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Three interpenetrated frameworks constructed by long flexible N,N'-bipyridyl and dicarboxylate ligands

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Abstract

Three interpenetrated polymeric networks, {[Co(bpp)(OH-BDC)] \cdot H₂O}_n (1) [Ni(bpp)_{1.5}(H₂O)(OH-BDC)]_n (2) and {[Cd(bpp)-(H₂O)(OH-BDC)] \cdot 2H₂O}_n (3), have been prepared by hydrothermal reactions of 1,3-bis(4-pyridyl)propane (bpp), 5-hydroxyisophthalic acid (OH-H₂BDC), with Co(NO₃)₂ \cdot 6H₂O, Ni(NO₃)₂ \cdot 6H₂O and Cd(NO₃)₂ \cdot 4H₂O, respectively. Single-crystal X-ray diffraction analyses reveal that the three compounds all exhibit interpenetrated but entirely different structures. Compound 1 is a fourfold interpenetrated *adamantanoid* structure with water molecules as space fillers, in which bpp adopts a TG conformation (*T* = *trans*, *G* = *gauche*). Compound 2 is an interdigitated structure from the interpenetrated long arms of one-dimensional molecular ladders, while bpp in 2 adopts both TT and TG conformations. Compound 3 is a twofold interpenetrated three-dimensional network from a one-dimensional metal-carboxylate chain bridged by TG conformational bpp. The hydrogen bonding interactions in 1–3 further stabilize the whole structural frameworks and play critical roles in their constructions. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

The rational design and construction of coordination polymers based upon assembly of metal ions and multifunctional organic ligands is an interesting research field. This not only stems from their potential application as functional materials but also from their intriguing structural topologies [1,2]. Among the various architectures, interpenetrated and intertwinded phenomena are frequently observed, especially in *adamantanoid* networks, polythreaded and interdigitated structures [3– 7]. In principle, the exploration of long ligands usually lead to large voids that may further result in interpenetrated or entangled structures [8–10], of which the most

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outstanding examples are the long dipyridyl ligands, such as 1,2-bis(4-pyridyl)ethane (bpe) and 1,2-di(4-pyridyl)ethylene (dpe). Using these ligands [11–17] or their mixture with other organic ligands [18–20], many desirable interpenetrated metal-organic networks have been constructed. However, the assembly of these neutral N-donor ligands with metal ions is heavily dependent on the presence of different counterions [21].

In this regard, our synthetic strategy was to select an analogue of bpe or dpe: 1,3-bis(4-pyridyl)propane (bpp), and introduce benzenedicarboxylic acid (5-hydroxyisophthalic acid, OH-H₂BDC) as an auxiliary ligand into the reaction systems, with the following considerations: (1) Bpp, compared to bpe or dpe, has a longer and more flexible conformation. Accordingly, it possesses TT, TG, GG and GG' conformations (T = trans, G = gauche) owing to the free twist of the propyl group (-CH₂-CH₂-CH₂-). Thereby

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it can adopt different conformations to take part in coordination [21-24]. (2) The aim of combining OH-H₂BDC into the reaction system is to simplify the control and modulation of the final results, because the deprotonated carboxylate groups, which possess rich coordination modes (Scheme 1), may act as anionic groups and afford neutral metal-organic frameworks. (3) The hydroxyl group (-OH) can provide hydrogen bonding interactions with other groups and further stabilize the structures. On the other hand, the architectures from mixed ligands of bpp and dior poly-carboxylate ligands, to our knowledge, are still rare to date [20,25,26], although some metal-organic frameworks from the direct assembly of bpp and metal ions have been investigated [22-24]. Herein, we wish to report the syntheses and characterizations of three interpenetrated coordination polymers, {[Co(bpp)-(OH-BDC)] · H₂O}_n (1), $[Ni(bpp)_{1,5}(H_2O)(OH-BDC)]_n$ (2) and { $[Cd(bpp)(H_2O)(OH-BDC)] \cdot 2H_2O$ }, assembly from bpp, OH-H₂BDC with Co^{II}, Ni^{II} and Cd^{II} ions, respectively. All of the three compounds display interpenetrated structures. Exo-bidentate bpp in 1 and 3 adopts a TG conformation, while bpp in 2 acts as a terminal and exo-bidentate ligand with TT and TG conformations, respectively.



