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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lsrt20>

Two New Metal-Organic Frameworks Based on 5-Bromoisophthalic Acid and 1,3-bi(4-pyridyl)propane: Hydrothermal Syntheses, Structures, and Magnetic Properties

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Accepted author version posted online: 14 Mar 2012. Published online: 01 May 2012.

To cite this article: Min-Le Han, Hai-Xia Wu, Ke-Yan Zhao & Zu-Qiang Zhang (2012) Two New Metal-Organic Frameworks Based on 5-Bromoisophthalic Acid and 1,3-bi(4-pyridyl)propane: Hydrothermal Syntheses, Structures, and Magnetic Properties, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 42:4, 590-595, DOI: [10.1080/15533174.2011.613890](https://doi.org/10.1080/15533174.2011.613890)

To link to this article: <http://dx.doi.org/10.1080/15533174.2011.613890>

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Two New Metal-Organic Frameworks Based on 5-Bromoisophthalic Acid and 1,3-bi(4-pyridyl)propane: Hydrothermal Syntheses, Structures, and Magnetic Properties

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Two new complexes, $[M((H_2O)(bpp)(Brip))_n]$ ($M = Co^{II}$ (1) and Ni^{II} (2)), $bpp = 1,3$ -bi(4-pyridyl)propane, $H_2Brip = 5$ -bromoisophthalic acid), have been synthesized through hydrothermal reaction. They were characterized by elemental analysis, IR spectra, thermal analysis, magnetic properties, and X-ray single-crystal diffraction. The two complexes belong to monoclinic system, $C2/c$ space group. The adjacent Co^{II} or Ni^{II} ions are bridged by $Brip$ to form an alternate 1D chain. Such 1D chains are further connected by bpp to generate a twofold interpenetrating diamondoid 3D network. Variable-temperature magnetic susceptibility measurements indicate the occurrence of weak ferromagnetic interactions between the Co^{II} (1) and Ni^{II} (2) ions, respectively.

Keywords 1,3-bi(4-pyridyl)propane, 5-bromoisophthalic acid, crystal structure, magnetic properties

INTRODUCTION

Recently, the design and construction of metal-organic frameworks (MOFs) is of great interest in the fields of crystal engineering. Major reasons for this interest stem from their intriguing variety of topologies and structural diversity, such as helices and diamondoid nets and because of their potential applications as functional materials, such as gas storage, catalysis, fluorescent, magnetism, ion exchange, and sensor technology.^[1–11] Interpenetrating nets are a longstanding fascination for chemists, and many interesting structures have been constructed and well discussed in several comprehensive reviews.^[12–23] A common strategy in the design of interpenetrating networks is the use of polycarboxylates and flexible N-donor building

blocks, as they can promote helical or looped structural patterns, through which other organic linkers can penetrate.

Among N-donors, 1,3-bi(4-pyridyl)propane, as a flexible dipyridyl ligand, has four different conformations, TT, TG, GG, and GG' [24] (the definition of TT, TG, GG, and GG' is designed to display quite different N-to-N distance of bpp ligands). It can be used to construct interpenetrating nets.^[24,25–31] In this work, we will describe the synthesis, structural characterization, and magnetic properties of two 3D twofold interpenetrating coordination frameworks, $[Co(H_2O)(bpp)(Brip)]_n$ (1) and $[Ni(H_2O)(bpp)(Brip)]_n$ (2).

EXPERIMENTAL

Materials and Physical Measurement

All chemicals purchased were of reagent grade and used without further purification. All the products were highly stable in air at ambient conditions. Elemental analyses (C, H, and N) were performed on a Flash 2000 organic elemental analyzer (Thermo Scientific, Madison, WI, USA). The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer (Madison, WI, USA) equipped with graphite-monochromatized $Mo K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Thermal analyses were performed on a SII EXStar6000 (SII Nano Technology Inc., Japan) TG/DTA6300 analyzer heated from 30 to 895°C under nitrogen. The infrared spectra (4000–600 cm^{-1}) were recorded on a NICOLET 6700 FT-IR spectrometer (Madison, WI, USA). Variable-temperature magnetic measurement were performed on the Quantum Design (Madison, WI, USA) SQUID MPMS XL-7 instruments in a magnetic field of 2000 Oe in the temperature of 2–300 K.

