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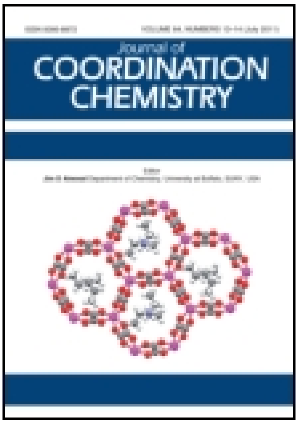

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Synthesis, characterization, and crystal structures of two coordination polymers from 3,5-bis(pyridin-4-ylmethyl) aminobenzoic acid

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Synthesis, characterization, and crystal structures of two coordination polymers from 3,5-bis(pyridin-4-ylmethyl) aminobenzoic acid

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Aqueous medium reactions of transition metal salts with HL under hydrothermal conditions at 90°C led to two new coordination polymers, $[M(L)_2(H_2O)_2] \cdot H_2O$ [$M = Co$(**1**) and Mn(**2**); HL = 3,5-bis(pyridin-4-ylmethyl)aminobenzoic acid]. HL contains both flexible N-donor groups [(pyridin-4-ylmethyl)amino] and carboxylate. The flexibility of (pyridin-4-ylmethyl) amino endows HL the ability to adopt varied conformations and coordination modes. Due to the presence of nitrogen and oxygen of HL and water in the reaction system, hydrogen-bonding interactions are available to assemble donor and acceptor building blocks. The two complexes are structurally similar to L^- doubly interconnecting M(II) to form 1-D chains. The extension of the 1-D chain through hydrogen-bonding forms fascinating 3-D supramolecular frameworks. FT-IR spectroscopy and thermal stability have been studied. The two compounds represent the first complexes containing 3,5-bis(pyridin-4-ylmethyl)amino benzoate.

Keywords: Cobalt; Manganese; Flexibility; Metal-organic frameworks

1. Introduction

Interest has been focused on crystal engineering of metal-organic frameworks (MOFs) due to their intriguing architectures and potential applications in heterogeneous catalysis, ion-recognition, nonlinear optics, and molecular adsorption [1]. Open frameworks have been devised and discussed in some comprehensive reviews [2]. The most feasible strategy for the design and construction of MOFs is to select suitable polyfunctional ligands as building blocks that enable the control of the variety of structural motifs [3]. Among popularly employed ligands, rigid or flexible N-, O-containing multidentate donors usually containing carboxylate- or pyridyl-groups are the building blocks [4]. Compared with rigid ligands, flexible ligands, such as 1,2,3,4,5,6-cyclohexanehexacarboxylic acid, bis(2-methylimidazo-1-yl)methane, and 2-(1H-imidazole-1-yl)acetic acid [5], may adopt varied conformations and coordination modes according to the different geometric requirements of the metal ions and offer MOFs with structural diversity. Apart from coordinative bonding as the primary

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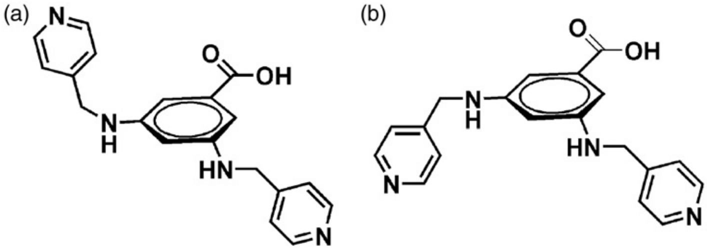
interaction to sustain MOFs, the use of non-covalent interactions such as hydrogen-bonding to arrange molecular building blocks has also evolved as a strategy for controlled assembly of extended supramolecular networks [6].