Scheme 1. The coordination modes of OH-BDC in compounds 1-3.

2. Experimental

2.1. Materials and physical measures

1,3-bis(4-pyridyl)propane and 5-hydroxyisophthalic acid were purchased from Aldrich and used without further purification, all the other reagents were commercially available and used as purchased. Thermal analyses were performed using a TGA/SDTA851 instrument with a heating rate of 15 °C/min in a nitrogen stream. IR spectra as KBr disks were recorded on a Magna 750 FT–IR spectrophotometer. Elementary analyses were carried out by the elementary analysis group of this institute on an Elementary Vario ELIII analyzer.

2.2. Syntheses of the compounds

2.2.1. Preparation of $\{[Co(bpp)(OH-BDC)] \cdot H_2O\}_n$ (1)

A mixture of Co(NO₃)₂ · 6H₂O (0.058 g, 0.20 mmol), 5-hydroxyisophthalic acid (0.032 g, 0.20 mmol), 1,3bis(4-pyridyl)propane (0.040 g, 0.20 mmol) and NaOH (0.016 g, 0.40 mmol) in distilled water (18 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated to 165 °C for 96 h. After cooling to room temperature over 24 h, cube-shaped red crystals of **1** were obtained. Yield: 41%. Elementary *Anal.* Calc. for C₂₁H₂₀CoN₂O₆ (455.32): C, 55.40; H, 4.43; N, 6.15. Found: C, 55.38; H, 4.51; N, 6.11%. IR (KBr, cm⁻¹): 3400 (m), 2927 (w), 1615 (s), 1575 (vs), 1401 (vs), 1373 (s), 1276 (s), 1018 (m), 785 (s), 723 (s), 519 (m).

2.2.2. Preparation of $[Ni(bpp)_{1.5}(H_2O)(OH-BDC)]_n$ (2)

A mixture of Ni(NO₃)₂ · 6H₂O (0.073 g, 0.25 mmol), 5-hydroxyisophthalic acid (0.045 g, 0.25 mmol), 1,3bis(4-pyridyl)propane (0.050 g, 0.25 mmol) and NaOH (0.020 g, 0.50 mmol) in distilled water (18 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated to 170 °C for 96 h. After cooling to room temperature over 24 h, block green crystals of **2** were obtained. Yield: 64%. Elementary *Anal*. Calc. for C_{27.5}H₂₇-NiN₃O₆ (554.23): C, 59.60; H, 4.91; N, 7.58. Found: C, 59.62; H, 5.02; N, 7.49%. IR (KBr, cm⁻¹): 3354 (w), 1616 (s), 1562 (vs), 1452 (s), 1412 (vs), 1357 (vs), 1277 (m), 1068 (m), 800 (s), 727 (s), 523 (m).

2.2.3. Preparation of $\{[Cd(bpp)(H_2O)(OH-BDC)] \cdot 2H_2O\}_n$ (3)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.077g, 0.25 mmol), 5-hydroxyisophthalic acid (0.045 g, 0.25 mmol), 1,3bis(4-pyridyl)propane (0.050 g, 0.25 mmol) and NaOH (0.020 g, 0.50 mmol) in distilled water (18 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated to 170 °C for 96 h. After cooling to room temperature over 24 h, block yellow crystals of **3** were obtained. Yield: 45%. Elementary *Anal.* Calc. for $C_{21}H_{24}CdN_2O_8$ (544.82): C, 46.30; H, 4.44; N, 5.14. Found: C, 46.31; H, 4.39; N, 5.18%. IR (KBr, cm⁻¹): 3385 (w), 1616 (s), 1554 (vs), 1427 (s), 1377 (vs), 1277 (m), 1227 (m), 1016 (m), 978 (w), 779 (s), 737 (s), 575 (m).