Syntheses of Complexes 1 and 2

Complex 1 was synthesized by hydrothermal method in a 25 mL Teflon-lined autoclave by heating a mixture of 5-bromoisophthalic acid (24.5 mg, 0.1 mmol), bpp (19.8 mg, 0.1 mmol), $Co(OAc)_2 \cdot 4H_2O$ (24 mg, 0.1 mmol), and KOH (11.2 mg, 0.2 mmol) in 15 mL water at 433 K for three days. And then slowly cooled down to room temperature. Red block single

Received 6 August 2011; accepted 9 August 2011.

The authors gratefully acknowledge the support of the Natural Science Foundation of Henan Province Educational Committee (12B150019) and the Youth Foundation of Luoyang Normal University (2011-QNJJ-003).

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crystals of **1** were obtained. Anal. Calcd. for $C_{21}H_{19}BrCoN_2O_5$ (%): C, 48.67; H, 3.70; N, 5.41. Found: C, 48.71; H, 3.65; N, 5.38. I.R. data (cm^{-1}): 1614s, 1575 m, 1543 m, 1380s, 1358s, 773s, 733s, 716s.

2 was synthesized in a similar way to that described for **1**, except that $Co(OAc)_2 \cdot 4H_2O$ was replaced by $Ni(OAc)_2 \cdot 4H_2O$. Green block crystals of **2** were obtained. Anal. Calcd. for $C_{21}H_{19}BrN_2NiO_5$ (%): C, 48.69; H, 3.70; N, 5.41. Found: C, 48.64; H, 3.67; N, 5.44. IR data (cm^{-1}): 1614s, 1538 m, 1447 m, 1423 m, 1358s, 1223 m, 820 m, 769s, 734s, 718s.

Single-Crystal X-Ray Diffraction

The crystallographic data collections for complexes **1** and **2** were carried out on a Bruker Smart Apex II CCD diffractometer with a graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using φ/ω scan technique at room temperature. The empirical absorption corrections were applied. The structures were solved by direct methods using the SHELXS-97^[32] program and refined by full-matrix least-squares on F^2 using the SHELXL-97^[33] program. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligands were placed in the geometrically calculated positions. The crystallographic data and structure refinement of complexes **1** and **2** are summarized in Table 1. Selected bond lengths (\AA) and bond angles ($^\circ$) as well as the hydrogen bond distances and angles are presented in Tables 2 and 3, respectively.

RESULTS AND DISCUSSION

Description of Crystal Structures

Figure 1 shows a perspective view of the title complexes with atomic numbering scheme. Complexes **1** and **2** crystallize in the same monoclinic space group $C2/c$, and the crystal structure analysis revealed that they have the same structure. Thus, only the structure of **1** is described here. The asymmetric unit of **1** contains one Co^{II} center, one Brip dianion, and one bpp ligand, as well as one coordinated water molecule. Both of the carboxylate groups of the acid are deprotonated. The Co^{II} ion is six-coordinated with a distorted octahedral ge-

