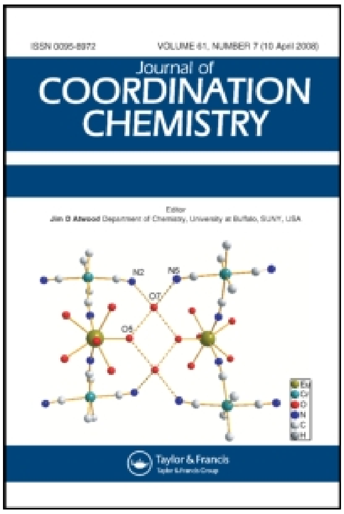

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Two new metal coordination polymers containing mixed ligands: hydrothermal synthesis and crystal structures of [Co_2(1,2,4,5-btc)$(phen)_2(H_2O)_6$]·$2H_2O$ and [Mn_3(1,2,4-btc)$_2$(phen)$_2$(H_2O)$_2$]*_n*

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Two new metal coordination polymers containing mixed ligands: hydrothermal synthesis and crystal structures of $[Co_2(1,2,4,5\text{-btc})(phen)_2(H_2O)_6] \cdot 2H_2O$ and $[Mn_3(1,2,4\text{-btc})_2(phen)_2(H_2O)_2]_n$

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Crystallisation of benzene-1,2,4,5-tetracarboxylic acid or benzene-1,2,4-tricarboxylic acid with divalent metal ions of Co, and Mn with 1,10-phenanthroline gives two new coordination solids, $[Co_2(C_{10}H_2O_8)(C_{12}H_8N_2)_2(H_2O)_6] \cdot 2H_2O$ (**1**) and $[Mn_3(C_9H_3O_6)_2(C_{12}H_8N_2)_2(H_2O)_2]_n$ (**2**). The three-dimensional supramolecular structure of compound **1** is constructed from discrete $[Co_2(C_{10}H_2O_8)(C_{12}H_8N_2)_2(OH_2)_6]$ dimers and isolated water molecules via interesting hydrogen-bonding and π–π stacking interactions. Compound **2** has an unusual (4, 6) network, and the network is furthermore extended into a three-dimensional supramolecular architecture by the aid of hydrogen bonding and π–π stacking interactions.

Keywords: Coordination polymers; Hydrothermal synthesis; Crystal structure; Supramolecular network

1. Introduction

Contemporary interest in metal–organic coordination frameworks stems from their structural diversity and, more importantly, their potential applications as materials in catalysis, host–guest chemistry, photochemistry, sorption, electrical conductivity, and magnetism [1–6]. To date, a variety of low-dimensional coordination polymers based on d-block transition metal ions and organic ligands have been prepared and exhibit potential applications in the field of functional materials [7]. The construction of metal–organic coordination polymers can be achieved using various organic aromatic polycarboxylate ligands via covalent interactions and/or intermolecular forces. Among the various aromatic polycarboxylate ligands, symmetrical polycarboxylate ligands, benzene-1,2,4,5-tetracarboxylic acid (1,2,4,5-btc), are of special interest because

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of the variety of coordinations toward transition metal ions [8–10]. In previous studies, carboxyl groups on the 1,2,4,5-btc induce versatile coordination modes with transition metal complexes and act as hydrogen bond donors and/or acceptors inter- and/or intramolecularly [11]. Besides symmetrically bridging ligands, recent studies [12–14] have shown that unsymmetrical benzene polycarboxylates, such as benzene-1,2,4-triacarboxylic acid (1,2,4-btc) can give unprecedented structures with novel topological features due to their coordination sites with differing donor ability [15].

Introduction of another organic ligand such as N-containing chelating bidentate ligand in the {metal/btc} system may introduce new character and structural evolution [7a, 16–18]. However, syntheses of compounds containing mixed ligands are more difficult to control than those containing only one ligand, due to the different solubility of the ligands and coordination competition of the ligands. Hydrothermal synthesis has been proved to be an effective and promising method for growing crystals of numerous inorganic compounds, providing special reaction conditions in which differential solubility problems are minimized.