2.2.4. X-ray crystallographic study

Measurement of 1 was conducted on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Reflections (14335) were collected at -100 °C, of which 4327 reflections were unique [27]. Intensity data for 2 and 3 were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at room temperature, the empirical absorption corrections were applied by using the SADABS program [28]. The structures for 1-3 were solved by direct methods [29] and refined on F^2 by full-matrix leastsquares using the SHELXL-97 program package [30]. The positions of H atoms were generated geometrically (C-H bond fixed at 0.96 Å), assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms before the final cycle of refinement. For 2, the carbon atom (C15) is handled as disordered at two posi-

Table 1 Crystallographic data for compounds 1–3 tions each with an occupancy of 50%. Crystal data and structure determination summaries for 1-3 are summarized in Table 1, selected bonds and angles in Table 2.

3. Results and discussion

3.1. Syntheses and characterizations

Compounds 1–3 were synthesized through the hydrothermal reactions of bpp, OH-H₂BDC with Co^{II}, Ni^{II} and Cd^{II} salts, respectively. Similar to the previous reports by us and some other groups, the -OH group of HO-H₂BDC is not involved in coordination to the transition metal ions and only serves as a donor for hydrogen bonds to stabilize the structures of 1-3 (see below), however, the -OH group as an electron-donating group may influence the self-assembly process although the reaction mechanism still remains unclear, because the expected results were not obtained when using misophthalic acid (H₂BDC) instead of HO-H₂BDC under the same hydrothermal condition. The IR spectra of the three compounds exhibit strong characteristic vibrational bands of the carboxylate groups. For 1, the characteristic bands of the carboxylate groups are shown at 1575 cm^{-1} for the antisymmetric stretching band and

	1	2	3
Empirical formula	C ₂₁ H ₂₀ CoN ₂ O ₆	C _{27.5} H ₂₇ N ₃ NiO ₆	C ₂₁ H ₂₄ CdN ₂ O ₈
Formula weight	455.32	554.23	544.82
<i>T</i> (K)	173(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	C2/c
a (Å)	10.96(5)	10.1547(2)	16.6695(11)
b (Å)	10.90(3)	17.8222(5)	17.1742(11)
<i>c</i> (Å)	16.29(5)	14.2077(3)	19.0262(12)
β (°)	103.806(14)	91.89	108.028(1)
$V(Å^3)$	1891(11)	2569.91(10)	5179.5(6)
Ζ	4	4	8
$D_{\text{calc}} (\text{Mg m}^{-3})$	1.599	1.432	1.397
Absorption coefficient (mm ⁻¹)	0.952	0.803	0.886
<i>F</i> (000)	940	1156	2208
Crystal size (mm)	$0.15 \times 0.10 \times 0.05$	$0.32 \times 0.26 \times 0.18$	$0.48 \times 0.28 \times 0.20$
θ Range for data collection (°)	2.03-27.48	1.83-25.08	3.15-25.02
Index ranges	$-14 \leqslant h \leqslant 14$,	$-12 \leqslant h \leqslant 11$,	$-7 \leqslant h \leqslant 19$,
-	$-14 \leqslant k \leqslant 14$,	$-10 \leq k \leq 21,$	$-20 \leq k \leq 17,$
	$-21 \leqslant l \leqslant 14$	$-16 \leq l \leq 11$	$-22 \leqslant l \leqslant 20$
Reflections collected	14335	7633	7460
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data $[I > 2\sigma(I)]$ /parameters	3447/279	3937/347	3295/298
Goodness-of-fit on F^2	1.131	1.115	1.325
R_1 indices $(I \ge 2\sigma(I))^a$	0.0563	0.0432	0.0587
wR_2 indices $(I \ge 2\sigma(I))^{b}$	0.1131	0.0980	0.1704
Largest difference peak and hole ($e \text{ Å}^{-3}$)	0.651 and -0.641	0.296 and -0.299	0.922 and -0.452

 $_{1}^{a} R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$

^b
$$wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$$
.