TABLE 1
Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	$C_{21}H_{19}BrN_2CoO_5$	$C_{21}H_{19}BrN_2NiO_5$
Molecular weight	518.22	518.00
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (\AA)	14.279(12)	14.602(5)
b (\AA)	18.573(16)	17.978(6)
c (\AA)	16.228(14)	16.997(6)
B ($^\circ$)	99.777(10)	106.590(5)
V (\AA^3)	4261(6)	4276(3)
Z	8	8
T (K)	296(2)	294(2)
D_{calc} ($g \cdot cm^{-3}$)	1.623	1.609
μ (mm^{-1})	2.728	2.811
$F(000)$	2088	2096
Max./min. transmission	0.5219/0.4334	0.6943/0.5898
θ range ($^\circ$)	2.35–25.50	2.27–25.50
Reflections collected	14242	15853
Independent reflections (R_{int})	3945 ($R_{int} = 0.0284$)	3964 ($R_{int} = 0.0805$)
Restraint/parameters	0/271	0/271
Goodness-of-fit (GOF) on F^2	0.973	1.017
R_1, wR_2 [$I > 2\sigma(I)$]	0.0319, 0.0573	0.0482, 0.1099
R_1, wR_2 [all data]	0.0516, 0.0643	0.1065, 0.1451
Largest diff. peak and hole ($e \cdot \text{\AA}^{-3}$)	0.490/–0.506	0.693/–0.723

$$R = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right], R_w = \left[\frac{\sum w [|F_o|^2 - F_c^2 |^2]}{\sum w (|F_o|^2)^2} \right]^{1/2}$$

ometry. The six-coordinated atoms come from two *cis*-nitrogen atoms of two bpp ligands, three carboxylate oxygen atoms of two Brip ligands, and one water molecule. The water oxygen atom (O5) and a pyridyl nitrogen (N2B) atom of bpp are axial of the

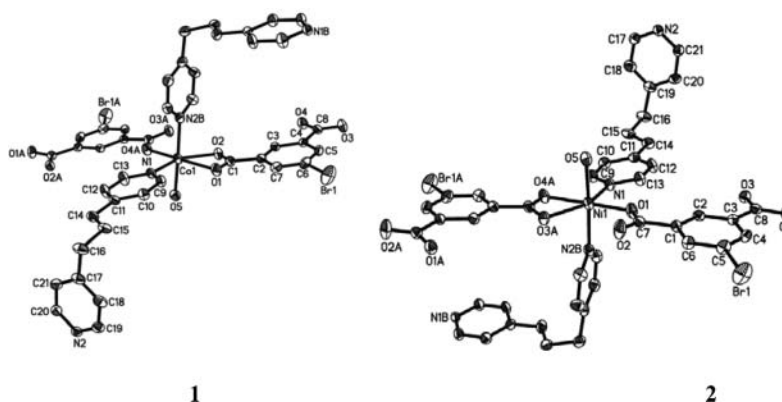


FIG. 1. Molecular structure of the title complexes. H atoms are omitted for clarity.

TABLE 2
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

1					
Co1-O4#1	2.028(2)	Co1-N1	2.120(2)	Co1-O2	2.177(3)
Co1-O5	2.131(3)	Co1-N2#2	2.165(3)	Co1-O1	2.252(2)
O4#1-Co1-N1	93.72(11)	O4#1-Co1-O5	83.21(8)	O4#1-Co1-O1	175.39(8)
N1-Co1-O5	90.00(8)	O4#1-Co1-N2#2	90.86(8)	N1-Co1-O1	90.59(10)
N1-Co1-N2#2	95.38(9)	O5-Co1-N2#2	172.25(8)	O5-Co1-O1	95.20(8)
O4#1-Co1-O2	116.41(9)	N1-Co1-O2	149.52(8)	N2#2-Co1-O1	90.33(8)
O5-Co1-O2	89.18(8)	N2#2-Co1-O2	89.00(8)	O2-Co1-O1	59.16(8)
2					
Ni1-O1	2.030(4)	Ni1-O5	2.066(4)	Ni1-N2#4	2.113(5)
Ni1-N1	2.073(4)	Ni1-O4#3	2.092(4)	Ni1-O3#3	2.296(4)
O1-Ni1-O5	88.19(16)	O1-Ni1-N1	91.85(17)	O1-Ni1-O3#3	115.25(15)
O5-Ni1-N1	92.31(16)	O1-Ni1-O4#3	174.78(16)	O5-Ni1-O3#3	86.63(14)
O5-Ni1-O4#3	89.41(15)	N1-Ni1-O4#3	92.87(17)	N1-Ni1-O3#3	152.80(16)
O1-Ni1-N2#4	90.82(17)	O5-Ni1-N2#4	172.65(16)	O4#1-Ni1-O3#3	59.96(14)
N1-Ni1-N2#4	95.00(18)	O4#3-Ni1-N2#4	90.97(16)	N2#2-Ni1-O3#3	87.21(16)

Symmetry codes: **1**: #1: $x, -y + 1, z - 1/2$; #2: $x + 1/2, -y + 3/2, z + 1/2$; **2**: #3: $x, -y + 1, z - 1/2$; #4: $x - 1/2, -y + 1/2, z - 1/2$.