Based on the aforementioned points, the aim of our research is to synthesize novel coordination polymers with symmetrical or unsymmetrical benzene carboxylates and N-containing chelating bidentate ligands under hydrothermal conditions. In this article, we report two new metal–organic polymers $[Co_2(C_{10}H_2O_8)(C_{12}H_8N_2)_2(H_2O)_6]\cdot 2H_2O$ (**1**) and $[Mn_3(C_9H_3O_6)_2(C_{12}H_8N_2)_2(H_2O)_2]_n$ (**2**). In both complexes, various types of hydrogen bonding or π–π interactions play important roles in reinforcing the metal–ligand ligations as well as in determining the shapes of the btc^{2-} anions. The details of the structures and properties of **1** and **2** are discussed in this report.

2. Experimental

2.1. *Materials and methods*

All chemicals were commercially purchased and used without further purification. The elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 C H N Elemental Analyser. Co and Mn were determined by a PLASMA-SPEC (I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}.

2.2. *Preparation of compounds*

A mixture of cobalt acetate tetrahydrate (0.1157 g, 0.5 mmol), benzene-1,2,4,5-tetracarboxylic acid (0.0450 g, 0.2 mmol), 1,10-phen (0.01 g, 0.056 mmol), NaOH (0.02 g, 0.5 mmol) and H_2O (6 mL) was stirred for 30 min in air and then sealed in a 15 mL Teflon-lined autoclave. After maintaining at 160°C for 5 days, the bomb was cooled at a rate of 10°C h^{-1} to room temperature. Pink crystals of **1** were collected by filtration and air-dried (yield: 78% based on Co). Anal. Calcd for $C_{34}H_{34}Co_2N_4O_{16}$: C, 46.80; H, 3.90; N, 6.42; O, 29.36; Co, 13.52. Found: C, 46.97; H, 3.56; N, 6.87; O, 29.48; Co, 13.12%. FT/IR data (cm^{-1}): 1670(w), 1583(s), 1540(s), 1517(s), 1480(s), 1428(s), 1388(s), 1279(w), 1225(w), 1158(w), 1142(s), 1107(m), 961(w), 900(s), 868(m), 854(s), 815(s), 776(s), 729(s), 678(s), 568(s), 466(s).

$$[Co_2(C_{10}H_2O_8)(C_{12}H_8N_2)_2(H_2O)_6] \cdot 2H_2O. \tag{1}$$

A mixture of $Mn(CH_3COO)_2 \cdot 2H_2O$ (0.1045 g, 0.5 mmol), adipic acid (0.073 g, 0.5 mmol), H_3btc (0.0562, 0.3 mmol), phen (0.0182 g, 0.1 mmol), NaOH (0.04 g, 1 mmol) and H_2O (6 mL) was stirred for 30 min in air. The mixture was sealed in a 15 mL Teflon-lined autoclave and heated at 160°C for 5 days. Then, the autoclave was cooled at $10°C\,h^{-1}$ to room temperature. Yellow block crystals of **2** were isolated in *c*. 60% yield based on Mn. Adipic acid is necessary for this reaction, though it is not incorporated into the structure of the title compound. It may function as a neutralising agent. Calcd for: Mn, 16.90; C, 51.67; H, 2.67; N, 5.74; O, 22.96%. Found: Mn, 16.87; C, 51.74; H, 2.59; N, 5.81; O, 22.99%. FT/IR data (cm^{-1}): 3536(m), 1679(s), 1621(s), 1583(s), 1540(m), 1157(s), 1301(w), 1194(w), 985(w), 903(m), 860(w), 820(m), 765(s), 731(m), 689(m), 660(s), 618(m), 530(s) and 420(s).

$$[Mn_3(C_9H_3O_6)_2(C_{12}H_8N_2)_2(OH_2)_2]_n. \tag{2}$$

2.3. *X-ray crystallography*

Details of the structure determinations are given in table 1. X-ray diffraction measurements were made with graphite-monochromatic Mo Kα radiation (= 0.71073 Å) using

Table 1. Crystal data and structure refinements for compounds **1** and **2**.