- - 1/2

Table 2

Selected bond lengths (Å) and angles (°) of compounds $1\!\!-\!\!3$

Compound 1	
Co-O(1)	1.986(4)
Co-O(3B)	1.978(6)
Co-N(2A)	2.047(4)
Co–N(1)	2.048(9)
O(3B)-Co-O(1)	100.2(2)
O(3B)-Co-N(2A)	118.0(2)
O(1)-Co-N(2A)	110.8(2)
O(3B)-Co-N(1)	112.1(3)
O(1)-Co-N(1)	100.0(2)
N(2A)-Co- $N(1)$	113.3(1)
Compound 2	
N1-O(1)	2.139(2)
N1-O(4B)	2.033(2)
$N_1 - N(1)$	2.103(3)
NI-O(2)	2.115(2)
Ni N(2)	2.000(2)
111-11(2)	2.105(5)
O(4B)–Ni–OW	94.1(8)
O(4B)-Ni-N(1)	91.4(9)
OW–Ni–N(1)	93.7(1)
O(4B)-Ni-N(2)	87.6(9)
OW–Ni–N(2)	88.6(9)
N(1)-Ni-N(2)	177.6(1)
O(4B)-Ni-O(2)	162.8(8)
OW–Ni–O(2)	102.4(8)
$N(1) - N_1 - O(2)$	92.4(9)
N(2)-N1-O(2)	87.9(9)
O(4B)-Ni=O(1)	100.9(8)
OW-NI=O(1) N(1) N: O(1)	163.5(8)
N(1)-NI=O(1) N(2) $Ni=O(1)$	92.7(9)
N(2)-NI=O(1)	83.4(9) 63.2(7)
O(2)-NI- $O(1)$	02.2(7)
Compound 3	
Cd–O(4A)	2.284(5)
Cd-N(2B)	2.324(6)
Cd-N(1)	2.341(5)
Cd-O(1)	2.355(5)
Cd–OW1	2.379(6)
Cd-O(2)	2.516(5)
Cd–O(3A)	2.614(5)
O(4A)CdN(2B)	86.4(2)
O(4A)-Cd-N(1)	98.1(2)
N(2B)-Cd-N(1)	96.4(2)
O(4A)-Cd-O(1)	135.5(2)
N(2B)-Cd-O(1)	138.0(2)
N(1)-Cd-O(1)	83.1(2)
O(4A)-Cd-OW1	84.8(2)
N(2B)-Cd-OW1	95.0(2)
N(1)-Cd-OW1	168.5(2)
O(1)-Cd-OW1	87.0(2)
O(4A)-Cd-O(2)	163.3(2)
N(2B)-Cd-O(2)	85.4(2)
N(1)-Cd-O(2)	97.2(2)
O(1)-Cd-O(2)	53.4(2)
OW1–Cd–O(2)	81.5(2)
O(4A)–Cd–O(3A)	52.1(2)
N(2B)-Cd-O(3A)	137.6(2)
N(1)-Cd-O(3A)	83.7(2)
O(1)-Cd- $O(3A)$	84.2(2)
OW1-Cd-O(3A)	89.4(2)
O(2)-Cd-O(3A)	136.8(2)

Symmetry code: for **1** (A) x + 1/2, -y + 5/2, z - 1/2; (B) x + 1/2, -y + 3/2, z + 1/2. **2** (B) x + 1, y, z. **3** (A) x, -y + 1, z - 1/2; (B) x - 1/2, y + 1/2, z.

