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Crystal structures and magnetic properties of three cobalt(II)–organic frameworks with nanoscale channels

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Three cobalt(II) coordination polymers, $\{[\text{Co}(\text{nip})(4,4'\text{-bpy})] \cdot 3\text{H}_2\text{O}\}_n$ (**1**), $[\text{Co}(\text{nip})(\text{bpe})]_n$ (**2**), and $[\text{Co}(\text{nip})(\text{bpp})(\text{H}_2\text{O})]_n$ (**3**), were hydrothermally synthesized by the reaction of cobalt nitrate hexahydrate and nip with 4,4'-bpy, bpe, and bpp [nip = 5-nitro-1,3-benzenedicarboxylate, 4,4'-bpy = 4,4'-bipyridine, bpe = 1,2-bis(4-pyridyl)ethane, bpp = 1,3-bis(4-pyridyl)propane], respectively. Co(II) displays different coordination in the three complexes, resulting in different structures with nanoscale channels. Compounds **1** and **2** form 2-D layer structures, but **3** has a two-fold interpenetrated 3-D framework. The magnetic properties associated with their crystal structures were investigated.

Keywords: Cobalt(II) coordination polymers; Magnetic properties; Nanoscale channel

1. Introduction

Synthesis of metal–organic frameworks (MOFs) from transition metals and organic ligands have been extensively developed for their crystallographic diversity and potential applications in catalysis, nonlinear optics, magnetism, electronics, catalysis, sorption, and molecular recognition [1–14]. Various structures with interesting compositions and topologies have been produced through a judicious choice of ligand and metal precursor [15–20], and those that can act as hosts to capture guest molecules have attracted much attention [21–23]. Benzenemulticarboxylates have been extensively employed to link metal ions to produce high-dimensional frameworks containing channels or cavities [24–26]. Flexible dipyrindine ligands such as 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,2-di(4-pyridyl)ethylene [27–30], and 1,3-bis(4-pyridyl)propane [31–33] can freely rotate to meet the requirement of coordination geometries of metal ions in the assembly process and are good candidates for producing beautiful structures and useful functional properties. The combination of benzenemulticarboxylates and dipyrindines with metal ions has resulted in various

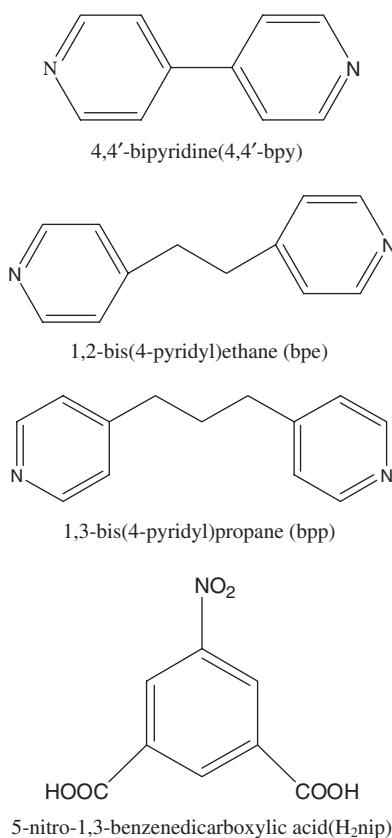
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supramolecular complexes with different structures and functions. In this article, we chose nip, 4,4'-bpy, bpe, bpp [nip = 5-nitro-1,3-benzenedicarboxylate, 4,4'-bpy = 4,4'-bipyridine, bpe = 1,2-bis(4-pyridyl)ethane, and bpp = 1,3-bis(4-pyridyl)propane] (scheme 1) to investigate whether similar ligands would give similar networks and the influence of ligand flexibility on the formation of supramolecular architectures. Hence we report here the syntheses and crystal structures of three new cobalt(II) coordination polymers, $\{[\text{Co}(\text{nip})(4,4'\text{-bpy})] \cdot 3\text{H}_2\text{O}\}_n$ (**1**), $[\text{Co}(\text{nip})(\text{bpe})]_n$ (**2**), and $[\text{Co}(\text{nip})(\text{bpp})(\text{H}_2\text{O})]_n$ (**3**), which all have nanoscale channels.

2. Experimental

2.1. General information

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and nip were purchased and used without purification. The 4,4'-bpy, bpe, and bpp were purchased from Fluka. C, H, and N analyses were determined on a Perkin Elmer 240°C analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer from 200 to 4000 cm^{-1} . Temperature-dependent



Scheme 1. Structures of ligands.

magnetic measurements were determined on a Quantum Design SQUID-XL7 magnetometer.