Empirical formula	$C_{42}H_{22}Mn_3N_4O_{14}$	$C_{34}H_{34}Co_2N_4O_{16}$
Formula weight	975.49	872.51
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	$a = 7.7799(2)$ Å $\alpha = 88.75°$ $b = 10.803(2)$ Å $\beta = 78.96°$ $c = 12.147(2)$ Å $\gamma = 69.74°$	$a = 7.4157(2)$ Å $\alpha = 66.61(3)°$ $b = 11.064(2)$ Å $\beta = 76.37(3)°$ $c = 12.222(2)$ Å $\gamma = 71.03(3)°$
Volume	939.0(3) $Å^3$	863.8(3) $Å^3$
Z	1	1
Dc	$1.725\ Mg\,m^{-3}$	$1.677\ Mg\,m^{-3}$
Absorption coefficient	$1.705\ mm^{-1}$	$1.045\ mm^{-1}$
$F(000)$	493	448
Crystal size	0.243 × 0.216 × 0.179 mm	0.142 × 0.135 × 0.127 mm
θ range for data collection	3.02–27.48°	2.24–27.48°
Limiting indices	$-10 \le h \le 10$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-9 \le h \le 9$, $-14 \le k \le 14$, $-15 \le l \le 15$
Reflections collected	9226	6152
Independent reflections	4237 [$R_{(int)} = 0.0309$]	3836 [$R_{(int)} = 0.0347$]
Completeness to $\theta = 27.48°$	98.7%	96.7%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4237/0/286	3836/0/285
Goodness-of-fit on F^2	0.967	1.136
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0341$, $wR_2 = 0.1096$	$R_1 = 0.0541$, $wR_2 = 0.1495$
R indices (all data)	$R_1 = 0.0405$, $wR_2 = 0.1226$	$R_1 = 0.0753$, $wR_2 = 0.1624$
Largest difference for peak and hole	0.552 and $-0.820\ e\,Å^{-3}$	0.358 and $-0.363\ e\,Å^{-3}$

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

Compound 1			
]Co(1)–O(1)	2.088(3)	Co(1)–O(5)	2.115(3)
Co(1)–O(6)	2.061(3)	Co(1)–O(7)	2.192(3)
Co(1)–N(1)	2.128(3)	Co(1)–N(2)	2.137(3)
O(6)–Co(1)–O(1)	99.66(12)	O(5)–Co(1)–N(2)	85.53(13)
O(6)–Co(1)–O(5)	175.41(14)	N(1)–Co(1)–N(2)	78.36(13)
O(1)–Co(1)–O(5)	83.16(12)	O(6)–Co(1)–O(7)	85.92(13)
O(6)–Co(1)–N(1)	86.23(13)	O(1)–Co(1)–O(7)	91.49(11)
O(1)–Co(1)–N(1)	93.19(12)	O(5)–Co(1)–O(7)	90.41(13)
O(5)–Co(1)–N(1)	97.27(13)	N(1)–Co(1)–O(7)	171.44(12)
O(6)–Co(1)–N(2)	92.29(13)	N(2)–Co(1)–O(7)	98.56(12)
O(1)–Co(1)–N(2)	164.92(11)		
Compound 2			
Mn(1)–O(3)	2.1066(15)	Mn(2)–O(2)#1	2.1466(15)
Mn(1)–O(1)	2.1296(18)	Mn(2)–O(2)	2.1466(15)
Mn(1)–O(5)#4	2.2191(17)	Mn(2)–O(7)	2.1818(16)
Mn(1)–N(1)	2.236(2)	Mn(2)–O(7)#1	2.1818(16)
Mn(1)–N(2)	2.275(2)	Mn(2)–O(4)#2	2.2604(15)
Mn(1)–O(6)#4	2.3290(2)	Mn(2)–O(4)#3	2.2604(15)
O(2)#1–Mn(2)–O(2)	180.00(9)	O(3)–Mn(1)–N(1)	112.45(7)
O(2)#1–Mn(2)–O(7)	86.91(6)	O(1)–Mn(1)–N(1)	88.26(7)
O(2)–Mn(2)–O(7)	93.09(6)	O(5)#4–Mn(1)–N(1)	149.87(6)
O(7)–Mn(2)–O(7)#1	180.00(10)	O(3)–Mn(1)–N(2)	95.44(6)
O(2)#1–Mn(2)–O(4)#2	88.75(6)	O(1)–Mn(1)–N(2)	160.77(7)
O(2)–Mn(2)–O(4)#2	91.25(6)	O(5)#4–Mn(1)–N(2)	91.45(8)
O(7)–Mn(2)–O(4)#2	93.37(6)	O(3)–Mn(1)–O(6)#4	145.49(6)
O(7)#1–Mn(2)–O(4)#2	86.63(6)	O(1)–Mn(1)–O(6)#4	84.28(7)
O(4)#2–Mn(2)–O(4)#3	180.00(4)	O(5)#4–Mn(1)–O(6)#4	57.75(6)
O(3)–Mn(1)–O(1)	85.71(6)	N(1)–Mn(1)–O(6)#4	100.17(7)
O(3)–Mn(1)–O(5)#4	94.54(7)	N(2)–Mn(1)–O(6)#4	104.62(7)
O(1)–Mn(1)–O(5)#4	107.62(7)		