1401 cm⁻¹ for the symmetric stretching band. The separation (Δ) between $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ is 174 cm⁻¹. For **2**, one antisymmetric stretching band

(1562 cm⁻¹) and two symmetric stretching bands (1412 and 1357 cm⁻¹) are exhibited, the Δ values are 150 and 205 cm⁻¹, respectively. For **3**, the typical antisymmetric and symmetric stretching bands of carboxylate groups are at 1564 and 1387 cm⁻¹, with a Δ value ca. 177 cm⁻¹. The results are consistent with the different coordination modes of the carboxylate groups in the three compounds, one coordination mode in **1** and **3**, two coordination modes in **2** (Scheme 1) [31].

To study the stability of the three compounds, thermogravimetric analyses (TGA) were performed on polycrystalline samples in nitrogen atmosphere. For 1, the weight loss of 4.08% from 160 to 279 °C is equivalent to the loss of one free water molecule per formula unit (ca. 3.96%), indicating the presence of hydrogen bonding interactions. After 317 °C, the decomposition of the framework starts. For 2, the thermogravimetric analysis shows that there is no weight loss up to 360 °C, where the entirely decomposition of 2 starts. For 3, the weight loss of 6.78% (calculated: 6.61%) from 45 to 134 °C, is attributed to the loss of two free water molecules per formula unit. Complete decomposition of the framework starts after 415 °C.

3.1.1. Crystal structure of compound 1

Single-crystal X-ray diffraction analysis reveals that **1** is a fourfold interpenetrated *adamantanoid* structure. As shown in Fig. 1, each Co^{II} center is in a distorted tetrahedral geometry, which is seldom displayed in cobalt-carboxylate compounds [32]. Two nitrogen atoms from different bpp ligands and two monodentate carboxylate oxygen atoms from different OH-BDC ligands coordinate to the metal center. The average distances of Co–N and Co–O are 1.986(4) and 2.048(1) Å, respectively. OH-BDC acts as a bis-monodentate ligand to link the Co^{II} centers (Scheme 1(a)). The hydroxyl group (–OH) does not take part in coordination, but it is involved in a



Fig. 1. ORTEP drawing of the coordination environment around Co^{II} in 1 with the thermal ellipsoids at the 30% probability level.

strong hydrogen bonding interaction with a free water molecule (O5–H···OW, 2.692 Å), which is consistent with the result of the TGA. Bpp in a TG conformation bridges the Co^{II} centers, the dihedral angle between the two pyridine rings is 80.6°. Thus, ten Co^{II} centers are connected by twelve bridging ligands, namely six bpp and six OH-BDC, generating a adamantanoid cage, which is further extended into a three-dimensional structure (Fig. 2). The separations of the adjacent $Co \cdot \cdot \cdot Co$ atoms bridged by bpp and OH-BDC are 12.657 and 9.711 Å, respectively. The long spacers between coordination sites result in large cavities within the adamantanoid cages. In order to minimize the big void cavities and stabilize the framework by nature, the potential voids are effectively filled via mutual interpenetration of three independent equivalent frameworks, generating a fourfold interpenetrated adamantanoid architecture (Fig. 3). Free water molecules are accommodated inside the framework and further shrink the void spaces. Another isomorphous complex, {[Zn(bpp)(OH-BDC)] $(H_2O)_{n}$, has been obtained and published by us in another report [26].

3.1.2. Crystal structure of compound 2

Compound **2** is a polythreaded structure constructed through interpenetration of long arms of neutral onedimensional molecular ladders. As shown in Fig. 4, each Ni^{II} center is in a highly distorted octahedral coordination geometry. Four oxygen atoms from one water mol-



Fig. 2. (a) View of a single *adamantanoid* cage. (b) Perspective view of the three-dimensional *adamantanoid* structure in **1**. For clarity only the Co^{II} centers are shown, with the bonds representing the bridging ligands.