Multidentate ligands with arene core and N-donor groups, such as (pyridin-4-ylmethyl)amino, may be preferred building blocks. Recently, we started a systematic study on metal(II) coordination with HL ligand [HL = 3,5-bis(pyridin-4-ylmethyl)aminobenzoic acid] to analyze the influence that intrinsic features of the ligand can exert on the structure and functional properties of resultant complexes. Compared with other N- or O-donors, HL possesses several distinctive features. First, the asymmetrical tripodal ligand contains both N- and O-donors [7]; second, in contrast to rigid aromatic carboxylic acids, HL may exhibit different coordination conformations such as *trans* and *cis*, based on the plane of benzene because of the flexibility of (pyridin-4-ylmethyl)amino groups (scheme 1). Flexible arms endow HL a peculiar characteristic in forming the MOFs with interesting architectures [8]. Third, hydrogen bonds may be available to play a role in the resulting supramolecular networks, critical in constructing and stabilizing supramolecular networks [9]. In this contribution we describe our preliminary research of the preparation, crystallography, and properties of two complexes with HL, $\{[Co(L)_2(H_2O)_2]\cdot H_2O$ (**1**) and $[Mn(L)_2(H_2O)_2]\cdot H_2O$ (**2**)$\}$ to explore coordination behavior of HL and prepare materials with interesting properties. The two complexes are structurally similar to L^- doubly interconnecting M(II) centers to form a 1-D chain. Hydrogen bonds array the complexes into 3-D supramolecular frameworks. Coordinated and uncoordinated (pyridin-4-ylmethyl)amino groups coexist in the complexes. The uncoordinated ones own a higher degree of freedom, helping to assemble donors and acceptors to form intermolecular N–H $\cdots$ O and O–H $\cdots$ N hydrogen bonds. Due to the existence of uncoordinated (pyridin-4-ylmethyl)amino groups, the compounds may be utilized as Lewis bases in heterogeneous catalysis [10]. The two compounds represent the first examples of complexes containing 3,5-bis(pyridin-4-ylmethyl)amino benzoate.

2. Experimental

2.1. *Materials and characterization*

Commercially available chemicals and solvents are of reagent grade and used as received. HL was readily prepared according to the reported literature [11]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C Elemental analyzer.



Scheme 1. Different conformations of HL: (a) the *trans* and (b) *cis* based on the plane of benzene.

Thermogravimetric analysis (TGA) was carried out on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10°C min^{-1} from 30°C to 800°C. FT-IR spectra were recorded from 400 to 4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets.

2.2. *Synthesis*

2.2.1. Synthesis of $[Co(L)_2(H_2O)_2] \cdot H_2O$ (1). A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (29.8 mg, 0.1 mmol), HL (66.8 mg, 0.2 mmol), and NaOH (8.0 mg, 0.2 mmol) in 12 mL of water was stirred for 10 min in air and then transferred to a 16 mL Teflon-lined stainless steel container and heated at 90°C for 3 days. After the mixture cooled to room temperature, **1** was isolated from the mixture in light brown block crystalline form by filtration and washed by water and ethanol several times with a yield of 48.34 mg (0.062 mmol, 62% based on HL). Anal. Calcd for $C_{38}H_{40}CoN_8O_7$ (%): C, 58.54; H, 5.17; N, 14.37. Found (%): C, 58.26; H, 5.42; N, 14.59.

2.2.2. Synthesis of $[Mn(L)_2(H_2O)_2] \cdot H_2O$ (2). Complex **2** was synthesized by the same procedure as for **1**, except that $MnCl_2 \cdot 4H_2O$ (19.79 mg, 0.1 mmol) was used instead of $Co(NO_3)_2 \cdot 6H_2O$ as the starting material. Light brown block crystals of **2** were isolated by filtration and washed by water and ethanol several times with a yield of 20.14 mg (0.055 mmol, 55% based on HL). Anal. Calcd for $C_{38}H_{40}MnN_8O_7$ (%): C, 58.84; H, 5.20; N, 14.45. Found (%): C, 58.69; H, 5.46; N, 14.19.