2.2. Synthesis of **1**

An aqueous mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0294 g, 0.1 mmol), H_2nip (0.0216 g, 0.1 mmol), 4,4'-bpy (0.0313 g, 0.2 mmol), and H_2O (10 mL) was placed in a 15 mL Teflon-lined stainless-steel vessel and heated at 180°C for 4.5 days. After the mixture was cooled to room temperature, pink needle-like crystals were filtered and washed with water. Yield: 0.0241 g, 50.39% based on Co, Anal. Calcd (%) for $\text{C}_{18}\text{H}_{17}\text{CoN}_3\text{O}_9$: H, 3.58; C, 45.20; N, 8.79. Found (%): H, 3.61; C, 45.23; N, 8.75. IR data (KBr, cm^{-1}): 3848m, 3742s, 3440m, 3087s, 2922m, 2360m, 1610s, 1534m, 787s, 629m.

2.3. Synthesis of **2**

Compound **2** was prepared by the same process as **1** with 4,4'-bpy replaced by bpe (0.0375 g, 0.2 mmol). After the mixture was cooled to room temperature, purple needle-like crystals were filtered and washed with water. Yield: 0.0226 g, 49.97% based on Co, Anal. Calcd (%) for $\text{C}_{20}\text{H}_{15}\text{CoN}_3\text{O}_6$: C, 53.11; H, 3.34; N, 9.29. Found (%): C, 53.21; H, 3.40; N, 9.35. IR data (KBr, cm^{-1}): 3810m, 3729s, 3421m, 3079s, 2935m, 1617s, 1533m, 789s, 542m.

2.4. Synthesis of **3**

Compound **3** was prepared by the same process as for **1** with 4,4'-bpy replaced by bpp (0.0408 g, 0.1 mmol), but the mixture was heated at 145°C for 4.0 days. After the mixture was cooled to room temperature, pink needle-like crystals were filtered and washed with water. Yield: 0.0233 g, 48.11% based on Co, Anal. Calcd (%) for $\text{C}_{21}\text{H}_{19}\text{CoN}_3\text{O}_7$: C, 52.08; H, 3.95; N, 8.68. Found (%): C, 52.10; H, 3.98; N, 8.65. IR data (KBr, cm^{-1}): 3841m, 3742s, 3419m, 3071s, 2925m, 1610s, 1541m, 782s, 543m.

2.5. X-ray crystallography

The structures of $\{[\text{Co}(\text{nip})(4,4'\text{-bpy})] \cdot 3\text{H}_2\text{O}\}_n$ (**1**), $[\text{Co}(\text{nip})(\text{bpe})]_n$ (**2**), and $[\text{Co}(\text{nip})(\text{bpp})(\text{H}_2\text{O})]_n$ (**3**) were determined by single crystal X-ray crystallography. Intensity data and unit-cell parameters for **1**, **2**, and **3** were measured at 298 K on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan mode. Empirical absorption corrections were applied using SADABS [34]. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using the SHELXL-97 program package [35]. Water hydrogens were refined subject to the restraint $\text{O-H} = 0.82(5) \text{ \AA}$; other hydrogens were located theoretically and refined anisotropically. A summary of the crystallographic data of **1**, **2**, and **3** is presented in table 1, with selected bond lengths and angles in table 2.

Table 1. Crystal data and structural refinement for 1–3.

Complex	1	2	3
Empirical formula	C ₁₈ H ₁₁ CoN ₃ O ₆ · 3H ₂ O	C ₂₀ H ₁₅ CoN ₃ O ₆	C ₂₁ H ₁₉ CoN ₃ O ₇
<i>M_r</i>	478.28	452.28	484.32
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pnna</i>
Unit cell dimensions (Å, °)			
<i>a</i>	10.1657(10)	9.6483(8)	16.8815(10)
<i>b</i>	10.3043(10)	10.1516(8)	13.9898(8)
<i>c</i>	11.0817(11)	11.5751(9)	18.0275(10)
α	117.093(2)	74.3660(10)	90
β	92.521(2)	78.6470(10)	90
γ	100.847(2)	68.7420(10)	90
Volume (Å ³), <i>Z</i>	1003.74(17), 2	1011.27(14), 2	4257.5(4), 8
Calculated density (mg m ⁻³)	1.562	1.485	1.511
Absorption coefficient (mm ⁻¹)	0.912	0.891	0.855
<i>F</i> (000)	394	462	1992
Goodness-of-fit on <i>F</i> ²	1.079	1.027	1.174
<i>R</i> ₁ [<i>I</i> > 2σ]	0.0371	0.0360	0.0710
<i>wR</i> ₂ (all data)	0.0914	0.0924	0.1539

