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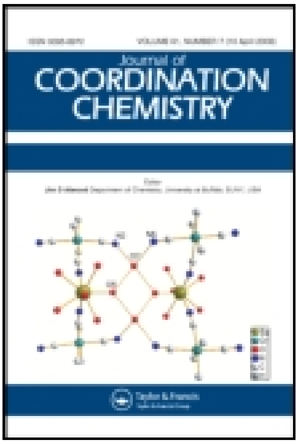

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Design and syntheses of two threefold interpenetrating 2-D networks

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Design and syntheses of two threefold interpenetrating 2-D networks

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Two new interpenetrating networks, $[Ni(2,2'\text{-bpy})(5\text{-npa})(bpe)_{0.5}(H_2O)]_n$ (**1**) and $[Ni(2,2'\text{-bpy})(5\text{-npa})(bpa)_{0.5}(H_2O)]_n$ (**2**) (2,2′-bpy = 2,2′-bipyridine, 5-npa = 5-nitroisophthalato, bpe = 1,2-bis(4-pyridyl)ethylene, bpa = 1,2-bis(4-pyridyl)ethane), have been synthesized and characterized by elemental analyses, IR spectroscopy, thermogravimetric analyses, X-ray powder diffraction, and single-crystal X-ray diffraction. Complexes **1** and **2** have similar structures and show a threefold interpenetrating topology constructed by three 2-D wave-like networks. Secondary building unit (SBU), $[Ni(2,2'\text{-bpy})(5\text{-npa})(H_2O)]_n$, was used as starting material of the multistep reaction. Replacing one coordination bond of chelating carboxyl group of SBUs by bpe and bpa afford the two threefold interpenetrating complexes.

Keywords: Secondary syntheses; Bipyridine-based ligand; Interpenetrating network

1. Introduction

The rational design and synthesis of metal–organic networks is of interest in material science since they may provide a new strategy for achieving solid functional materials with potential applications in catalysis, gas storage, magnetism, and optics [1–4]. A variety of architectures have been obtained using simple ligands, such as 4,4-bipyridine and 1,2-bi(4-pyridyl)ethane [5]. Use of longer bis(pyridine) spacers afforded very interesting structural motifs, such as double helices, multiple sheets, interpenetrated ladders, and interpenetrated diamondoid nets [6–13]. The design of coordination polymers from spacer ligands is highly influenced by the nature of coordination of the metal ion, the structural characteristics of the polydentate organic ligand [14], the metal, ligand ratio, the counteranion, solvent, reaction temperature, pH, and templating agent [15–17]. Thus, the crystal engineering of networks with desired topologies and specific properties using spacer ligands remains a difficult challenge. The most effective approach is by using secondary building units (SBUs) as the designing material to obtain tailor-made structures with required structures and properties starting from well-characterized inorganic and organic species [18–21]. As the SBUs already have their own geometry and properties, by choosing appropriate linkers, target

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structures with predictable properties can be obtained by multistep reactions. In this article, two interpenetrating networks were synthesized by polystep reactions.

2. Experimental

2.1. *Materials and instrumentation*

All reagents and chemicals were commercially obtained and used without purification. The crystal structure was obtained on a Bruker Smart-1000 CCD diffractometer. X-ray powder diffraction (XRPD) measurements were recorded on a Bruker D8 advance diffractometer at 40 kV, 40 mA for Cu-Kα ($\lambda = 1.5406$ Å), with a step size of 0.01° in θ and a scan speed of 0.1 s per step size. Thermal gravimetric analyses from 50°C to 1000°C were carried out under N_2 at a heating rate of 5°C min^{-1} using a TA-Q600 instrument. Carbon, hydrogen, and nitrogen were determined using an EA 1112 elemental analyzer. IR spectra (KBr disc) were recorded on an EQUINOX55 (Bruker) spectrophotometer.