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

a Rigaku R-AXIS RAPID IP diffractometer. An empirical absorption correction (multiscan) was applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXL crystallographic software package [19, 20]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **1** were located from difference Fourier maps. The hydrogen atoms of water were located from the difference Fourier map and refined freely. For **2**, the hydrogen atoms were placed in idealized positions. The selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of compound 1*

The X-ray single crystal diffraction reveals that compound **1** is built from $[Co_2(C_{10}H_2O_8)(C_{12}H_8N_2)_2(H_2O)_6]_n$ dimers and coordinated water molecules. There is one crystallographically independent Co centre in the structure of **1**. The Co centre adopts a distorted octahedral geometry with two nitrogens of a chelating phen ligand, one oxygen of a carboxylate group and three oxygen donors from coordinated water molecules. The two Co–N bond lengths are 2.128(3) and 2.137(3) Å,

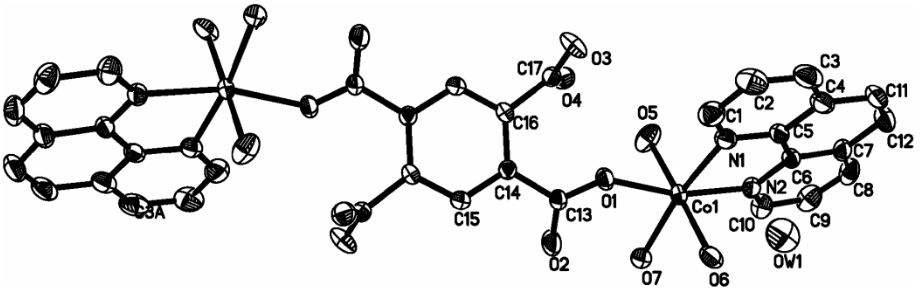

Figure 1. ORTEP drawing of compound **1**. Hydrogen atoms are omitted for clarity.

Table 3. Hydrogen bonds (Å and °) for structures **1** and **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
Compound 1				
O5–H13···O1	0.806	2.631	2.789	92.74
O5–H13···O4	0.806	1.928	2.728	114.55
O5–H14···O7A	0.877	1.887	2.762	175.46
O6–H6···O7	0.753	2.786	2.900	91.11
O6–H4···OW1	0.904	1.808	2.712	175.72
O6–H4···N1	0.904	2.731	2.863	89.13
O6–H5···O3A	0.685	1.932	2.612	172.08
O7–H7···O4A	0.753	2.064	2.790	162.24
O7–H7···O2	0.865	1.726	2.584	171.74
OW1–H···O3B	0.863	1.882	2.738	171.68
Compound 2				
O7–H7B···O2A	0.930	2.863	2.977	87.86
O7–H7···O6A	0.930	1.952	2.841	159.37

respectively. The Co–OW bond lengths vary from 2.061(3) to 2.192(3) Å, and the Co–O (carboxylate) bond length is 2.088(3) Å. The O(N)–Co(1)–N(O) angles range from 83.16(12) to 175.41(14)°. As far as each 1,2,4,5-btc ligand is concerned, it adopts a bridging monodentate coordination mode to link two metal atoms, with the –2,4 carboxyl groups idle. The valence sum calculations [21] give the value of 1.4345 for the uncoordinated oxygen atoms O2, 1.4661 for O3 and 1.4268 for O4, suggesting that they are deprotonated. This result is consistent with the IR spectrum in which no characteristic bond around 1700 cm^{-1} can be observed [22]. All Co1 and Co(1A) centres are linked by one 1,2,4,5-btc ligand to form a dimer (figure 1).