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

1			
Co(1)–N(1)	2.019(2)	Co(1)–O(1)	2.2586(19)
Co(1)–O(5)C	2.0241(19)	Co(1)–O(2)B	1.9503(19)
Co(1)–N(2)A	2.004(2)		
O(2)B–Co(1)–N(2)A	92.54(9)	N(1)–Co(1)–O(5)C	88.67(9)
O(2)B–Co(1)–N(1)	85.89(9)	O(2)B–Co(1)–O(1)	122.51(8)
N(2)A–Co(1)–N(1)	177.44(9)	N(2)A–Co(1)–O(1)	91.94(9)
O(2)B–Co(1)–O(5)C	152.25(8)	N(1)–Co(1)–O(1)	90.61(8)
N(2)A–Co(1)–O(5)C	91.80(8)	O(5)C–Co(1)–O(1)	84.69(7)
2			
Co(1)–O(6)A	2.0299(16)	Co(1)–N(1)	2.1543(18)
Co(1)–O(5)B	2.0420(14)	Co(1)–N(2)C	2.1624(18)
Co(1)–O(2)	2.1307(15)	Co(1)–O(1)	2.2667(17)
O(6)A–Co(1)–O(5)B	105.41(6)	O(2)–Co(1)–N(2)C	87.94(6)
O(5)B–Co(1)–O(2)	157.04(6)	N(1)–Co(1)–N(2)C	176.50(7)
O(6)A–Co(1)–N(1)	92.64(7)	O(6)A–Co(1)–O(1)	156.43(6)
O(5)B–Co(1)–N(1)	94.66(7)	O(5)B–Co(1)–O(1)	97.36(6)
O(2)–Co(1)–N(1)	89.50(7)	O(2)–Co(1)–O(1)	59.91(6)
O(6)A–Co(1)–N(2)C	90.04(7)	N(1)–Co(1)–O(1)	91.46(7)
O(5)B–Co(1)–N(2)C	86.79(7)	N(2)C–Co(1)–O(1)	85.19(7)
O(6)A–Co(1)–O(2)	96.92(6)		
3			
O(1)–Co(1)	2.139(3)	Co(1)–O(3)A	2.043(3)
O(2)–Co(1)	2.287(3)	Co(1)–N(1)	2.128(3)
O(7)–Co(1)	2.105(3)	Co(1)–N(2)B	2.167(4)
O(3)–Co(1)C	2.043(3)	O(3)A–Co(1)–O(7)	86.74(12)
O(7)–Co(1)–N(1)	91.94(12)	O(3)A–Co(1)–N(1)	92.98(12)
O(3)A–Co(1)–O(1)	173.81(12)	O(1)–Co(1)–N(2)B	91.69(13)
O(7)–Co(1)–O(1)	89.51(12)	O(3)A–Co(1)–O(2)	115.74(12)
N(1)–Co(1)–O(1)	92.06(12)	O(7)–Co(1)–O(2)	86.32(11)
O(3)A–Co(1)–N(2)B	91.60(13)	N(1)–Co(1)–O(2)	151.03(12)
O(7)–Co(1)–N(2)B	174.60(12)	O(1)–Co(1)–O(2)	59.04(11)
N(1)–Co(1)–N(2)B	93.27(12)	N(2)B–Co(1)–O(2)	89.79(12)

Symmetry transformations used to generate equivalent atoms for **1**: A *x*, *y*, *z* + 1; B $-x + 1$, $-y + 1$, $-z + 2$; C $-x + 2$, $-y + 1$, $-z + 2$; for **2**: A $-x + 1$, $-y + 2$, $-z + 1$; B *x*, *y* – 1, *z*; C *x* – 1, *y*, *z* + 1; for **3**: A $x + 1/2$, *y*, $-z + 1$; B $-x + 1/2$, $y - 1/2$, $-z + 1/2$; C $x - 1/2$, *y*, $-z + 1$.

3. Results and discussion

In the asymmetric unit of **1**, each cobalt was five-coordinate in a highly distorted trigonal bipyramidal geometry (figure 1), consisting of three oxygens from three different nip carboxylates in the equatorial plane and two nitrogens from two different 4,4'-bpy occupying axial positions. The N–Co–N angle was close to 180° and the N–Co–O angles were close to 90°, but angles in the equatorial plane were 122.51(8), 84.69(7), and 152.25(8)°. This may be caused by Jahn–Teller effect and the uncoordinated oxygen of monodentate carboxylate. The Co–N bond lengths were 2.019 and 2.004 Å, and the Co–O distances were 1.950, 2.024, and 2.259 Å; all bond lengths and angles fall within commonly observed ranges [36].