2.3. *X-ray crystallography*

Crystallographic data collections for **1** and **2** were carried out on a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated (Mo-Kα) radiation ($\lambda = 0.71073$ Å) at 293(2) K using ω scan modes at different fixed positions of the phi angle. The diffraction data were integrated using SAINT, which was also used for intensity corrections for the Lorentz and polarization effects. Multi-scan absorption correction was applied using SADABS. The structures of **1** and **2** were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 crystallographic software package [12]. Hydrogens except the ones in (–NH–) of (pyridin-4-ylmethyl)amino group and water molecules in **1** and **2** were added geometrically and allowed to ride on their parents. The hydrogens in (–NH–) and water were located from Fourier maps directly. The contribution of these hydrogens was included in the structure factor calculations. The crystallographic details and selected bond lengths and angles are provided in tables 1 and 2, respectively.

3. Results and discussion

3.1. *Preparation and FT-IR spectroscopy*

The hydrothermal reactions at 90°C of stoichiometric amounts of corresponding metal salts with HL in the presence of NaOH provided single crystals of **1** and **2** analyzed as $[M(L)_2(H_2O)_2] \cdot H_2O$ [M = Co(1) and Mn(2)], which are stable in air.

Table 1. Crystallographic data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{38}H_{40}CoN_8O_7$	$C_{38}H_{40}MnN_8O_7$
Formula weight	779.71	775.72
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	10.8203(9)	10.842(5)
b	9.3214(8)	9.320(5)
c	18.1877(16)	18.308(5)
β	92.324(1)	92.452(5)
Volume (Å^3), Z	1832.9(3), 2	1848.3(14), 2
Calculated density (Mg m^{-3})	1.413	1.394
Absorption coefficient	0.530	0.418
$F(000)$	720	810
θ range for data collection (°)	1.88–28.01	2.23–25.00
Limiting indices	$-14 \leq h \leq 13$; $-9 \leq k \leq 12$; $-23 \leq l \leq 23$	$-12 \leq h \leq 11$; $-11 \leq k \leq 10$; $-21 \leq l \leq 21$
Reflections collected/unique	11,149/4346 ($R_{\mathrm{int}} = 0.0660$)	8779/3173 ($R_{\mathrm{int}} = 0.0324$)
Data/restraints/parameters	4346/4/250	3173/2/238
Completeness (%)	98.3	98.0
Goodness-of-fit on F^2	0.978	1.264
R_1/wR_2 [$I > 2\sigma(I)$]	0.0438/0.1140	0.0890/0.1697
R_1/wR_2 [all data]	0.0627/0.1239	0.0999/0.1744
Largest difference peak and hole (e Å^{-3})	0.544 and −0.558	0.545 and −0.390

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

Complex **1**			
Co1–O1	2.1026(14)	Co1–O1W	2.1210(14)
Co1–N1(#2)	2.1584(17)		
O1–Co1–O1W	91.21(6)	O1–Co1–N1(#3)	90.49(6)
O1–Co1–O1W(#1)	88.79(6)	O1–Co1–N1(#2)	89.51(6)
O1W–Co1–N1(#3)	89.83(6)	O1(#1)–Co1–O1W	88.79(6)
O1W–Co1–N1(#2)	90.18(6)	O1(#1)–Co1–N1(#3)	89.51(6)
O1W(#1)–Co1–N1(#3)	90.18(6)	O1(#1)–Co1–O1W(#1)	91.21(6)
O1(#1)–Co1–N1(#2)	90.49(6)	O1W(#1)–Co1–N1(#2)	89.83(6)
O1–Co1–O1(#1)	180.00(7)	N1(#3)–Co1–N1(#2)	180.0
O1W–Co1–O1W(#1)	180.00(4)		
Complex **2**			
Mn1–O1	2.157(3)	Mn1–O1W	2.188(3)
Mn1–N1(#3)	2.261(4)		
O1–Mn1–O1W	89.19(12)	O1–Mn1–N1(#3)	89.98(13)
O1–Mn1–O1W(#4)	90.81(12)	O1–Mn1–N1(#5)	90.02(13)
O1W–Mn1–N1(#3)	89.65(14)	O1(#4)–Mn1–O1W	90.81(12)
O1W–Mn1–N1(#5)	90.35(14)	O1(#4)–Mn1–N1(#3)	90.02(13)
O1W(#4)–Mn1–N1(#3)	90.35(14)	O1(#4)–Mn1–O1W(#4)	89.19(12)
O1(#4)–Mn1–N1(#5)	89.98(13)	O1W(#4)–Mn1–N1(#5)	89.65(14)
O1–Mn1–O1(#4)	180.00(13)	N1(#3)–Mn1–N1(#5)	180.000(1)
O1W–Mn1–O1W(#4)	180.000(1)		

