ligands (4,4'-bpt and 3,3'-bpt) and carboxylic acid ligands (H<sub>2</sub>AIP).

between yield and ratio. Thus 1 : 1 : 1 may be the best strategy, in which the yield is high and the product is relatively clean. For **2**, the small amount of red crystals of **2** were very carefully picked from the large number of purple crystals of  $[\text{Co}(\text{AIP})]$ , which was reported [13]. To improve the yield of **2**, we changed the solvent, temperature, pH, systematic decrease in AIP and increase in 3,3'-bpt, all of which were unsuccessful.

For the three complexes, although we cannot predict what metal-ligand ratios give what products, the different oriented pyridyl groups of the triazole-containing dipyridine isomers as well as the geometric needs of the carboxyl ligands and metal salts are important factors in preparation of the coordination polymers.

### 3. Description of the crystal structures

#### 3.1. Structural description of 1–3

**3.1.1.  $\{[\text{Ni}_2(\text{AIP})_2(4,4'\text{-bpt})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}\}_n$  (**1**).** The asymmetric unit of **1** contains one independent Ni(II), an AIP, and half a 4,4'-bpt. As depicted in figure 1(a), Ni1 is six coordinate in a slightly distorted octahedral environment, provided by water O5 and AIP N4B occupying the axes, three carboxylate O1A, O2A, and O3 and one pyridyl N1 composing the equatorial plane. Each AIP is coordinated to three Ni (figure 1(b)), two through carboxyl and amino bridges and the third chelating coordination by the other carboxyl. Ni(II) is bridged by three AIP to adjacent Ni(II) cations and each AIP links with three Ni(II) cations to afford a mononuclear reticular structure. The Ni(II) cations can be considered as three-connected nodes and are linked by three 3-coordinate AIP linkers to form a (6, 3) honeycomb type net in the crystallographic *bc* plane (figure 1(c)). The neighboring layers are further linked by 4,4'-bpt to generate a double-deck cross column type architecture and the interlayer Ni $\cdots$ Ni distance is 14.07(1) Å (figure 1(d) and (e)).

A more revealing description from this framework can be achieved by topology analysis. Considering the coordination modes of AIP, which can be viewed as a three-connected node, and Ni as four-connected nodes, the structure can be simplified to a (3,4)-connected topology with the short Schläfli symbol of  $(6^3)(6^5.8)$ .

**3.1.2.  $\{[\text{Co}(\text{AIP})(3,3'\text{-bpt})]\cdot \text{H}_2\text{O}\}_n$  (**2**).** As shown in figure 2(a) and (b), **2** has a 3-D polymeric coordination layer structure. The asymmetric unit of **2** has one crystallographically independent Co(II) displaying a distorted octahedral coordination. Co1 is coordinated by four equatorial oxygens from three AIP and two apical nitrogens from two 3,3'-bpt ligands. Each AIP links three Co(II) centers, one carboxylic group chelating to one Co, and the other carboxylic groups coordinating to two Co ions through a *syn-syn* mode, giving a  $[\text{Co}(\text{CO}_2)_2\text{Co}]$  dimeric unit. Adjacent dimeric units are linked through coordination by two carboxylates of AIP, resulting in the generation of a 2-D (4,4)-sql layer architecture in the crystallographic *ac* plane. The layer is further connected by parallel 3,3'-bpt pillars to generate a 3-D open framework with 1-D solvent-filled channel (figure 2(c) and (d)). Owing to steric hindrance of dicarboxylate, the charge balance, and coordination of the metal ion, AIP is difficult to form a 3-D structure in the absence of bridging ligands. The appropriate subsidiary 3,3'-bpt is favorable for a self-filling structure (the “*syn-anti*” 3,3'-bpt bridge in the interlayer region bridges the diagonal of a single window in the (4,4)-sql net).