Along the basal plane, pairs of cobalts were bridged by pairs of nip ligands as μ_3 -bridges in **1**. Nip had two bridging styles, forming a 16-membered ring and an eight-membered ring, respectively. Each pair of such rings were interconnected to form a 1-D chain of $[\text{Co}_2(\text{nip})_2]_n$ (figure 2). The chains were further connected by 4,4'-bpy to form a 2-D layer structure (figure 3). The long 4,4'-bpy ligands are pillars between the chains, in which the planar ladders generate the rectangular cavity. The length of the cavity was established by the distance between cobalts of adjacent ladders ($d(\text{Co}\cdots\text{Co})=11.082\text{ \AA}$) and the height of the cavity was established by adjacent Co \cdots Co distance (7.940 Å) in the side of the $[\text{Co}_2(\text{nip})_2]_n$ ladder, while the depth of the cavity was the Co \cdots Co distance (4.172 Å) within the dicobalt core $[\text{Co}_2(\text{CO}_2)_2]$. The structure could also be regarded as two grid sheets with (4,4) net topology, which were constructed through Co centers bridged by nip parallel to *a*-axis and 4,4'-bpy parallel to *c*-axis, which were linked by μ_2 -bridging carboxylates of nip resulting in the unprecedented 2-D layer framework. The most striking feature of **1** was that the adjacent 2-D layers were parallel and stacked without interpenetrating to generate nanoscale rectangular channels, filled with water molecules.

When 1,2-bis(4-pyridyl)ethane was used instead of 4,4'-bpy, a similar structure was obtained for **2** but with a different coordination environment of the central cobalt. The cobalt(II) is six coordinate by a chelating carboxylate of nip with Co–O1 and Co–O2 distances of 2.267 and 2.131 Å, two μ_2 -bridging carboxylates of two nips with Co–O distances of 2.030 and 2.042 Å, and two nitrogens of two bpe at *trans*-positions with Co–N distances of 2.154 and 2.162 Å (figure 4). The nitrogens were located in axial positions with N–Co–N angle of 176.50(7)°. *Trans* O–Co–O angles of 156.43(6) and 157.04(6)° around Co were found.

The basic building block of **2** was a dicobalt carboxylate moiety bridged by two carboxylates with Co \cdots Co distance of 4.526 Å. The dicobalt cores were linked by 4-exo-tridentate nip ligands resulting in a 1-D belt of $[\text{Co}_2(\text{nip})_2]_n$, as shown in figure 5. Then 1-D adjacent belts were further interlinked through dpe to generate an infinite 2-D layer structure, which contained two kinds of large channels with dimensions of $13.532 \times 7.068\text{ \AA}^2$ and $13.532 \times 4.526\text{ \AA}^2$ similar to the one shown in figure 3 for **1**.

When bpp in **3** replaced 4,4'-bpy in **1** or bpe in **2**, the structure of **3** was completely different, with a remarkable 3-D extended interpenetrating framework; it had the same interpenetrating structure as the analogous Ni-complex [37], and they are isotypous. Cobalt(II) was six-coordinate in a distorted octahedral geometry. Each cobalt(II) was surrounded by three carboxylates (O1, O2, and O3A) from two nip ligands, two

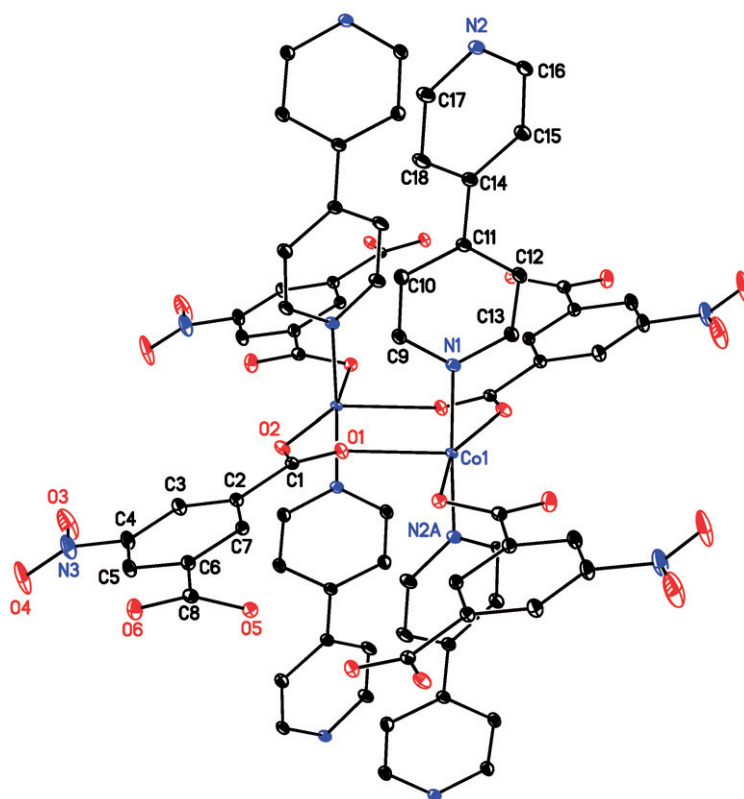


Figure 1. ORTEP plot of **1** showing 10% probability displacement ellipsoids. Only the contents of the asymmetric unit are labeled. Hydrogen atoms and water molecules are omitted for clarity. A = $x, y, z + 1$.