Symmetry transformations used to generate equivalent atoms: #1: $2-x, -y, 1-z$; #2: $2-x, 1-y, 1-z$; #3: $x, -1+y, z$; #4: $2-x, -y, 2-z$; #5: $2-x, 1-y, 2-z$.

Table 3. Hydrogen-bonding geometries (Å, °) of **1** and **2**.

D–H···A	d(D–H)	d(H···A)	∠DHA	d(D···A)	Symmetry operator of A
Complex **1**					
N3–H3N···O1W	0.83	2.20	174	3.03	$x, -y+1/2, z-1/2$
O1W–H1WA···N2	0.83	1.95	166	2.77	$x, -y-1/2, z+1/2$
O2W–H2W···O2	0.88	1.86	159	2.71	$x, -y+1/2, z-1/2$
O2W–H2WA···O2	0.91	1.79	171	2.70	$-x+1, y+1/2, -z+1/2$
Complex **2**					
N3–H3N···O1W	0.90	2.16	162	3.03	$x, -y+1/2, z-1/2$
O1W–H1W···N2	0.91	1.87	174	2.77	$x, -y-1/2, z+1/2$
O2W–H2WA···O2	1.24	1.58	145	2.69	$-x+1, y+1/2, -z+3/2$
O2W–H2W···O2	1.05	1.82	142	2.72	$x, -y+1/2, z-1/2$

IR spectra of **1** and **2** are similar, so **1** will be discussed in detail as an example. The absence of bands from 1680 to 1760 cm^{-1} indicates complete deprotonation of carboxylic groups of HL [13]. Characteristic bands of carboxylates are at 1541–1606 cm^{-1} for asymmetric stretches and 1456–1401 cm^{-1} for symmetric stretches [14]. The value of $\Delta\nu = \nu_{as}(COO)–\nu_s(COO)$, which is used to determine the coordination mode of carboxylate, follows the order: $\Delta\nu_{monodentate} > \Delta\nu_{ionic} > \Delta\nu_{bridging} > \Delta\nu_{chelate}$ [15]. However, strong hydrogen-bonding with monodentate carboxylates can decrease the $\Delta\nu$ value. The $\Delta\nu$ corresponding to monodentate carboxylate in **1** (145 cm^{-1}) is significantly smaller than expected. Strong intermolecular hydrogen bonds exist between lattice water and the carboxylate oxygen (table 3). Such low values of $\Delta\nu$ have been reported for other monodentate carboxylates with C = O group involved in strong hydrogen-bonding [16]. In all these cases, results of X-ray analysis unambiguously defined the binding of carboxylate. In **1**, bands at 1502 cm^{-1} are assigned to C–H stretches of benzene. Bands at 3350 cm^{-1} are assigned to NH stretches of L^-, and broad bands at 3520 cm^{-1} correspond to the vibrations of lattice water [17].

3.2. *Structural description*

Determination of the structures of **1** and **2** by X-ray crystallography show similar molecular structures. Each of the two complexes crystallizes in the monoclinic system with space group $P2_1/c$ (table 1). Thus, only **1** will be discussed in detail here.