2.2. *Synthesis of SBUs*

The complex was prepared according to the method we reported previously [22]. A mixture of $NiSO_4{\cdot}6H_2O$ (0.5 mmol, 0.1342 g), 5-nitroisophthalato(5-npa) (0.5 mmol, 0.1075 g), NaOH (100 µL, 10 mol L^{-1}), 2,2′-bipyridine(2,2′-bpy) (0.5 mmol, 0.0775 g), and H_2O (20 mL) was heated in a 30 mL stainless-steel reactor with a Teflon liner at 150°C for 48 h, and then slowly cooled to room temperature to give blue block single crystals of $[Ni(2,2'\text{-bpy})(5\text{-npa})(H_2O)]_n$. The blue crystalline product was filtered and washed with water. Yield: 70% based on Ni. Anal. Calcd for $C_{18}H_{13}N_3NiO_7$ (%): C, 48.98; H, 2.95; N, 9.52. Found (%): C, 49.29; H, 2.99; N, 9.74. IR (KBr): 3407, 1721, 1640, 1609, 1541, 1451, 1397, 1341 cm^{-1}.

2.3. *Synthesis of two threefold interpenetrating frameworks*

An aqueous solution (15 mL) of SBU (0.02 mmol, 0.0996 g) and 1,2-bis(4-pyridyl) ethylene(bpe) (0.01 mmol, 0.0186 g) in a 30 mL Teflon-lined stainless-steel reactor was heated at 160°C for 72 h and then slowly cooled to room temperature to give green block single crystals of **1**. The green crystalline product was filtered and washed with water. Yield: 80% based on Ni. Anal. Calcd for $C_{24}H_{18}N_4NiO_7$ (%): C, 54.07; H, 3.40; N, 10.51. Found (%): C, 54.18; H, 3.51; N, 10.54. IR (KBr): 3396, 1676, 1608, 1566, 1388, 1348, 783, 734, 668 cm^{-1}.

Complex **2** was synthesized in the same way as **1** using 1,2-bis(4-pyridyl)ethane(bpa) (0.01 mmol, 0.0188 g) in the place of bpe. Yield: 82% based on Ni. Anal. Calcd for $C_{24}H_{19}N_4NiO_7$ (%): C, 53.97; H, 3.59; N, 10.49. Found (%): C, 54.18; H, 3.71; N, 10.58. IR (KBr): 3419, 1636, 1588, 1406, 1388, 823, 834, 868 cm^{-1}.

Table 1. Crystallographic data for **1** and **2**.

	Complex **1**	Complex **2**
Empirical formula	$C_{24}H_{18}N_4NiO_7$	$C_{24}H_{19}N_4NiO_7$
Formula weight	533.11	534.12
Temperature (K)	298	298
Crystal system	Monoclinic	Monoclinic
Space group	$p2_1/C$	$p2_1/C$
Unit cell dimensions (Å, °)		
a	16.625(3)	16.578(3)
b	8.9824(18)	8.9853(18)
c	18.741(8)	17.908(4)
β	119.94(2)	113.99(3)
Volume (Å^3), Z	2425.2(12), 4	2437.1(9), 4
Calculated density (g cm^{-3})	1.460	1.456
Absorption coefficient (mm^{-1})	0.852	0.848
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0456$, $wR_2 = 0.1155$	$R_1 = 0.0436$, $wR_2 = 0.1209$
R indices (all data)[a]	$R_1 = 0.0611$, $wR_2 = 0.1281$	$R_1 = 0.0488$, $wR_2 = 0.1250$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|.wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

2.4. *X-ray crystallographic studies*

Intensity data for the SBU and the two threefold interpenetrating frameworks were measured on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied using SADABS [23]. The structures for SBU and the two threefold interpenetrating networks were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXL-97 program package [24]. The positions of hydrogens were generated theoretically (C–H fixed at 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbons before the final cycle of refinement. Crystal data and structure determination summaries are given in table 1.