TABLE 3
Distance (Å) and angles (°) of hydrogen bonding for complexes **1** and **2**

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
Complex 1				
O(5)-H(1W)...O(2)#5	0.82	2.11	2.832(3)	145.6
O(5)-H(2W)...O(3)#6	0.84	1.85	2.676(3)	168.0
Complex 2				
O(5)-H(2W)...O(3)#7	0.83	1.99	2.750(5)	152.1
O(5)-H(1W)...O(2)#8	0.82	1.91	2.703(6)	161.5

Symmetry codes: **1**: #5: $-x, -y + 1, -z + 2$; #6: $-x, y, -z + 5/2$; **2**: #7: $-x + 2, y, -z + 1/2$; #8: $-x + 2, -y + 1, -z$.

distorted octahedral coordination sphere of M, with an O5-M-N2B angle of $172.25(8)^\circ$ for **1** and $172.65(16)^\circ$ for **2**. The Co-N bond lengths are 2.120(2) and 2.165(3) Å and the Co-O ones are in the range of 2.028(2)–2.252(2) Å. The Ni-N bond lengths

are 2.073(4) and 2.113(5) Å and the Ni-O ones are in the range of 2.030(4)–2.296(4) Å. Each Brip ligand acts as a μ_2 -bridge linking two M ions, in which one carboxylate group adopts a monodentate mode while another adopts a chelating mode

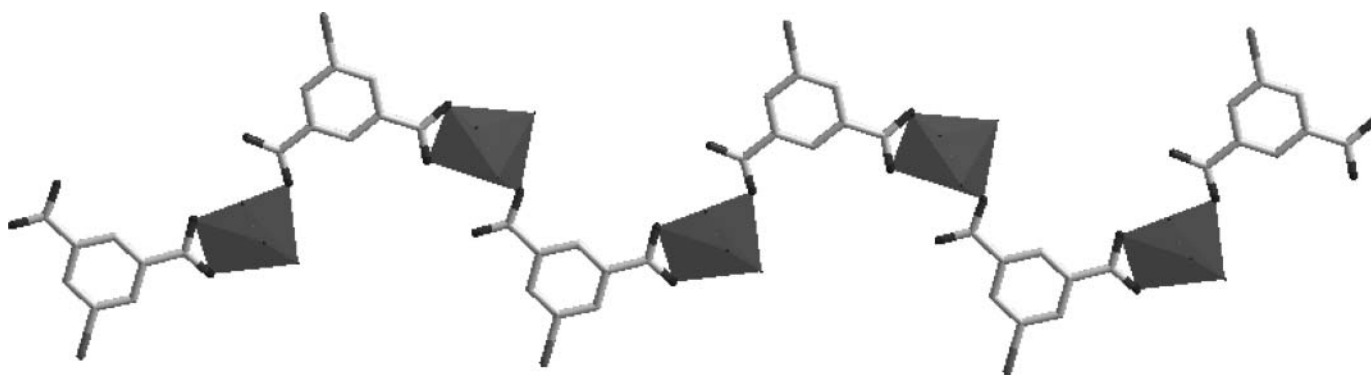


FIG. 2. Polyhedral view of 1D chains of complexes **1** and **2**.

coordinating to one M ion. And the bpp ligands with a GG' conformation providing a N-to-N separation with the distance of 8.543 Å link the adjacent M ions. Based on the previous connection, the adjacent M ions are bridged by Brip to form an alternating 1D chain (Figure 2). Such 1D chains are further connected through bpp ligands to generate a 3D network with diamondoid topology with the Schläfli symbol of (6₂. 6₂. 6₂. 6₂. 6₂. 6₂.) (Figure 3). The large distances between the metal ions result in large cavities within the network, and thus one identical framework fill this space to generate a twofold interpenetrating network (Figure 3). Hydrogen bonds between the coordinated water molecules and the carboxylate groups of the Brip ligands further stabilize the structure (Table 3).