As shown in figure 1, in the asymmetrical unit of **1**, there is half a Co(II), one L^-, one coordinated water molecule, and half a crystallization water molecule. Each Co(II) is six-coordinate by two nitrogens from two different L^-, two carboxylate oxygens from two different L^-, and two oxygens from two coordinated water molecules in a slightly distorted octahedral coordination geometry, $[CoN_2O_4]$ (figure 1). From crystallographic symmetry, the six coordinating atoms around Co(II) can be simplified into three pairs [Co1–O1 = 2.1026(14) Å, Co1–N1(#2) = 2.1584(17) Å, Co1–O1W = 2.1210 (14) Å], and the very small average deviation (approximately 0.02 Å) of the bond length is just the reflection of the almost standard octahedral coordination geometry [O1–Co1–O1(#1) = N1(#2)–Co1–N1(#3) = O1W–Co1–O1W(#1) = 180°, O1–Co1–O1 W = 91.21(6)°, O1W–Co1–N1(#2) = 90.18(6)°, O1W–Co1–N1(#3) = 89.83(6)°]. Even so, slight distortion of the overall molecular structure exists, which might originate from

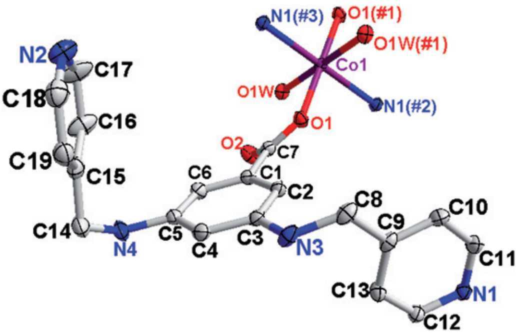
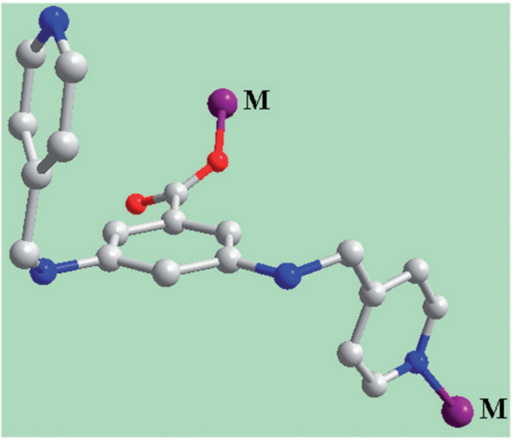


Figure 1. Diagram showing the coordination geometry of Co(II) in **1** with 30% probability displacement ellipsoids. Hydrogens were omitted for clarity. Symmetry transformations: (#1) $2-x$, $-y$, $1-z$; (#2) $2-x$, $1-y$, $1-z$; (#3) x, $-1+y$, z.



Scheme 2. Schematic representation of the coordination conformations and modes of L^- in **1** and **2**.

the Jahn–Teller effect based on electronic degenerate ground state of high-spin Co(II) ion with d^7 $[(t_{2g})^5(e_g)^2]$ electron configuration [18].

L^- is a counterion in the complex after deprotonation of carboxylic groups. The carboxylate in L^- adopts μ_1-$\eta^1:\eta^0$-monodentate coordination; two flexible arms of L^- are on the two sides of the central benzene plane, defined as *trans* (schemes 1 and 2), and one (pyridin-4-ylmethyl)amino group is coordinated. Thus, L^- is bidentate in the complex. Co(II) ions are doubly interconnected by L^- to yield a 1-D double-chain (figure 2) containing 24-membered non-coplanar metallacycles with intermetallic separations of $Co \cdots Co = 9.321$ Å.