3. Results and discussion

The SBU is a chain structure bridged by chelating and monodentate 5-npa; Ni(II) is six-coordinate with a distorted octahedral geometry (figure 1). We replaced the coordinated water by 4,4′-bipyridine (4,4′-bpy), thus two chains are bridged by 4,4′-bpy forming a ladder-like coordination polymer [22]. Replacing the coordinated solvent with a rigid linker could provide a method for the synthesis of predictable structures, and replacing one coordination bond of the chelating carboxylate may also be an important step in the multistep reaction. The bonds of chelating carboxylate are longer than monodentate ones, so they can be replaced. The octahedral geometry of Ni(II) is much distorted, but if one bond of the chelating carboxylate is replaced by a monodentate spacer, the octahedral geometry may be more regular. When replacing one chelating carboxylate with a bridging ligand, the chain structure may turn into a ring structure, and if the bridging ligand is long enough, the ring structure may interlock. In order to get an interpenetrating structure, we chose a rigid linker, bpe,

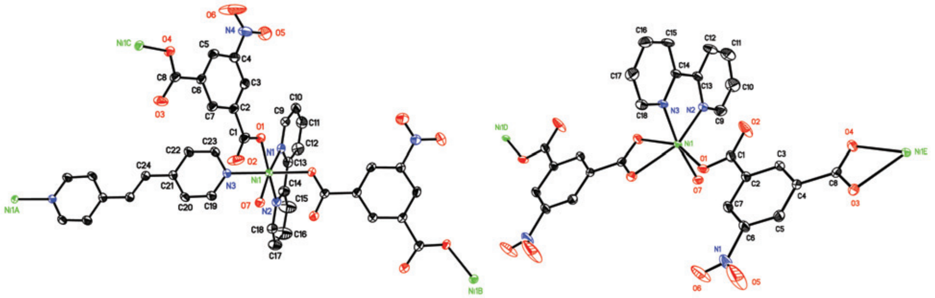

Figure 1. The coordination environment of nickel(II) of **1** (left) and SBU (right) with the atom numbering, showing displacement ellipsoids at 30% probability level. Hydrogens are omitted for clarity. Symmetry code: A = $-x+2$, $-y+2$, $-y+1$; B = x, $0.5-y$, $0.5+z$; C = x, $0.5-y$, $z-0.5$; D = $x-1$, y, z; E = $1+x$, y, z.

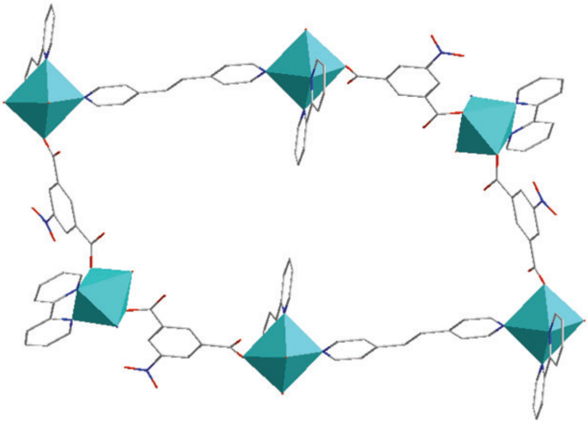

Figure 2. Perspective view of the six-membered ring structure of **1**. Hydrogens are omitted for clarity.

as bridging ligand to replace the chelating carboxylate. Choosing semi-rigid linker bpa can also get a similar structure.