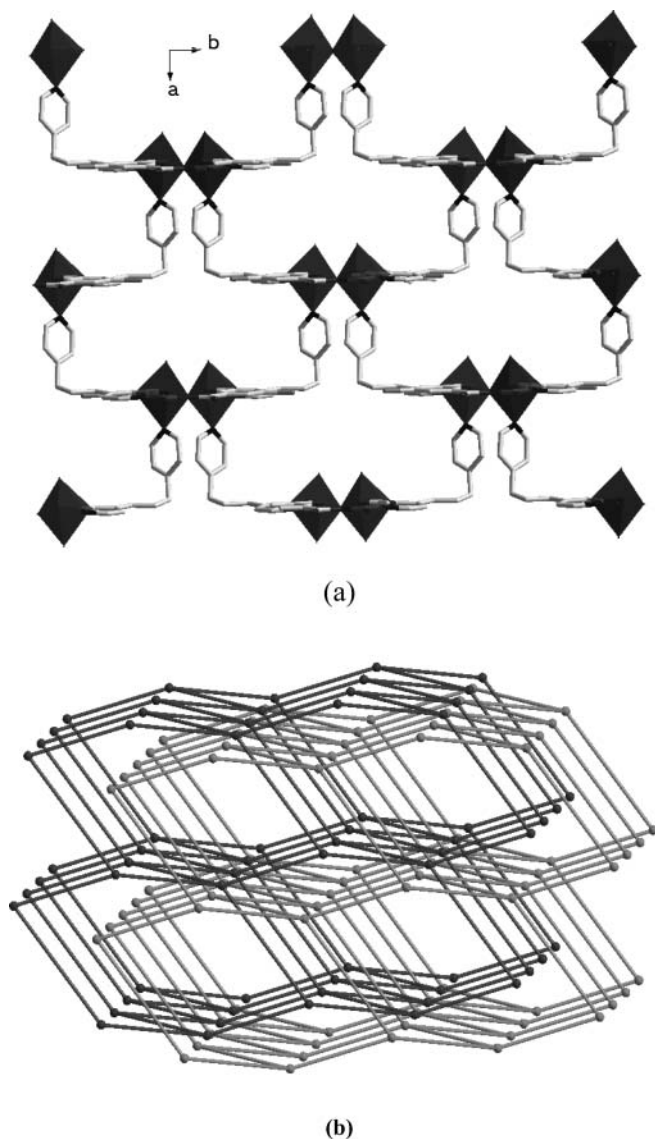


FIG. 3. (a) Polyhedral view of 3D network of complexes **1** and **2**. (b) Topology of complexes **1** and **2**.

Thermal Analysis

To investigate thermal stabilities of **1** and **2**, we studied them by TGA in Figure 4. The experiments were performed on samples consisting of numerous single crystals of **1** and **2** under N₂ atmosphere with a heating rate of 10°C•min⁻¹. For complex **1**, weight loss begins at 235°C, and coordinated water molecules are lost from 235°C to 270°C (calcd. 3.5%, obsd. 3.3%) and then a rapid weight loss was detected, which is attributed to the decomposition of complex **1**. For complex **2**, the first weight loss of 3.6% between 127°C and 174°C indicates the loss of coordinated water molecules (calcd. 3.5%) and the residue remains unchanged until about 310°C, and then a rapid weight loss was detected, which is attributed to the decomposition of complex **2**.