Fig. 3. Perspective view of the fourfold interpenetrated *adamantanoid* network in **1** with bridging ligands and water molecules omitted for clarity.



Fig. 4. ORTEP drawing of the coordination environment around Ni^{II} in **2** with the thermal ellipsoids at the 30% probability level.

ecule, one mono- and one chelating carboxylate groups of different OH-BDC ligands comprise the equatorial plane. Two nitrogen atoms from different conformational bpp ligands occupy the axial positions with the N1–Ni–N2 bond angle being 177.6(1)°. The deviation of the Ni^{II} center from the O₄ equatorial mean plane of the octahedron toward the apical nitrogen atom is 0.232 Å. The Ni–N and Ni–O bond distances are all within the normal ranges. OH-BDC behaves as a bridge through its mono- and chelating carboxylate groups to link different metal centers (Scheme 1(b)). Likewise, the hydroxyl group (–OH) does not participate in coordination, it is involved in a hydrogen bonding interaction with the coordinated water molecule [OW–H···O5ⁱ 2.803 Å, (i) x + 1/2, -y + 1/2, z + 1/2]. The most interesting feature of this structure is that there are two types of conformational bpp ligands with different coordination modes [22]. One with the two pyridyl rings being parallel adopts a TG conformation through bridging two Ni^{II} centers. The other possesses a TT conformation and serves as a terminal ligand, the dihedral angle between the two pyridyl rings is 79.6°. As shown in Fig. 5, the TG conformational bpp ligand and OH-BDC engage neighboring Ni^{II} centers into a one-dimensional neutral molecular ladder containing $[Ni_4(bpp)_2(OH-BDC)_2]$ rectangles $(14.023 \times$ 10.155 \AA^2). The TT conformational bpp ligand behaves as a lateral arm of the ladder through its one pyridyl ring coordinating to a Ni^{II} center, which prevents the formation of an extended motif. It is noteworthy that due to the absence of large solvent or guest molecules to fill the void space in the molecular ladder during assembly process, the terminal TT conformational bpp as long arms are threaded into $[Ni_4(bpp)_2(OH-BDC)_2]$ rectangles of an adjacent molecular ladder. Each rectangle is oppositely penetrated by two lateral arms from different molecular ladders, but there are no $\pi \cdots \pi$ interactions between the two mutual parallel and stagger pyridyl rings (Fig. 6). Such penetration not only effectively fills into the void space of the rectangles, but also results in a polythreaded polymeric structure. The hydrogen bonding interactions between coordinated water molecules and uncoordinated carboxylate oxygen atoms of OH-BDC [OW-H···O3ⁱⁱ 2.589 Å; symmetry code: (ii) x + 1, y, z] as well as the above-mentioned between the coordinated water molecules and hydroxyl



Fig. 5. Space-filling representation of a one-dimensional neutral molecular ladder with long arms.



Fig. 6. Perspective view of the polythreaded polymeric structure in **2**, with the bonds representing OH-BDC and exo-bidentate bpp.

groups of OH-BDC further stabilize the whole structural framework. Although some polythreaded architectures from molecular ladders with both inner rungs and lateral arms have been reported [33–35], the structural motif constructed by bpp with different conformations and a dicarboxylate ligand is still unprecedented.

3.1.3. Crystal structure of compound 3

Compound 3 is a twofold interpenetrated threedimensional framework with free water molecules as space fillers. As shown in Fig. 7, each Cd^{II} center is in a distorted pentagonal bipyramidal geometry. Two chelating carboxylate groups from different OH-BDC ligands and one pyridyl nitrogen atom from a bpp ligand comprise the equatorial basal plane, one water molecule and one pyridyl nitrogen atom from the other bpp ligand occupy the apical sites [OW1–Cd–N1 $168.5(2)^{\circ}$]. The Cd^{II} center is displaced about 0.221 Å