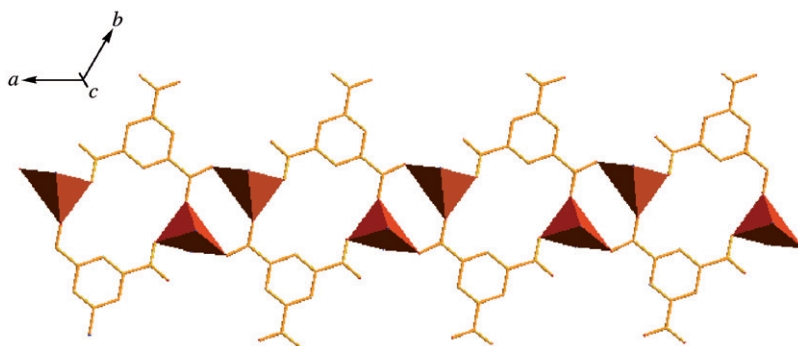


Figure 2. Perspective view of the 1-D structure of **1** bridged by nip.

nitrogens (N1 and N2B) from two bpp ligands, and one oxygen from a water (O7), as shown in figure 6. The water (O7) and a pyridyl nitrogen (N2B) are axial of the distorted octahedral coordination sphere of Co, with an O7–Co–N2B angle of 174.640° . The Co–O_{carboxylate} distances ranged from 2.042 to 2.288 Å and Co–N distances were 2.127 and 2.167 Å. Six cobalts were bridged by two nip and four bpp ligands

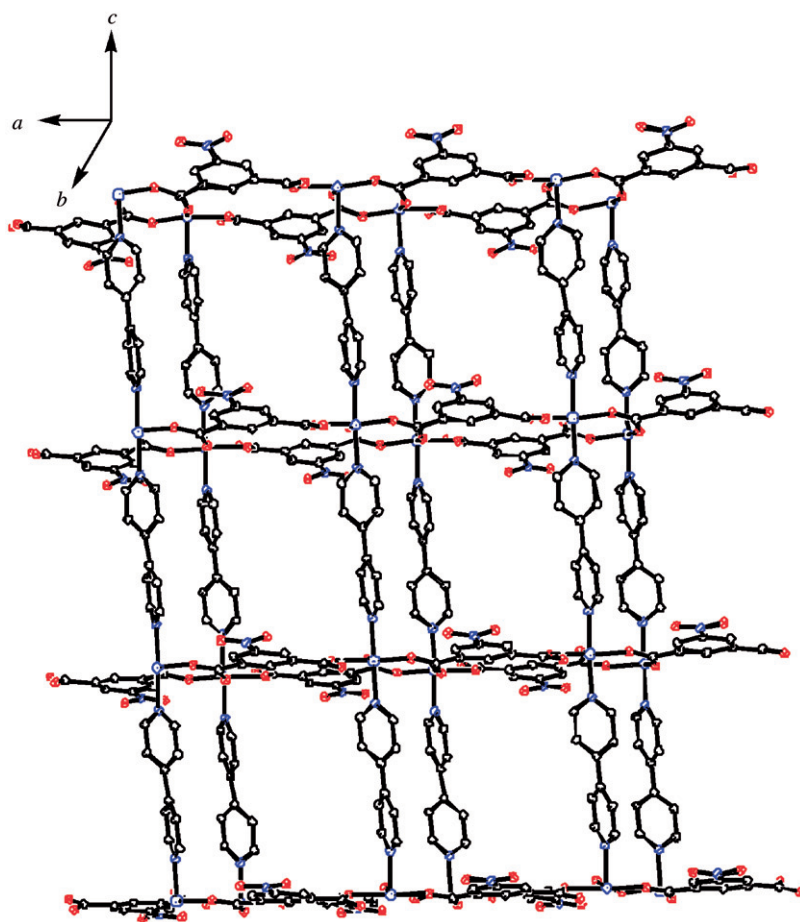


Figure 3. The perspective view of the rectangular cavity of **1** along the *c* axis.

forming a Co_6 ring, which was the basic building block for the 3-D framework of **3** (figure 7). In the Co_6 ring, the bpp and nip ligands separate cobalts at 11.244 and 8.858 Å, respectively. The bpp have GG conformation [37] to connect Co(II) ions (the definition of GG, TT, and TG is designed to display quite different N-to-N distances of bpp ligands). The Co_6 rings were fused to form the ultimate 3-D framework of **3**, which contained large channels with dimensions $13.990 \times 17.009 \text{ \AA}^2$. The 3-D networks further interlocked with each other in a two-fold interpenetrating mode, reducing the void volume in **3** (figure 8). (There are mistakes in the description of the Ni-derivative [37].)