Hydrogen bonds exist extensively in the complex. There are three kinds (figure 3) of intermolecular hydrogen bonds: (1) hydrogen bonds ($O2 \cdots H2W–O2W–H2WA \cdots O2$) with four hydrogens from two lattice water molecules (H2W and H2WA) doubly interconnect two carboxylate oxygens (O2) from adjacent 1-D chains to generate a dimer across the inversion center. The distances of oxygens of the nearest lattice water

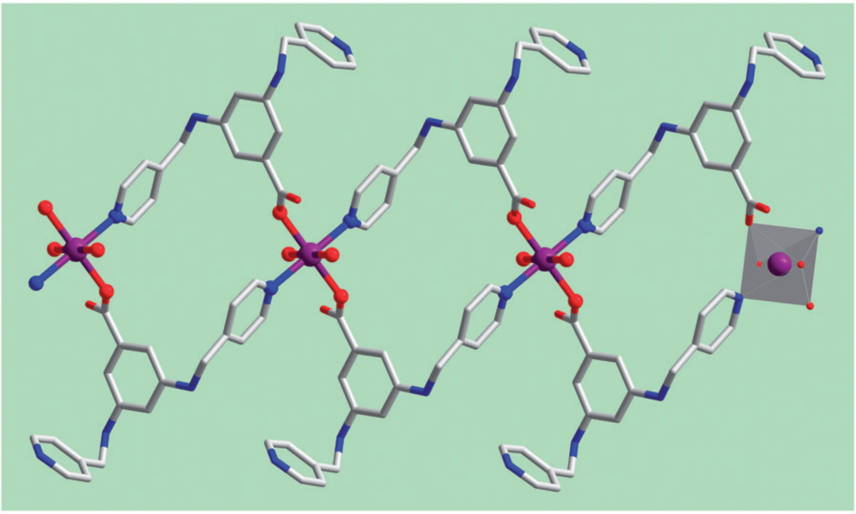


Figure 2. View of the 1-D zigzag double-chain linking *via* L^- doubly interconnecting Co(II) ions.

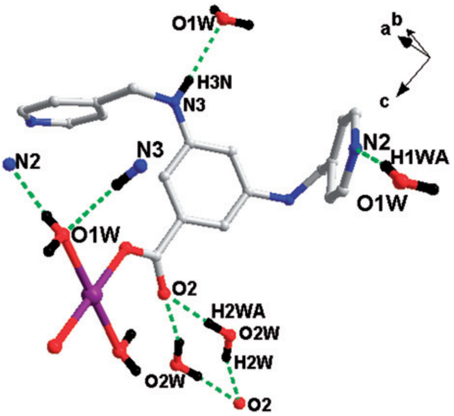


Figure 3. Three kinds of hydrogen-bonding interactions in **1**.

molecules is just 1.962 Å, which indicates that there may be O · · · O contacts within the dimer units. Ignoring other hydrogen bonds, this kind of intermolecular interaction links adjacent chains to form a 2-D network (figure 4). (2) Hydrogen bonds (N3–H3N · · · O1W) exist between hydrogens (H3N) from coordinated (pyridin-4-ylmethyl)amino groups and oxygens of coordinated water. (3) Hydrogen bonds (O1W–H1WA · · · N2) exist between hydrogens (H1WA) of coordinated water molecules and nitrogens from uncoordinated (pyridin-4-ylmethyl)amino groups. Hydrogen-bonding interactions (2) and (3) further connect the 1-D chains to construct a 3-D MOF (figure 5).

Complex **2**, $\{[Mn(L)_2(H_2O)_2] \cdot H_2O\}$ has the very similar structure to **1** except a little difference in the bond lengths and angles, presented in table 2.