Fig. 7. ORTEP drawing of the coordination environment around Cd^{II} in **3** with the thermal ellipsoids at the 30% probability level.

from the equatorial plane towards the axial donor atom. The Cd-O and Cd-N bond distances are in the range 2.284(5)-2.614(5) Å and 2.324(6)-2.341(5) Å, respectively. Different from 1 and 2, OH-BDC acts as a chelating bis-bidentate ligand (Scheme 1(c)) and bridges different Cd^{II} centers to give rise to a one-dimensional metal-carboxylate chain (Fig. 8). Exo-bidentate bpp adopts a TG conformation with the dihedral angle between two pyridyl rings being 79.4°, which is similar to that in 1. Thus bpp links the adjacent one-dimensional chain into a three-dimensional framework with large channels (Fig. 9). The $Cd \cdots Cd$ distances bridged by bpp and OH-BDC are 11.967 and 10.117 Å, respectively. In order to shrink the void space and stabilize the final product, the three-dimensional network is interpenetrated into itself to generate an interwining network (Fig. 10). Free water molecules are accommodated in the residual empties and further stabilize the structural framework through extensive hydrogen bonding interactions between coordinated water molecules and carboxylate oxygen atoms of OH-BDC [OW1-H···O1¹ 2.679 Å, (i) -x + 1, -y + 1, -z + 1], between coordi-



Fig. 8. View of a one-dimensional metal-carboxylate chain.



Fig. 9. Perspective view of the three-dimensional network possessing large channels along the c-axis in **3**.



Fig. 10. Perspective view of the twofold interpenetrated three-dimensional network with free water molecules along the c-axis in **3**.

nated water molecules and free water molecules $[OW1-H\cdots OW3^{ii} 2.856 \text{ Å}, (ii) -x + 1, y, -z + 3/2]$, between free water molecules and carboxylate oxygen atoms of OH-BDC $[OW2-H\cdots O2^{ii} 2.900 \text{ Å}]$, between free water molecules and free water molecules $[OW4-H\cdots OW5 2.116 \text{ Å}]$, as well as between hydroxyl groups of OH-BDC and free water molecules $[O5-H\cdots OW5 2.700 \text{ Å}]$.

4. Conclusions

The hydrothermal reactions of 1,3-bis(4-pyridyl)propane (bpp), 5-hydroxyisophthalic acid (OH-H₂BDC) and different metal salts produced three interpenetrated or polythreaded coordination polymers. The long flexible bpp adopts different conformations to link the metal ions. Owing to the existence of large voids from long metal-metal distances bridged by bpp and OH-BDC, all of the three compounds exhibit interpenetrated structures. This research also demonstrated that the presence of anionic groups (carboxylate groups) can simplify the design and construction of the compounds.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited in the Cambridge Crystallographic Data Center as supplementary publication, CCDC Nos. 240643–240645 for complexes **1–3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internet) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). or www at http://www.ccdc.cam.ac.uk].

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References

- R. Robson, B.F. Abrahams, S.R. Batten, R.W. Gable, B.F. Hoskins, J. Liu, Supramolecular Architecture, American Chemical Society, Washington, DC, 1992, p. 256.
- [2] M. Moulton, L.P. Wu, T. Kuroda-Sowa, Adv. Inorg. Chem. 46 (1999) 173.
- [3] M.J. Zaworotko, Chem. Soc. Rev. (1994) 283.
- [4] O.R. Evans, W.B. Lin, Acc. Chem. Res. 35 (2002) 511.
- [5] K. Biradha, M. Fujita, Chem. Commun. (2002) 1866.
- [6] M. Kondo, T. Joshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, Angew. Chem. Int. Ed. Engl. 36 (1997) 1844.
- [7] K.N. Power, T.L. Hennigar, M.J. Zaworotko, New J. Chem. (1998) 177.
- [8] S.R. Batten, R. Robson, Angew. Chem. Int. Ed. 37 (1998) 1460.
- [9] X.L. Wang, C. Qin, E.B. Wang, L. Xu, Z.M. Su, C.W. Hu, Angew. Chem. Int. Ed. 43 (2004) 5036.
- [10] F.A. Almeida Paz, Y.Z. Khimyak, A.D. Bond, J. Rocha, J. Klinowski, Eur. J. Inorg. Chem. (2002) 2823.
- [11] A.J. Blake, N.R. Champness, S.S.M. Chung, W.S. Li, M. Schröder, Chem. Commun. (1997) 1005.
- [12] D. Hagrman, R.P. Hammond, R. Haushalter, J. Zubieta, Chem. Mater. 10 (1998) 2091.
- [13] S.R. Batten, A.R. Harris, P. Jensen, K.S. Murray, A. Ziebell, J. Chem. Soc., Dalton Tran. (2000) 3829.