3.1. Magnetic properties

Magnetic measurements were performed on samples of **1–3**. The temperature dependences of magnetic susceptibility of **1–3** in the forms of χ_M versus *T* are displayed

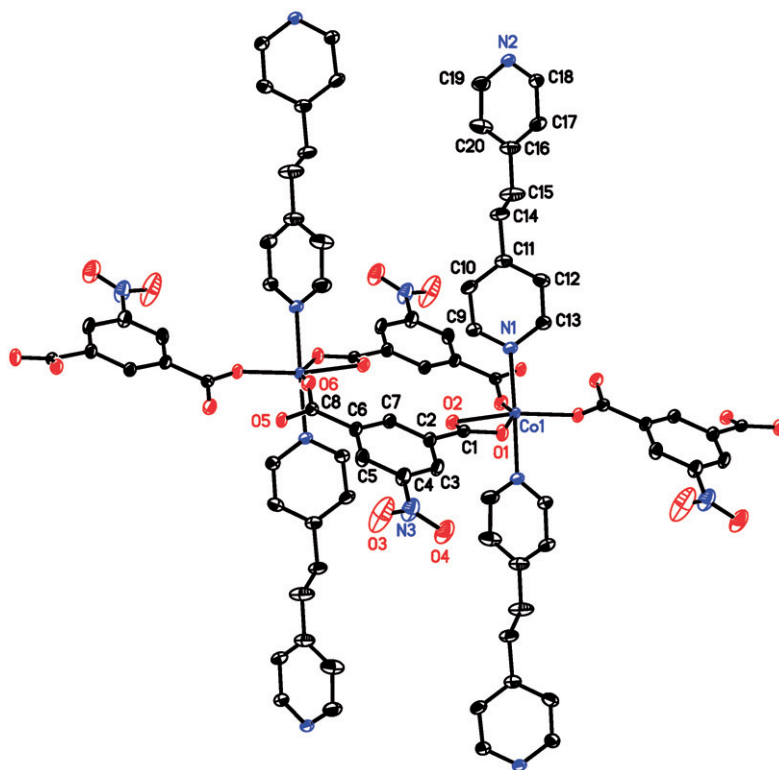


Figure 4. ORTEP plot of **2** showing 30% probability displacement ellipsoids. Only the contents of the asymmetric unit were labeled. Hydrogen atoms are omitted for clarity.

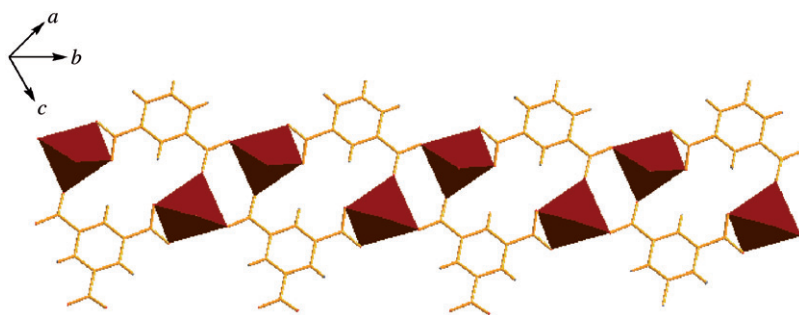


Figure 5. Perspective view of the 1-D structure of **2** bridged by nip.

in figure 9, with $\chi_M T$ versus T plots as inserts. **1** and **2** had similar topology, but their magnetisms are different. In **1**, the value of $\chi_M T$ first decreased, then slightly increased; as the temperature cooled to 2 K, the value of $\chi_M T$ decreased dramatically. This magnetic feature indicates antiferromagnetic coupling between cobalt ions [38, 39]. In **2**, the value of $\chi_M T$ first decreased and as the temperature cooled to 2 K, the value of $\chi_M T$