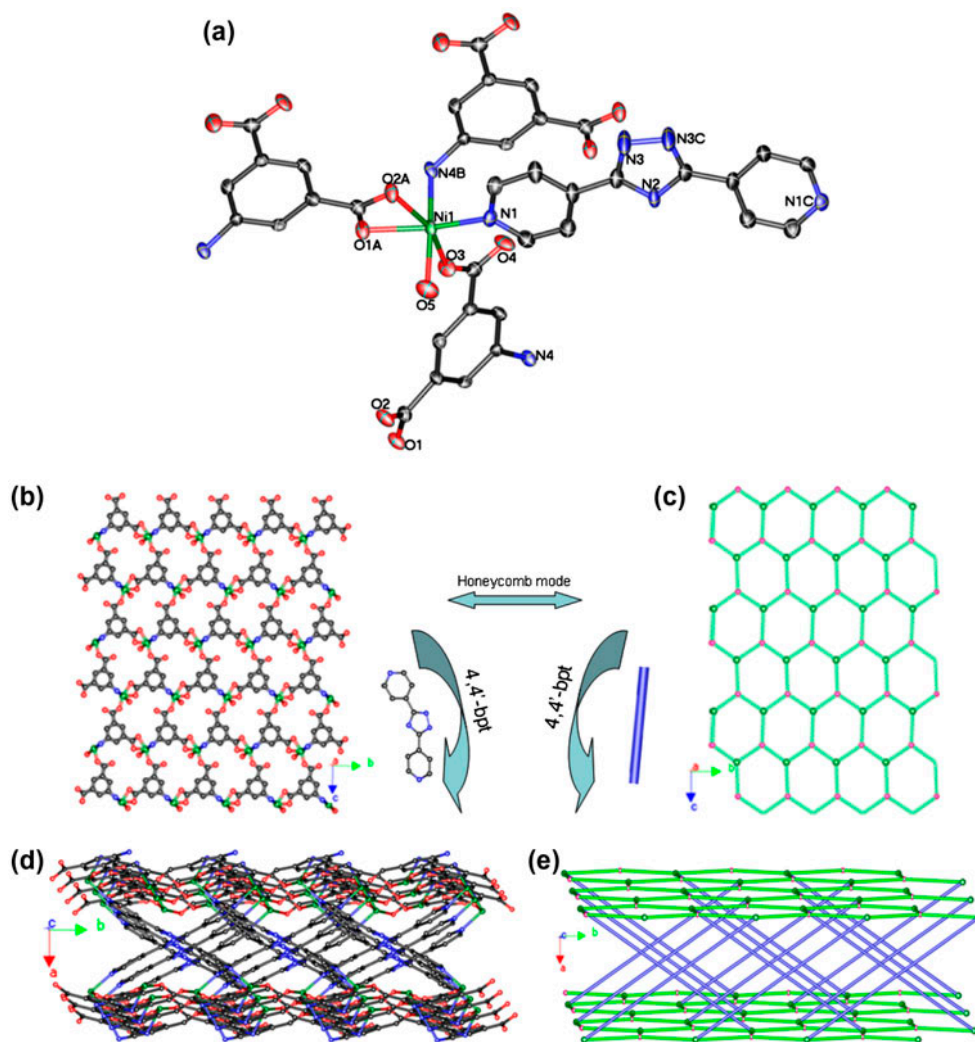


Figure 1. (a) The local coordination environments of Ni(II) in **1**; (b) view of 2-D network formed by AIP; (c) the simple form of the 2-D honeycomb network; (d) the (3,4)-connected cross-pillared architecture down the crystallographic *c* axis, and (e) its schematic description.

Better insight into the nature of this 3-D coordination polymeric network can be achieved by topological analysis. In **2**, each  $[\text{Co}(\text{CO}_2)_2\text{Co}]$  dimeric unit links eight nearest neighbors through AIP and 3,3'-bpt, so we can define it as an eight-connected node, with AIP and 3,3'-bpt as linkers. Therefore, the structure can be described as a body-centered cubic structure (bcu, normally called the CsCl net) with the Schläfli symbol of  $4^2 6^4$  [14].

