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Hydrothermal syntheses and crystal structures of two rectangular grid coordination polymers based on unique prismatic $[M_8(\mathrm{ip})_8(4,4'\text{-bipy})_8]$ building blocks [M = Ni(II) or Cd(II), ip = isophthalate, bipy = bipyridine]

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Abstract

Two new coordination polymers formulated as [Ni(ip)(4,4′-bipy)] (**1**) and [Cd(ip)(4,4′-bipy)]H_2O (**2**) have been hydrothermally prepared and structurally characterized. They crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$ for **1** and monoclinic space group $P2/c$ with $Z = 4$ for **2**, respectively. The dinuclear $[M_2L_4(\mathrm{carboxylate})_4]$ units in each complex are bridged by V-shaped ip and linear 4,4′-bipy spacers to form unique prismatic $[M_8(\mathrm{ip})_8(4,4'\text{-bipy})_8]$ building blocks, which are further inter-connected through the mixed organic ligands to generate two-dimensional rectangular grids. The packing modes of the two two-dimensional grids are slightly different in the orientations of the ip aromatic rings with respect to the planes of the rectangular grid coordination polymers.

Keywords: Coordination polymer; Hydrothermal syntheses; Nickel; Cadmium; Crystal structure

1. Introduction

It is quite apparent that controlled assembly of coordination polymers in the solid state offers potential for the development of rational strategies for design of new functional crystalline materials [1]. A designed and predictable coordination polymer framework may be exemplified by careful selection of metal coordination geometry and organic “spacer” ligands, which can create various supramolecular architectures sustained by strong covalent coordinate bonds or by weaker bonding forces, such as π–π interactions and/or hydrogen bondings. As well as an enormous amount of different dimensional frameworks having been reported based on single metal units (SMUs) and organic ligands, strong attentions have been also paid on the assembly of coordination polymers based on dinuclear metal units (DMUs), which are mainly tunable in two types (Scheme 1). Obviously, if the monocarboxylate ligands are substituted with dicarboxylate as well as terminal ligands (L) are substituted with linear bifunctional “spacer” or “rod” ligands such as 4,4′-bipyridine (4,4′-bipy), the extended structures with predictable topologies of general formula $[M_2(\mathrm{dicarboxylate})_2\mathrm{L}]$ and $[M_2(\mathrm{dicarboxylate})_2\mathrm{L}_2]$ will be produced for types I and II, respectively. Furthermore, these frameworks are tunable as the length and width of the spacer ligand controls the size of the cavities in the extended structures. Very recently several such complexes based on types I and II of DMUs have been reported [2,3], including the three-dimensional coordination polymers with cuboidal structural units based on type II of DMUs [3]. Herein we report two novel neutral rectangular grid coordination polymers constructed with isophthalate (a V-shaped dicarboxylate, designated as ip hereafter), 4,4′-bpy and type II of DMUs, namely [Ni(ip)(4,4′-bipy)] (**1**) and [Cd(ip)(4,4′-bipy)]·H_2O (**2**).

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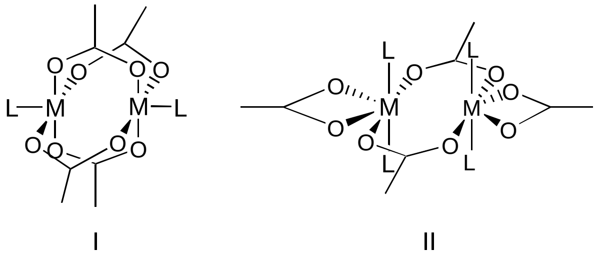


Scheme 1. Two types of carboxylate-bridged dinuclear metal structures.

2. Experimental

All reagents were commercially available and used as received. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT–IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer.