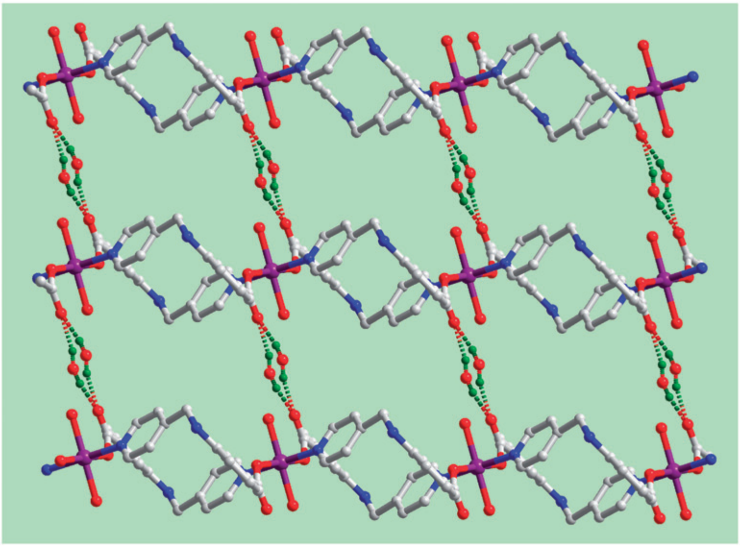


Figure 4. The 2-D supramolecular layer extended from the 1-D chain in **1** through hydrogen bonds of the dimer across the inversion center. Uncoordinated (pyridin-4-ylmethyl)amino groups were omitted for clarity.

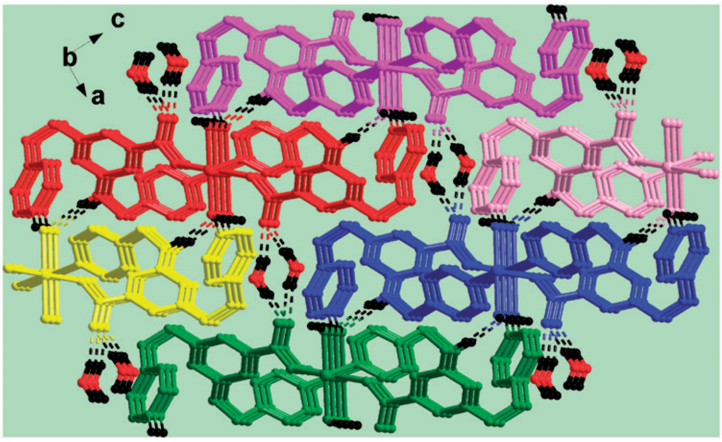


Figure 5. View of the 3-D MOF of **1** constructed from hydrogen bonds.

3.3. *Thermogravimetric analysis*

TGA of **1** and **2** have been recorded in N_2 with a heating rate of $10^\circ C\,min^{-1}$ from 30°C to 800°C. The TGA curves of **1** and **2** exhibit similar thermal behaviors (Supplementary material). Two overlapped steps (91–206°C for **1** and 97–199°C for **2**) correspond to the release of two coordinated water molecules and one lattice water molecule and the observed weight losses of 6.72% for **1** and 7.29% for **2** are close to the calculated value (6.93% and 6.96%, respectively). A steep step occurs at 329°C for **1** and 338°C for **2** associated with rapid decomposition of the framework; continuous decomposition of **1** and **2** proceeded above 800°C, so the final residuals for them have not been calculated.

4. Conclusion

Two new complexes with a 1-D double-chain containing 24-membered non-coplanar metallacycles were synthesized from HL through hydrothermal reaction at 90°C. Compared with other reported pyridyl and carboxylate-containing ligands and complexes, such as 3,5-bis(pyridin-2-ylmethyl)aminobenzoic acid, 4-(pyridin-4-ylmethoxy)benzoic acid, 4-(pyridin-3-ylmethyl)aminobenzoic acid, and 4-(pyridin-3-yl)benzoic acid [19], HL exhibits several features. First, HL is more flexible than the above-mentioned ligands, so it can show more coordination conformations. Second, HL contains one carboxylate and two pyridyl-containing groups, so it may possess more coordination, but one flexible arm does not coordinate. So, a critical issue is how to make full use of potential coordination. In future research, rigid auxiliary ligands such as 1,4-benzenedicarboxylic acid may be introduced to enhance rigidity and construct higher dimensional complexes.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC-821537 (for **1**) and CCDC-821538 (for **2**)). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Figure S1 describes the coordination environment of Mn^{2+} ion in **2**, figure S2 demonstrates three kinds of hydrogen-bonding interactions in **2**, and figure S3 shows the TGA curves of **1** and **2**. This supporting information for the article is available online or from the authors on request.

Acknowledgments

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