From figure 1 we can see each Ni(II) is six-coordinate in **1** and surrounded by two carboxylate oxygens from two different 5-npa dianions, three nitrogens from a bpe, and a 2,2′-bpy and one water molecule. Carboxylate is monodentate and one coordination bond of the chelating carboxylate was replaced by bpe. Compared to SBU, the octahedral geometry of **1** is more regular, and the nitrogen from bpe and the oxygen from a 5-npa dianion lie on the axes. A better insight into the structure of **1** can be achieved by the application of a topological approach, that is, by reducing multidimensional structures to simple node and linker nets [25]. According to the simplification principle, the Ni(II) is defined as a three connected node, while bpe and 5-npa serve as linkers. On the basis of this concept of chemical topology, the overall structure is a distorted six-membered ring, the shortest circuit here (figure 2). The distorted six-membered ring is connected by four 5-npa dianions and two bpe ligands. In the six-membered ring, the Ni···Ni distances bridged by bpe and 5-npa are 13.613(3)

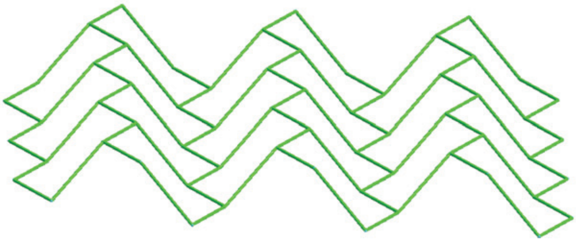

Figure 3. The 2-D wave-like sheet of **1**.

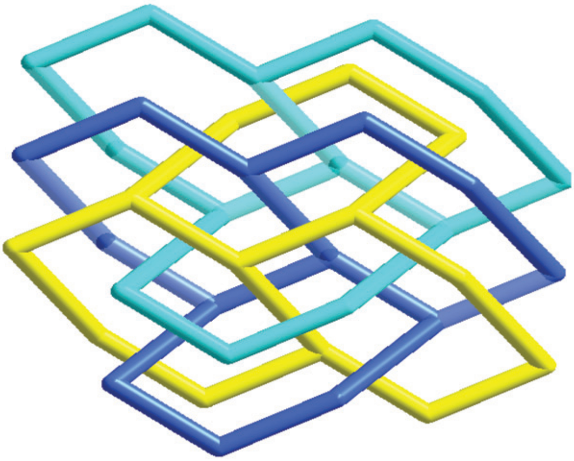

Figure 4. Perspective view of the threefold interpenetration structure in **1**.

and 10.853(4) Å, respectively. Ni(II) is a three-connected node and six-membered rings are connected by bpe and 5-npa forming a 2-D wave-like sheet (figure 3).

Large networks tend to interpenetrate to fill the voids within a single net. Bpe is a long linker and the six-membered ring is large enough to interpenetrate as by design. From figure 4 we can see that three six-membered rings are interlocked, directly leading to the formation of a 2-D threefold interpenetrated network.

IR spectra of **1** and **2** were performed as KBr pellets from 4000 to 500 $\mathrm{cm^{-1}}$. These polymers showed asymmetric vibration bands of the carboxylates [26–28] at 1676–1566 $\mathrm{cm^{-1}}$ for **1**, 1636–1588 $\mathrm{cm^{-1}}$ for **2**, and symmetric vibrations at 1388–1348 $\mathrm{cm^{-1}}$ for **1**, 1406–1388 $\mathrm{cm^{-1}}$ for **2**. The stretching vibration at 3396 $\mathrm{cm^{-1}}$ for **1** and 3419 $\mathrm{cm^{-1}}$ for **2** showed the presence of coordinated water. Strong bands at 1566 and 1588 $\mathrm{cm^{-1}}$ for **1** and **2** confirmed the presence of 2,2′-bpy and bpe (bpa), consistent with the X-ray analysis. Because of interpenetrating, **1** became more stable, losing coordinated water near 240°C (3.63%), calculated (3.38%). When heated above 270°C, the compound lost other ligands in sequence and decomposed (figure 5). The XPRD patterns of **1** as a powder agreed with the XPRD patterns simulated by the single-crystal structure, indicating that the powder and the single crystal are in the same phase (figure 5).