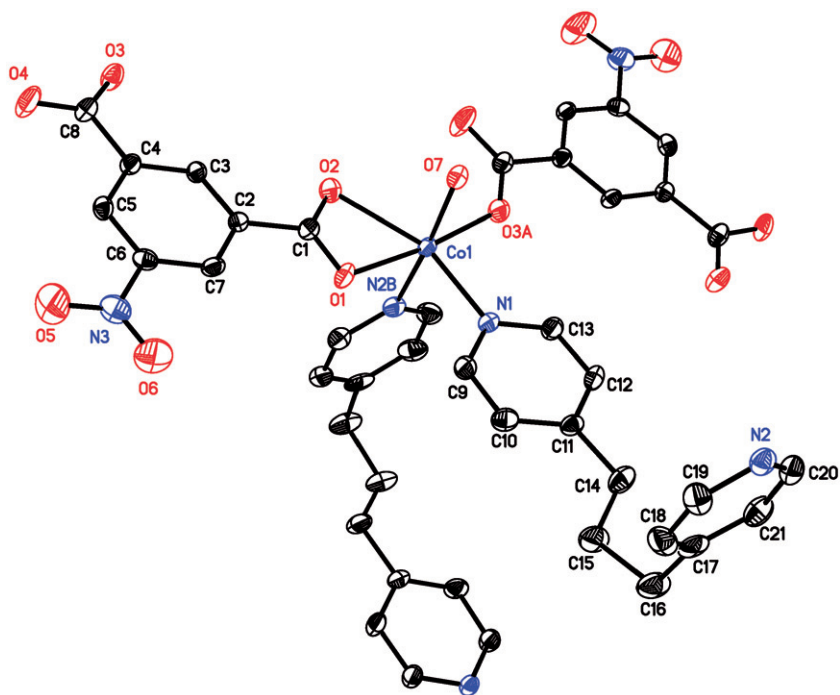


Figure 6. ORTEP plot of **3** showing 30% probability displacement ellipsoids. Only the contents of the asymmetric unit and mentioned atoms are labeled. Hydrogen atoms are omitted for clarity. A = $x + 1/2$, y , $-z + 1$; B = $-x + 1/2$, $y - 1/2$, $-z + 1/2$.

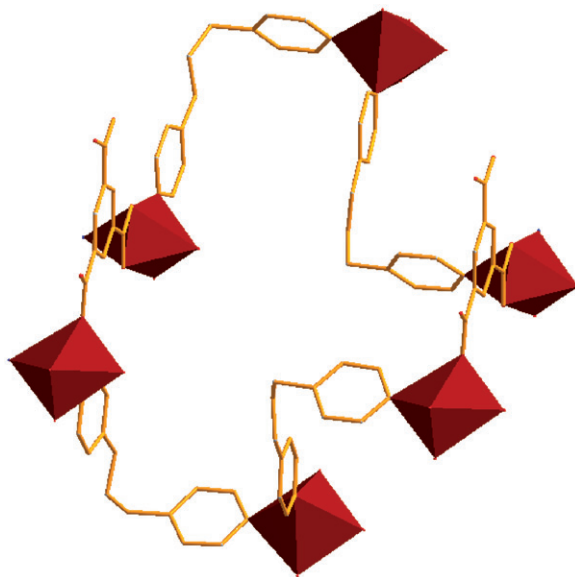


Figure 7. The Co₆ ring bridged by two nip and four bpp ligands in **3**.

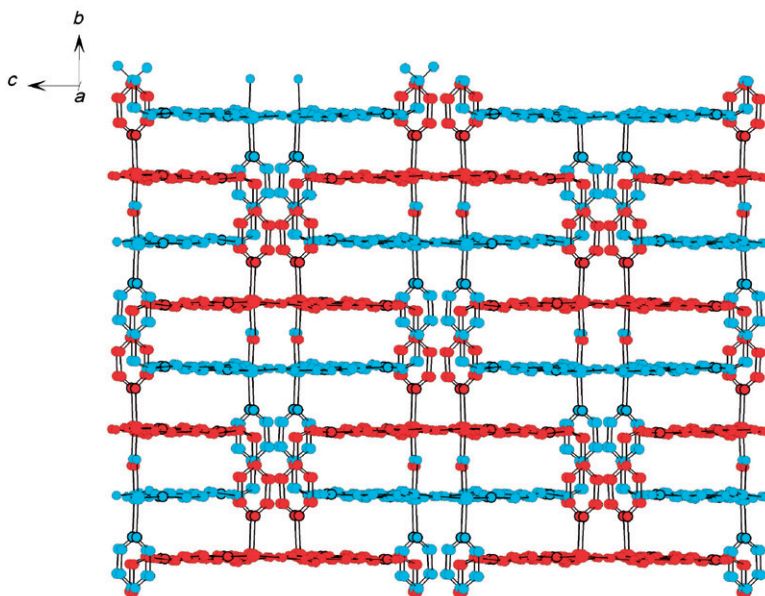


Figure 8. The perspective view along the *b* axis of the 3-D two-fold interpenetrating topology structure of **3**.

decreased dramatically. This magnetic feature indicated no coupling between cobalt ions in **2**. The magnetic behavior of **3** indicates almost no magnetic interactions because of the long distance between Co(II) ions. Such magnetic feature (relationship of $\chi_M T$ and T) from the paramagnetism of mononuclear metal might be due to the spin-orbital coupling or local zero-field splitting of Co(II) [40].