Magnetic Properties

The magnetic susceptibilities, χ_M , of **1** and **2** were measured in the 2–300 K temperature range at 2,000 G, and shown as $\chi_M T$ and χ_M versus T plots in Figure 5. For complex **1**, the experimental $\chi_M T$ value at 300 K is 2.93 cm³ K mol⁻¹, which is greater larger than that expected for the spin-only one for a high-spin cobalt ion (1.87 cm³·mol⁻¹·K with $g = 2.0$), but is close to the value of 3.37 cm³·mol⁻¹·K expected when the spin momentum and the orbit momentum exist independently ($\mu_{LS} = [L(L + 1) + 4S(S + 1)]^{1/2}$, $L = 3$, $S = 3/2$). This is due to the occurrence of an unquenched orbital contribution typical of the ⁴T_{1g} ground state in six-coordinated cobalt(II) complexes. Upon cooling, the value continuously increases reaching a maximum value of 3.33 cm³·mol⁻¹·K at 76 K, and then decreases upon further cooling. The $\chi_M T$ values increase with the decrease of the temperature, typical of the presence of intradimeric ferromagnetic interaction, and the decrease of $\chi_M T$ may be attributed to intermolecular antiferromagnetic interaction and/or the zero-field splitting term of the Co(II) ion.^[34] The

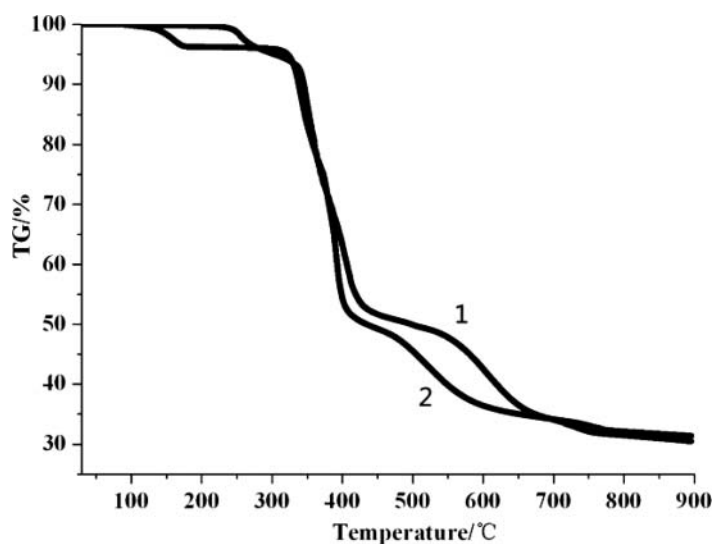


FIG. 4. The TGA curves for complexes **1** and **2**.