Synthesis of [Ni(ip)(4,4′-bipy)] (**1**). An aqueous mixture (8 cm^3) containing H_2ip (0.083 g, 0.5 mmol), NaOH (0.040 g, 1.0 mmol), $Ni(NO_3)_2 \cdot H_2O$ (0.145 g, 0.5 mmol) and 4,4′-bipy (0.078 g, 0.5 mmol) was placed in a Parr Teflon-lined stainless-steel vessel (23 cm^3), and the vessel was sealed and heated to 180°C for 7 d and then cooled at 5°C/h to 100°C and held for 10 h, followed by slow cooling to room temperature. Green plate-like crystals of **1** were mechanically separated, washed with water and dried in air (yield: 0.047 g, ca. 25%). Calc. for $C_{18}H_{12}N_2NiO_4$: C, 57.05; H, 3.19; N, 7.39. Found: C, 57.20; H, 3.07; N, 7.30%. FT–IR data (cm^{-1}): 3065w, 1609vs, 1576m, 1548s, 1484m, 1452m, 1408vs, 1223w, 1107w, 1069w, 832w, 812m, 740m, 721m and 629m.

Synthesis of [Cd(ip)(4,4′-bipy)]·H_2O (**2**). An aqueous mixture (8 cm^3) containing H_2ip (0.083 g, 0.5 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol) and 4,4′-bipy (0.078 g, 0.5 mmol) was placed in a Parr Teflon-lined stainless steel vessel (23 cm^3). Triethylamine (0.7 cm^3, 5 mmol) was added to this heterogeneous mixture, and the vessel was sealed and heated to 140°C for 20 h and then cooled to 100°C at a rate of 5°C/h, and held for another 10 h, followed by further cooling to room temperature. Colorless plate-like crystals of **2** were mechanically separated, washed with water and dried in air (yield: 0.135 g, 60%). Calc. for $C_{18}H_{14}CdN_2O_5$: C, 47.97; H, 3.13; N, 6.22. Found: C, 48.05; H, 3.01; N, 6.20%. FT–IR data (cm^{-1}): 3432br, 3057w, 1603vs, 1551s, 1483w, 1442 m, 1388vs, 1222w, 1072w, 1007w, 810m, 743m, 721m and 629m.

X-ray crystallography. Diffraction intensities were collected at 21°C on a Siemens R3m and a Bruker CCD diffractometer employing graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) for **1** and **2**, respectively, and absorption corrections were applied [4]. The structures were solved with direct methods and refined with full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs, respectively [5,6]. Non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å). Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [7]. The crystallographic data for **1** and **2** are listed in Table 1, and the selected bond lengths (Å) and bond angles (°) are given in Table 2, respectively. Drawings were produced with SHELXTL [8].

Table 1
Crystal data and structure refinement

	1	**2**
Formula	$C_{18}H_{12}N_2NiO_4$	$C_{18}H_{14}CdN_2O_5$
fw	379.01	450.71
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2/c$
a (Å)	9.242(4)	10.229(1)
b (Å)	10.137(5)	11.690(1)
c (Å)	10.144(6)	16.064(2)
α (deg)	77.58(2)	90
β (deg)	77.64(1)	104.09(2)
γ (deg)	71.48(1)	90
V (Å^3)	869.1(8)	1863.3(4)
Z	2	4
D_c ($g\,cm^{-3}$)	1.448	1.607
μ(MoKα) (mm^{-1})	1.140	1.202
No. unique data	4037	13101
No. data with $I \geqslant 2\sigma(I)$	3796	5395
R_1, wR_2	0.0501, 0.1387	0.0584, 0.1858

3. Results and discussion

Complexes **1** and **2** are structurally very similar and represent a class of rectangular grid coordination polymers that are based on type II of DMUs. In **1** two equivalent Ni(II) atoms separated at 4.416(2) Å are bridged by *syn-anti* carboxylate ends of ip ligands, as shown in Fig. 1(a). Each Ni(II) atom is in a distorted octahedral geometry, being coordinated by two *trans*-related μ-4,4′-bipy ligands [Ni–N 2.114(3) and 2.107(3) Å] at the axial positions, two oxygen atoms [Ni–O 2.184(3) and 2.115(3) Å] from the chelate carboxylate end of the ip ligand and two oxygen atoms [Ni–O 2.056(3) and 2.034(3) Å] from the bridging carboxylate ends of the ip ligands in the equatorial plane.