**3.1.3.  $\{[\text{Ni}(\text{AIP})(3,3'\text{-bpt})]\cdot\text{H}_2\text{O}\}_n$  (**3**).** The asymmetric unit of **3** contains one independent Ni(II) (figure 3(a)) displaying a slightly distorted octahedral geometry via coordination to N1 from bpt and O1, O3A, and O4A in the equatorial plane, and N5C and N6B from 3,3'-bpt and AIP in axial positions. As shown in figure 3(b) and (c), each AIP is coordinated



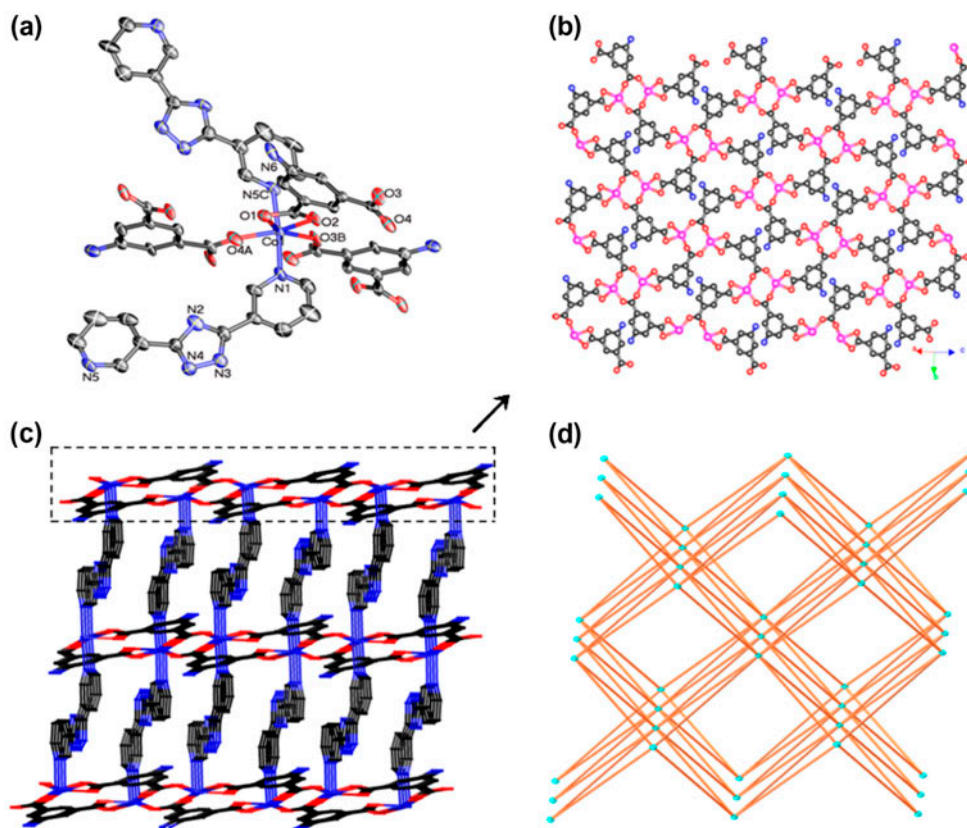


Figure 2. (a) The local coordination environments of Co(II). (b) View of 2-D network formed by AIP. (c) The overall 3-D network. (d) Schematic representation of the  $(4^2 6^4)$ -CsCl topology of **2**.

to three Ni ions, two through carboxyl and amine bridges and the third in a chelating coordination by the other carboxyl. Complex **3** also has a (6, 3) honeycomb structure in the crystallographic  $bc$  plane, like **1**. The neighboring layers are further linked by 3,3'-bpt to generate a double-layer architecture. The distances between Ni(II) centers separated by 3,3'-bpt and AIP are 7.780(1) and 12.33(2) Å, respectively. Moreover, 3,3'-bpt bridging the Ni(II) ions lead to infinite 1-D left- and right-handed helical chains with a  $2_1$  screw axis along the  $b$  axis [15], in which the helical pitch is equal to the length of the  $b$  axis (figure 3(d)). The left- and right-handed helical pillars alternate along the  $c$  direction (figure 3(d)) [16–18].