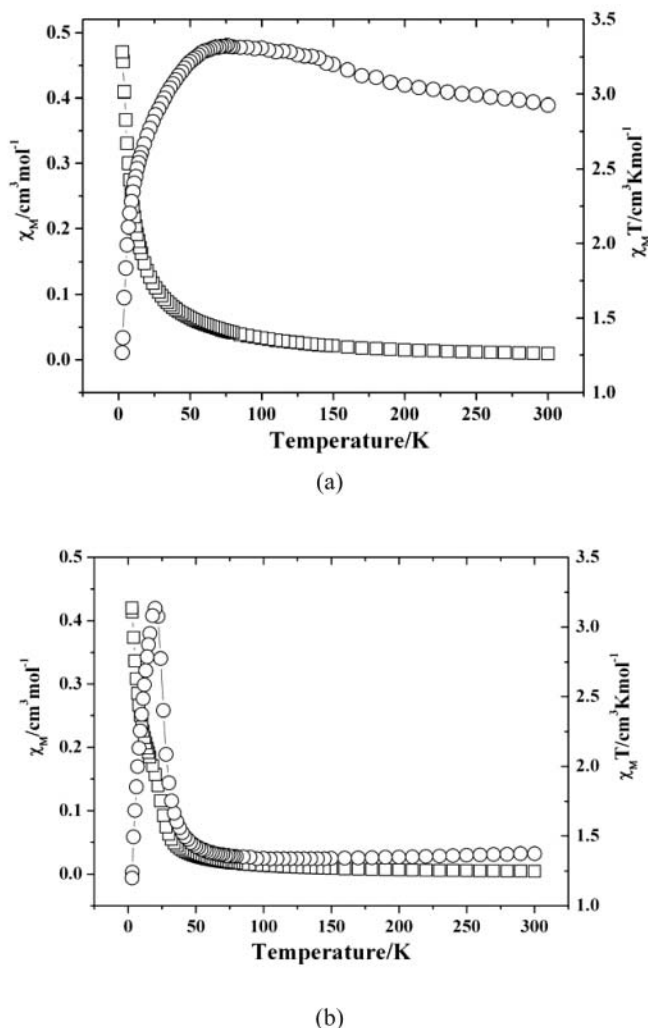


FIG. 5. Temperature dependence of χ_M and $\chi_M T$ versus T for complexes **1** (a) and **2** (b).

temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) obeys the Curie-Weiss law above 76 K with $C = 2.80 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, $\theta = 16.17 \text{ K}$, and $R = 1.274 \times 10^{-4}$, the positive θ value supports the presence of overall ferromagnetic interactions.

For complex **2**, at room temperature, $\chi_M T$ value is equal to $1.37 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, a value that is as expected for a magnetically isolated spin triplet ($1.21 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ with $g = 2.20$). As the temperature is lowered, the $\chi_M T$ value increases to maximum at 20 K of $3.14 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, and then abruptly decreases to $1.2 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. The increase of $\chi_M T$ with decreased temperature clearly indicates ferromagnetic coupling interactions between the metal centers. And the decrease of $\chi_M T$ may be attributed to intermolecular antiferromagnetic interaction and/or the zero-field splitting term of the Ni(II) ion.^[34] The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) obeys the Curie-Weiss law above 32 K with $C = 1.35 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, $\theta =$

1.65 K , and $R = 2.572 \times 10^{-4}$, the positive θ value supports the presence of overall ferromagnetic interactions.

CONCLUSIONS

In summary, two new complexes, $[\text{M}((\text{H}_2\text{O})(\text{bpp})(\text{Brip}))_n]$ ($\text{M} = \text{Co}^{\text{II}}$ (**1**) and Ni^{II} (**2**), $\text{bpp} = 1,3\text{-bi}(4\text{-pyridyl})\text{propane}$, $\text{H}_2\text{Brip} = 5\text{-bromoisophthalic acid}$), have been synthesized and characterized. The two complexes have twofold interpenetrating diamondoid 3D networks. Variable-temperature magnetic susceptibility measurements indicate the occurrence of weak ferromagnetic interactions between the Co^{II} (**1**) and Ni^{II} (**2**) ions, respectively.

SUPPLEMENTARY MATERIALS

The atomic coordinates and other parameters of structure **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (nos. 824627 and 824628, respectively; deposit@ccdc.cain-ac.uk or <http://www.ccdc.ac.uk>).

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Graphic Abstract-Pictogram:

Title: Syntheses, Structures, and Magnetic Properties of Two New Metal-Organic Frameworks Based on 5-bromoisophthalic acid and 1,3-bi(4-pyridyl)propane

Two new complexes, $[\text{M}((\text{H}_2\text{O})(\text{bpp})(\text{Brip}))]_n$ ($\text{M} = \text{Co}^{\text{II}}$ (**1**) and Ni^{II} (**2**), bpp = 1,3-bi(4-pyridyl)propane, $\text{H}_2\text{Brip} = 5\text{-bromoisophthalic acid}$), have been synthesized through hydrothermal reaction. Complexes **1** and **2** have the same structure. The adjacent metal ions are bridged by Brip to form an alternate 1D chain. Such 1D chains are further connected by bpp to generate a twofold interpenetrating diamondoid 3D network. Moreover, thermal stabilities and magnetic properties of complexes **1** and **2** have also been investigated.