It should be noted that the basic Ni_2 subunits in **1** belong to the type II of DMUs, and are analogous to those in the three-dimensional coordination polymers reported previously by us [3]. On the other hand, due to ip employed in **1** is a V-shaped dicarboxylate ligand, both the interconnection of the DMUs and the coordination mode of ip are very different from those

Table 2
Selected bond lengths (Å) and angles (deg) for complexes **1** and **2**

Complex **1**			
Ni(1)–O(1)	2.184(3)	Ni(1)–O(4b)	2.034(2)
Ni(1)–O(2)	2.115(3)	Ni(1)–N(1)	2.114(3)
Ni(1)–O(3a)	2.056(3)	Ni(1)–N(2a)	2.107(3)
O(1)–Ni(1)–O(2)	61.8(1)	O(3a)–Ni(1)–O(4b)	109.4(1)
O(1)–Ni(1)–O(4b)	95.2(1)	O(3a)–Ni(1)–N(1)	86.3(1)
O(1)–Ni(1)–N(1)	89.4(1)	O(3a)–Ni(1)–N(2a)	90.3(1)
O(1)–Ni(1)–N(2a)	93.7(1)	O(4b)–Ni(1)–N(1)	88.1(1)
O(2)–Ni(1)–O(3a)	93.3(1)	O(4b)–Ni(1)–N(2a)	93.1(1)
O(2)–Ni(1)–N(1)	89.2(1)	N(1)–Ni(1)–N(2a)	176.6(1)
O(2)–Ni(1)–N(2a)	91.0(1)		
Complex **2**			
Cd(1)–O(1)	2.280(4)	Cd(1)–O(4b)	2.393(5)
Cd(1)–O(2)	2.298(4)	Cd(1)–N(1)	2.328(3)
Cd(1)–O(2a)	2.812(4)	Cd(1)–N(2a)	2.311(3)
Cd(1)–O(3b)	2.352(4)		
O(1)–Cd(1)–O(2)	49.0(1)	O(2a)–Cd(1)–N(1)	86.6(1)
O(1)–Cd(1)–O(4b)	85.8(1)	O(2a)–Cd(1)–N(2a)	86.7(1)
O(1)–Cd(1)–N(1)	90.2(1)	O(3b)–Cd(1)–O(4b)	54.3(1)
O(1)–Cd(1)–N(2a)	91.7(1)	O(3b)–Cd(1)–N(1)	90.3(1)
O(2)–Cd(1)–O(2a)	78.7(1)	O(3b)–Cd(1)–N(2a)	92.7(1)
O(2)–Cd(1)–N(1)	87.8(1)	O(4b)–Cd(1)–N(1)	92.9(1)
O(2)–Cd(1)–N(2a)	88.1(1)	O(4b)–Cd(1)–N(2a)	94.3(1)
O(2a)–Cd(1)–O(3b)	92.2(2)	N(1)–Cd(1)–N(2a)	172.7(1)

Symmetry codes: (a) $x, y, z-1$; (b) $-x, -y, -z+1$ for **1**; (a) $-x+1, y, -z+1/2$; (b) $x, y+1, z$ for **2**.