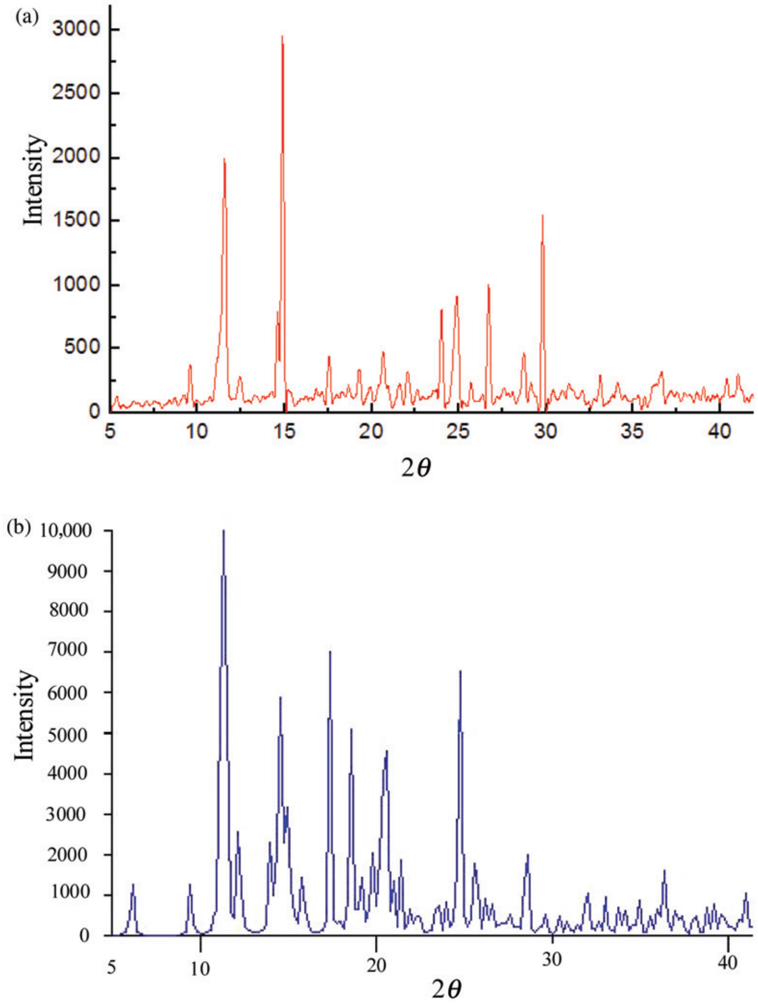

Figure 5. XPRD patterns of **1**: (a) Complex **1** powder and (b) XPRD simulated by the single-crystal structure.

It was difficult to synthesize the title complex starting with $NiSO_4 \cdot 6H_2O$, 2,2′-bpy, bpe(bpa), and 5-npa because a mixture was obtained. By preparing the SBU, we obtained pure interpenetrated network with high yield. As the SBU already had its own geometry, the structure of the title complex could be predicted.

4. Conclusions

Two similar threefold interpenetrating networks, $[Ni(2,2'\text{-bpy})(5\text{-npa})(bpe)_{0.5}(H_2O)]_n$ and $[Ni(2,2'\text{-bpy})(5\text{-npa})(bpa)_{0.5}(H_2O)]_n$, were synthesized based on a well-designed SBU, $[Ni(2,2'\text{-bipy})(5\text{-npa})(H_2O)]_n$. The two predicted networks were obtained by replacing one of the coordination bonds of chelating carboxylate in the SBU with bpe and bpa. Replacing the coordinated water in this SBU by 4,4′-bpy, a ladder-like coordination polymer was obtained [22]. Thus, by replacing the weak coordinated bond in the designed SBU with space linkers, target structures could be obtained, which is a most effective approach to obtain tailor-made structures with the required structures and properties.

Supplementary material

CCDC-691708, 802390, and 802391 contain the supplementary crystallographic data of SBUs and two interpenetrating frameworks 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: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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