4. Conclusion

Cobalt can produce various structural motifs with beautiful topologies and useful functional properties such as magnetic characterization [41] and luminescence properties [42]. Many cobalt coordination polymers have been constructed [43, 44], but most are formed by different ligands through hydrogen bonding and/or π – π interactions [45, 46]. In this article, we chose similar dipyridine ligands, which can freely rotate to meet the requirements of the coordination geometries of metal ions in the assembly process. Our purpose is to investigate whether similar ligands could obtain similar networks and to study the influence of the flexibility of the ligand on the formation of supramolecular architectures.

Three new complexes formed by cobalt and nip with 4,4'-bpy, bpe, and bpp have been synthesized and characterized. The flexible dipyridines influenced nip coordination. There were bridging and monodentate coordination in **1**, bridging and chelating coordination in **2** and **3**. Similar ligands could lead to similar structures but different supramolecular architectures because of the flexibility of the ligands. **1** and **2** both

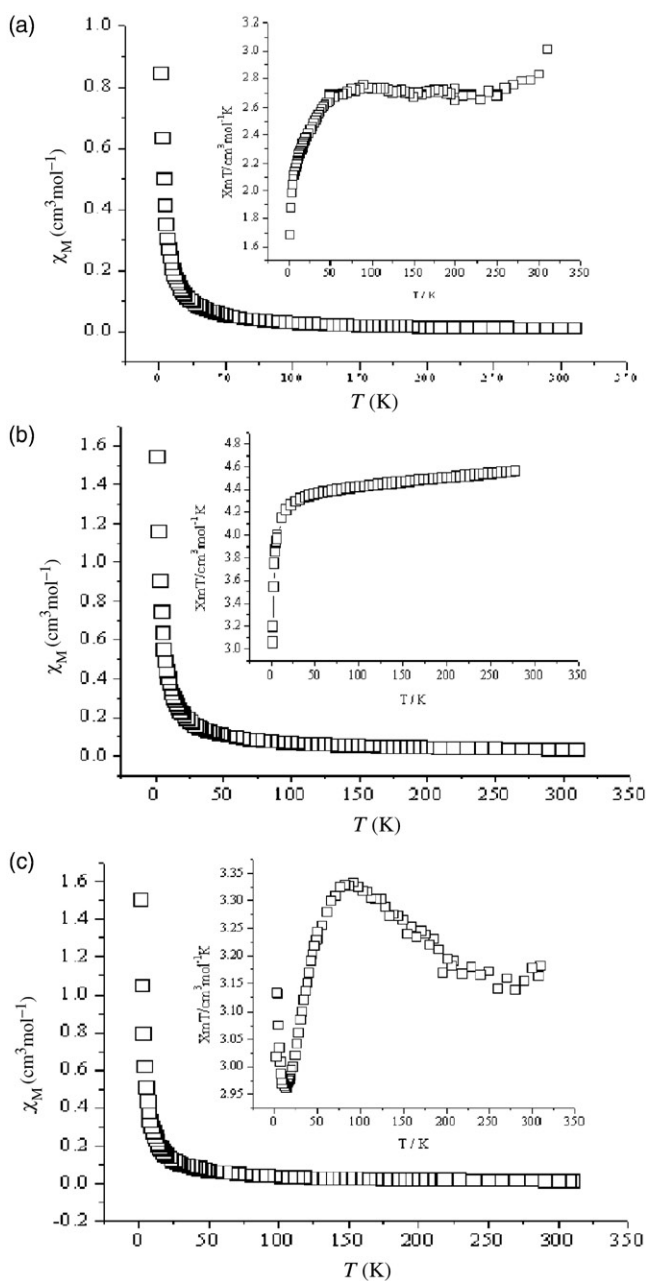


Figure 9. $\chi_M(T)$ vs. T plots for 1–3, and the inserts are the plots of $\chi_M T$ vs. T . Magnetic susceptibility was measured in an applied field of 2Koe. (a) $\chi_M(T)$ vs. T plot for 1. (b) $\chi_M(T)$ vs. T plot for 2. (c) $\chi_M(T)$ vs. T plot for 3.

exhibited noninterpenetrated 2-D layer framework, while **3** has an interpenetrating 3-D structure. Different structures resulted in different magnetic properties, and magnetism is dominated by structure. Further studies involving other long, flexible bidentate ligands and metal ions are in progress.

Supplementary material

CCDC 741379–741381 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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