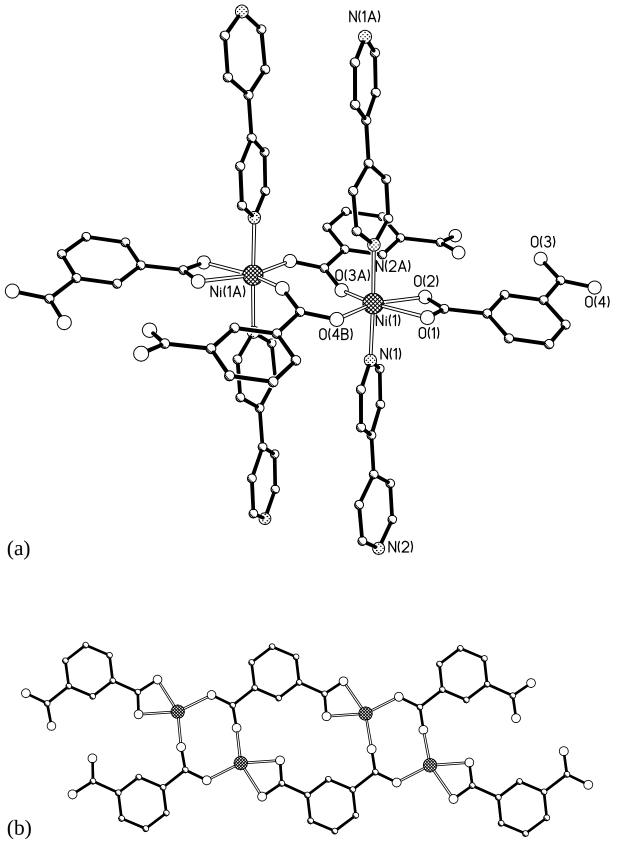
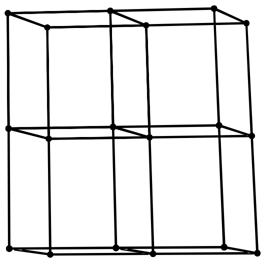


Fig. 1. Perspective views of the coordination environment (a) and the $[Ni_2(ip)_2]_n$ chain (b) in **1**.



Scheme 2. A prismatic building block (solid line).

in the previous work [3]. Each ip ligand in **1** functions in an unusual chelate-bridging bis-bidentate mode. In contrast, the linear dicarboxylate ligand terephthalate (tp) acts in either the chelating bis-bidentate or bridging bis-bidentate mode in the three-dimensional coordination polymers (see Scheme 1 in Ref. [3]). Consequently, the DMUs in **1** are inter-connected through the ip spacers to generate interesting one-dimensional ribbons with a distance between the adjacent Ni_2 subunits of ca. 10.14 Å, as shown in Fig. 1(b). The linkages of such ribbons through the μ-4,4′-bipy ligands in the axial positions of the coordination octahedra further generate an infinite two-dimensional neutral framework featuring interesting prismatic $[Ni_8(ip)_8(4,4'\text{-bipy})_8]$ building blocks with dimensions of ca. $4.42 \times 10.14 \times 11.34$ Å (Scheme 2), in which each apex of the prismatic building block is occupied by a Ni(II) atom. These prismatic building blocks in **1** are thus significantly different from the cuboid $[Co_{16}(tp)_8(4,4'\text{-bipy})_8]$ structural units described previously [3]. To our knowledge, neutral rectangular grids with mixed ligands are very unusual [9], and the building block in **1** is unprecedented (see Fig. 2).

In **2** the local coordination environment around the Cd(II) atom can be described as a greatly distorted pentagonal bipyramid [Fig. 3(a)] with an intra-dinuclear Cd⋯Cd separation of 3.966(2) Å. The distances of Cd(1)–O bonds associated with the oxygen atoms from the bridging carboxylate ends of ip ligands [Cd(1)–O(1) 2.280(4) and Cd(1)–O(2a) 2.298(4) Å] are slightly shorter than that of Cd1–O bonds associated with the oxygen atoms from the chelate carboxylate end of the ip ligand [Cd(1)–O(3b) 2.352(4) and Cd(1)–O(4b) 2.393(4) Å]. On the other hand, although the Cd(1)–O(2) distance [2.812(4) Å] is much longer than the other four Cd–O bands, similar cases of such long cadmium-ligand bonds have been found in $[Cd(py)(ip)]_2$ and [Cd(tp)(4,4′-bipy)] [10,3], as well as in other Cd-carboxylate distance [11]. The weak Cd(1)–O(2) bonding interactions in **2** should be responsible to the shorter intra-dinculear metal–metal separation in comparison to that found in **1** [12].