- [14] J.M. Knaust, S. Lopez, S.W. Keller, Inorg. Chim. Acta 324 (2002) 81.
- [15] L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, Chem. Commun. (2000) 1319.
- [16] C.V. Krishnamohan Sharma, R.D. Rogers, Chem. Commun. (1999) 83.
- [17] M. John Plater, M.R.S.J. Foreman, R.A. Howie, J.M.S. Skakle, Inorg. Chim. Acta 318 (2000) 175.
- [18] V. Niel, M.C. Muòoz, A.B. Gaspar, A. Galet, G. Levchenko, J.A. Real, Chem. Eur. J. 8 (2002) 2446.
- [19] J.Y. Lu, A.M. Babb, Inorg. Chem. 40 (2001) 3261.
- [20] J. Luo, M. Hong, R. Wang, R. Cao, L. Han, Z. Lin, Eur. J. Inorg. Chem. (2003) 2705.
- [21] S.R. Batten, J.C. Jeffery, M.D. Ward, Inorg. Chim. Acta 292 (1999) 231.
- [22] M.V. Marinho, M.I. Yoshida, K.J. Guedes, K. Krambrock, A.J. Bortoluzzi, M. Hörner, F.C. Machado, W.M. Teles, Inorg. Chem. 43 (2004) 1539.
- [23] L. Carlucci, G. Ciani, M. Moret, D.M. Proserpio, S. Rizzato, Angew. Chem. Int. Ed. 39 (2000) 1506.
- [24] M.J. Plater, M.R.S.J. Foreman, T. Gelbrich, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (2000) 1995.
- [25] Z.Y. Fu, S.M. Hu, J.C. Dai, J.J. Zhang, X.T. Wu, Eur. J. Inorg. Chem. (2003) 2670.
- [26] X.J. Li, R. Cao, D.F. Sun, W.H. Bi, Y.Q. Wang, X. Li, M.C. Hong, Cryst. Growth Des. 4 (2004) 775.
- [27] Crystalclear: ver 1.36; Molecular Structure Corporation; Rigaku, MSC/SSI, 491, South Orem Blvd, Orem, UT84058, 2001.
- [28] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, 1996.
- [29] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, 1997.
- [30] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, 1997.
- [31] H.X. Zhang, B.S. Kang, A.W. Xu, Z.N. Chen, Z.Y. Zhou, A.S.C. Chan, K.B. Yu, C. Ren, J. Chem. Soc., Dalton Trans. (2001) 2559.
- [32] E. Lee, Y. Kim, D.Y. Jung, Inorg. Chem. 41 (2002) 501.
- [33] M.L. Tong, H.J. Chen, X.M. Chen, Inorg. Chem. 39 (2000) 2235.
- [34] M.A. Withersby, A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M. Schröder, Angew. Chem. Int. Ed. 36 (1997) 2627.
- [35] O.S. Jung, S.H. Park, K.M. Kim, H.G. Jang, Inorg. Chem. 37 (1998) 5781.