From the topological point of view, this double-layer network can be simplified by considering one nickel connecting three AIP and two 3,3'-bpt are five-connected nodes. The coordination of AIP can be viewed as a three-connected node. Thus, the (3,5)-connected topology net with the short Schläfli symbol of  $(6^3)(4^3.6^7)$  could be observed.

Most complexes of similar mixed-ligands are 1-D chain, 2-D network, or 3-D structures [19]. From the above structural descriptions, **1** and **3**, synthesized under similar conditions, have double-layer structures. As the bpt ligands have different degrees of bending caused by the changing position of the pyridine which could form different connection modes between layers [20] as cross, helical, parallel pillared structures [21]. 5-Aminoisophthalic acid ( $H_2AIP$ ) which has two carboxylic groups and one amino group may be completely or

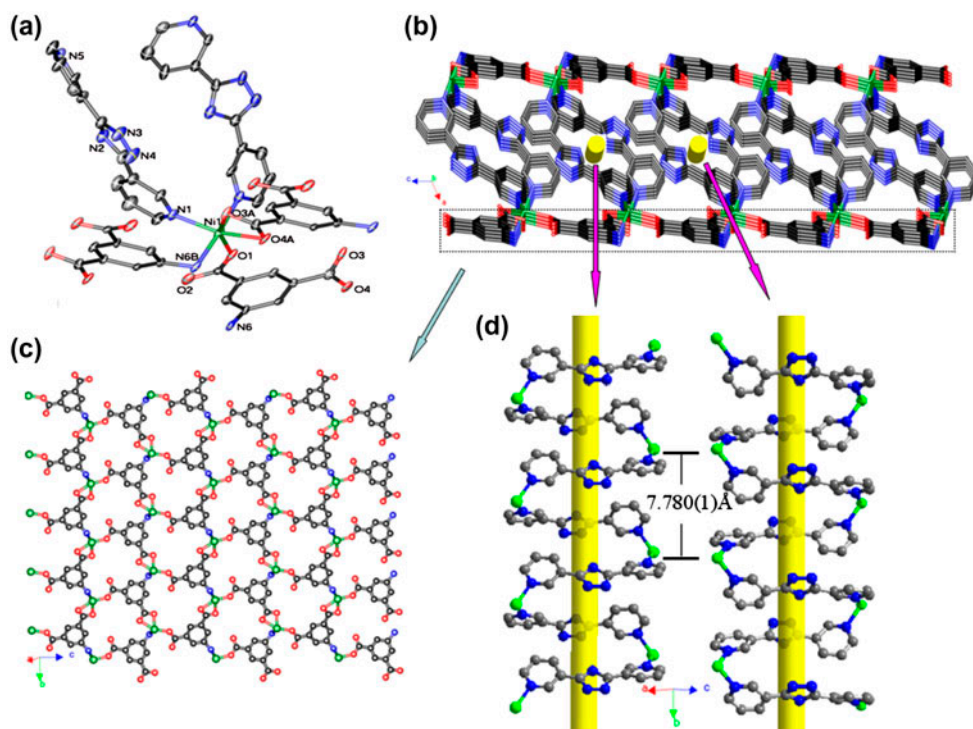


Figure 3. The local coordination of Ni(II) in **3**. (b) The (3,5)-connected helical-pillared architecture down the crystallographic  $c$  axis. (c) View of 2-D network formed by AIP. (d) 1-D left and right-handed helical chains.

partially deprotonated, resulting in coordination to Co(II)/Ni(II) ions to build layered structures. The stable layered structure which consists of metal and AIP is useful for formation of 2-D and 3-D pillared complexes. To form a double-layer structure, 5-aminoisophthalic acid is better than isophthalic acid [22].