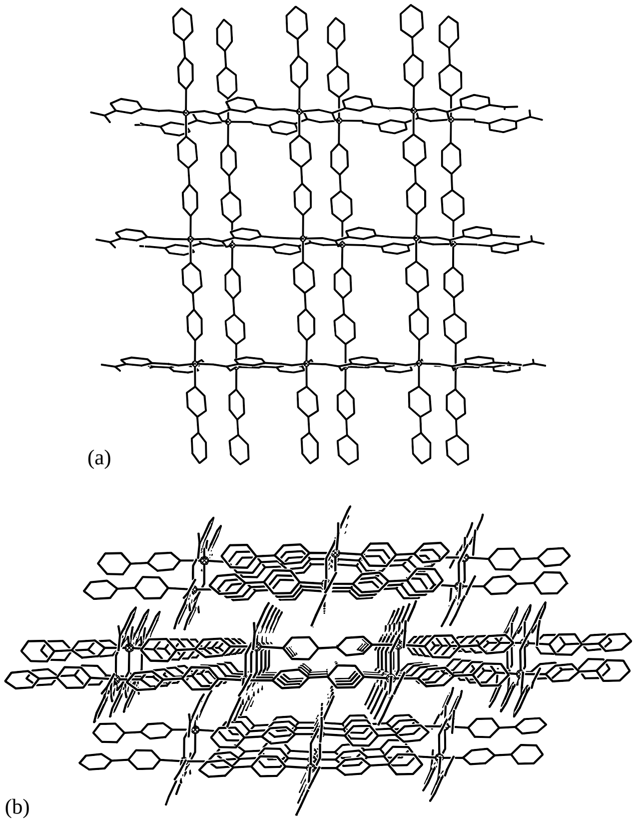


Fig. 2. Perspective views of the two-dimensional framework (a) and the inter-layer π–π stacking mode (b) in **1**.

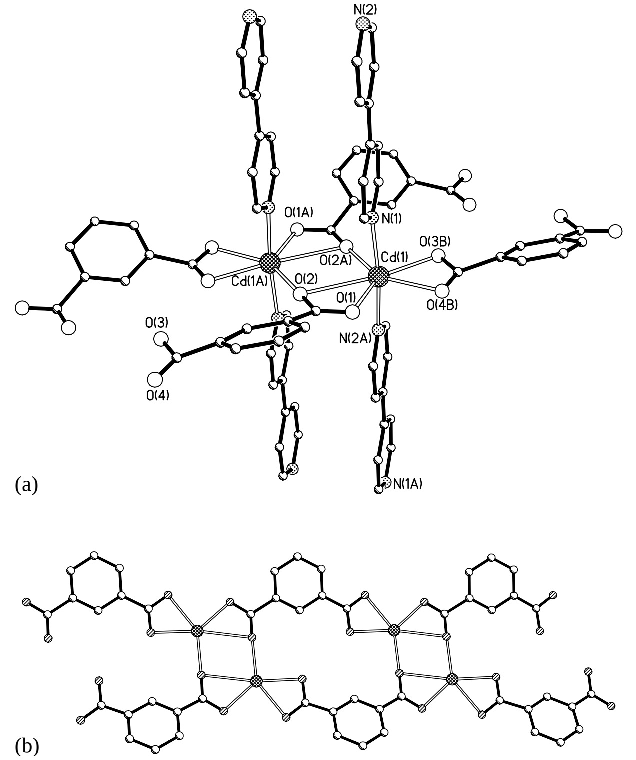


Fig. 3. Perspective views of the coordinaion environment (a) and the $[Cd_2(ip)_2]_n$ chain in **2**.

The axial Cd–N distances [2.328(3) and 2.311(3) Å] are similar to those found in related Cd-4,4′-bipy coordination polymers [13]. The two pyridyl rings of the 4,4′-bipy ligand are approximately coplanar, in contrast to that in **1** being twisted by ca. 50°. The dinuclear Cd_2 unit is inter-connected through ip ligands to generate one-dimensional ribbons with the distance of ca. 10.23 Å between adjacent Cd_2 subunits [Fig. 3(b)], which is slightly greater than that in **1**, and the one-dimensional ribbons are covalently linked by the μ-4,4′-bipy ligands to form an infinite two-dimensional framework with prismatic $[Cd_8(ip)_8(4,4'\text{-bipy})_8]$ building blocks, which have dimensions of ca. $3.97 \times 10.27 \times 11.69$ Å, as illustrated in Fig. 3(b) and Scheme 2.

The molecular packings of **1** and **2** are shown in Figs. 2(b) and 4(b), respectively. Although the space groups are different, there are only minor differences in the dimensional sizes of the coordination polymer grids between **1** and **2**. However, careful examination shows that there are still subtle differences in the packing fashions due to the different orientation of ip rings with respect to the plane of the rectangular grid. In **1** and **2**, adjacent grids are staggered in such a way that they are slipped in one direction by ca. 40%, i.e., in an ABAB fashion. In **1**, the ip rings lying in both sides of the grid

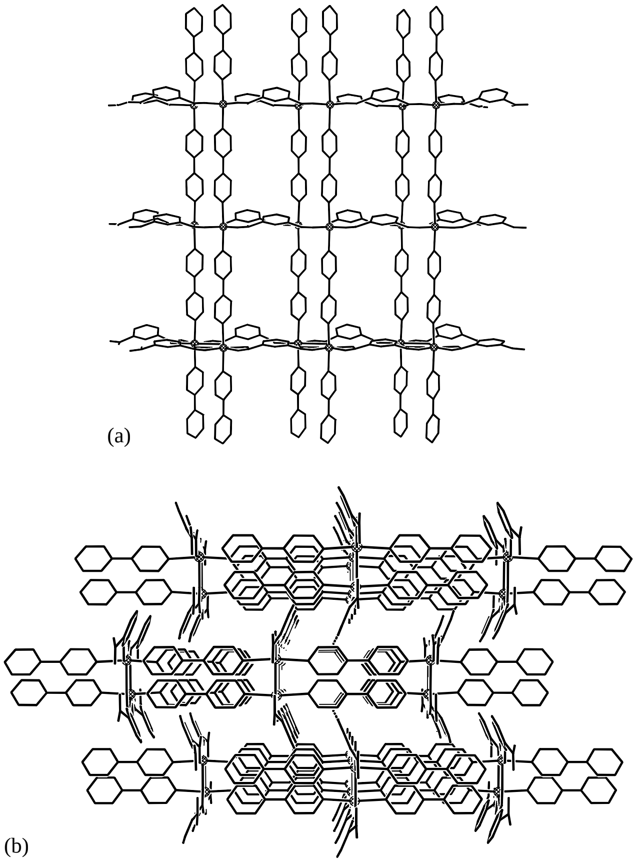


Fig. 4. Perspective views of the two-dimensional framework (a) and the inter-layer π–π stacking mode (b) in **2**.

adopt an orientation that can be regarded as being *trans* to one another, and favor the face-to-face π–π stacking interactions between the ip aromatic groups from adjacent layers, the shortest intermolecular face-to-face aromatic ring separation is ca. 3.73 Å, close to the values of the π–π stacking interactions in pure aromatic compounds [14]. In contrast, the ip rings in **2** lying in both sides of the grid are oriented on the same direction in a *cis* arrangement, and more favor the face-to-face π–π stacking interactions between the ip aromatic groups from adjacent layers, resulting in a shorter intermolecular face-to-face separation of ca. 3.57 Å, which indicate stronger π–π interactions. Presumably, the different orientations of the ip groups may be attributed to the different coordination modes of the carboxylate groups in **1** and **2**.

In summary, we have developed a synthetic route for the construction of rectangular grid coordination polymers using selected mixed organic ligands, which feature the DMUs and unique prismatic octanuclear building blocks.

Acknowledgments

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