### 3.2. Properties of 1–3

**3.2.1. X-ray powder diffraction (XRPD) results.** To confirm the phase purity of the sample, X-ray powder diffraction (XRPD) experiments have been carried out for **1** and **3**. The XRPD experimental and computer-simulated patterns of **1** and **3** are shown in figure 4. The phase purity of bulk products of the complexes was further confirmed by XRPD, and each XRPD pattern of the as-synthesized sample is consistent with the simulated one [23]. Unfortunately, **2** was difficult to crystallize and not enough of **2** was collected for TG/XRPD measurement.

**3.2.2. Thermal stabilities of 1 and 3.** Thermal properties of **1** and **3** were investigated by thermogravimetric analysis (Supplementary material). The first weight loss of **1** of 13.8% from 28 to 159 °C corresponds to release of lattice and coordinated water (Calcd 13.4%). The second step of weight loss (45.2%) from 386 to 477 °C corresponds to the removal of two AIP (Calcd 45%), and then, a series of complicated weight losses were observed until heating ends. The first weight loss of **3** of 3.87% from 251 to 317 °C corresponds to release

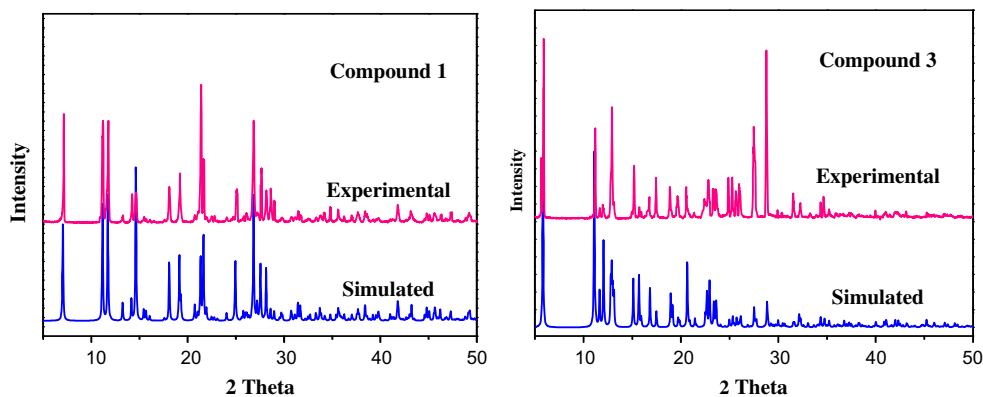


Figure 4. The simulated and experimental powder XRD patterns for **1** and **3**.

of coordinated water (Calcd 3.76%). The second step of weight loss (39.8%) from 402 to 480 °C corresponds to the removal of AIP (Calcd 39.9%). The residual framework starts to decompose beyond 480 °C with a series of complicated weight losses and does not stop until heating ends at 1000 °C.

#### 4. Conclusions

We have synthesized three pillared coordination polymers under the similar solvothermal conditions using bpt and 5-aminoisophthalic acid. Complex **1** has a (3,4)-connected topology with the short Schläfli symbol of  $(6^3)(6^5.8)$ . Complex **2** has a 3-D pillared layer structure with eight-connected topology with the Schläfli symbol of  $4^{24}6^4$ . Complex **3** shows a 2-D double-layer architecture with (3,5)-connected topology. AIP with a variety of coordination modes plays a very important role in the formation of the stable layered structures. For bpt, changing the position of the pyridyl N forms different connections between layers. **1** and **3** have the same coordination in the surface layer and the double layers are very similar. The results suggest that employing carboxylate and bpt is a useful strategy to design and synthesize MOFs with columnar architecture.

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#### Supplementary data

CCDC 921403–921405 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplemental data for this article can be accessed <http://dx.doi.org/10.1080/00958972.2013.854341>.

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