There exist π–π intermolecular interactions among aromatic groups of 1,10-phen ligands (shown in figure S1). The distance between aromatic units is 3.358–3.384 Å. Furthermore, the adjacent dimers are parallel with a supermolecular framework from inter- and intra-molecular hydrogen-bonding interactions. The intramolecular hydrogen-bonding interactions (table 3) can be found between the coordinated water molecule and the carboxyl oxygen of the 1,2,4,5-btc (O5···O4 2.728 Å, O4···O7C 2.790 Å and O3···O6 2.612 Å) and the isolated water molecule and the carboxyl oxygen of the 1,2,4,5-btc (OW1B···O3 2.738 Å), while the intermolecular hydrogen bonding interactions exist in coordinated water molecules (O7C···O5BA 2.762 Å) from different units, and the isolated water molecule and coordinated water

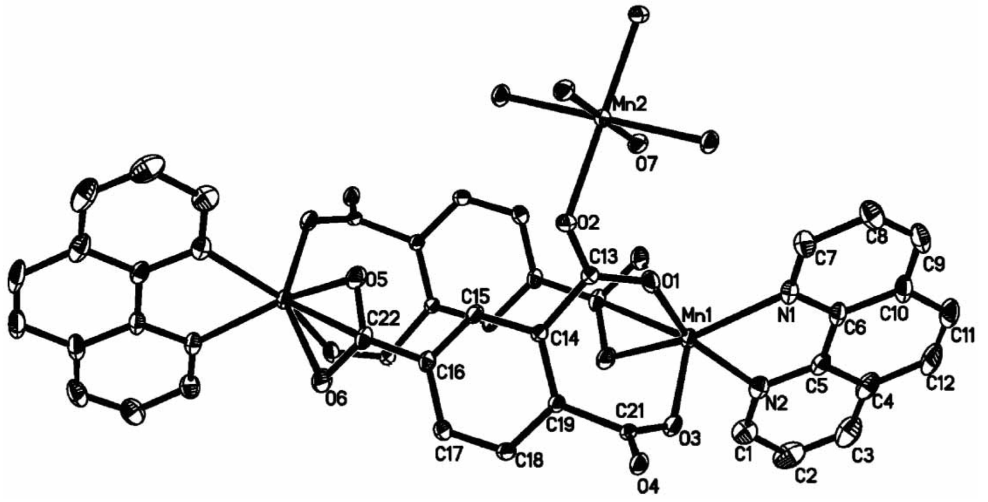

Figure 2. ORTEP drawing of compound **2**. Hydrogen atoms are omitted for clarity.

molecule (O6C···OW1 2.712 Å). Interestingly, the hydrogen-bonding interactions form a 'chair' conformation shape among the O5, O7, O4AA, O4D, O7DA and O5C, and a planar hexagonal shape among O3D, O3E, OW1A, OW1D, O6CA and O6A (figure 3). Obviously, the hydrogen-bonding interactions enhance the stability of the compound. To the best of our knowledge, such supramolecular framework has not been reported in the mixed 1,2,4,5-btc and phen system.

3.2. *Crystal structure of compound 2*

Compound **2** consists of [$Mn_2(phen)_2(1,2,4\text{-btc})_2$] dimers and [$Mn(H_2O)_2$] fragments (figure 2). There are two crystallographically unique Mn centres in the structure of **2**. The Mn(1) centre coordinates to two nitrogens of one chelating phen ligand and four oxygens from three different carboxylate groups. The average Mn(1)–N bond length is about 2.255 Å, and the Mn(1)–O bond lengths vary from 2.1066 to 2.2604 Å. The O(N)–Mn(1)–N(O) angles are in the range of 86.63(6)–160.77(7)°. Thus, Mn(1) displays a distorted octahedral coordination geometry. The Mn(3) site is similar to the Mn(1) centre. The Mn(2) has two oxygens of coordinated water and four oxygens from four different carboxyl groups. The average Mn(2)–O bond length is *c*. 2.1961 Å, while the O–Mn(2)–O angles are in the range of 57.75(6)–180.00(1)°. The Mn(2) centre also possesses a distorted octahedral coordination environment. Three carboxyl groups have two different kinds of coordination modes, bidentate chelating and monodentate double-bridging. All Mn(1) and Mn(3) centres are linked by two 1,2,4-btc ligands to form a dimer along the *a* axis. Adjacent chains are connected by Mn(2) octahedra to form a novel 2D (4, 6) network, as shown in figure 4(a). The four-membered ring consists of four Mn octahedra connected by two btc units, while the six-membered ring contains six Mn octahedra linked by four 1,2,4-btc moieties. These four- and six-membered rings distribute alternately on the 2-D layer along the *ab* plane.

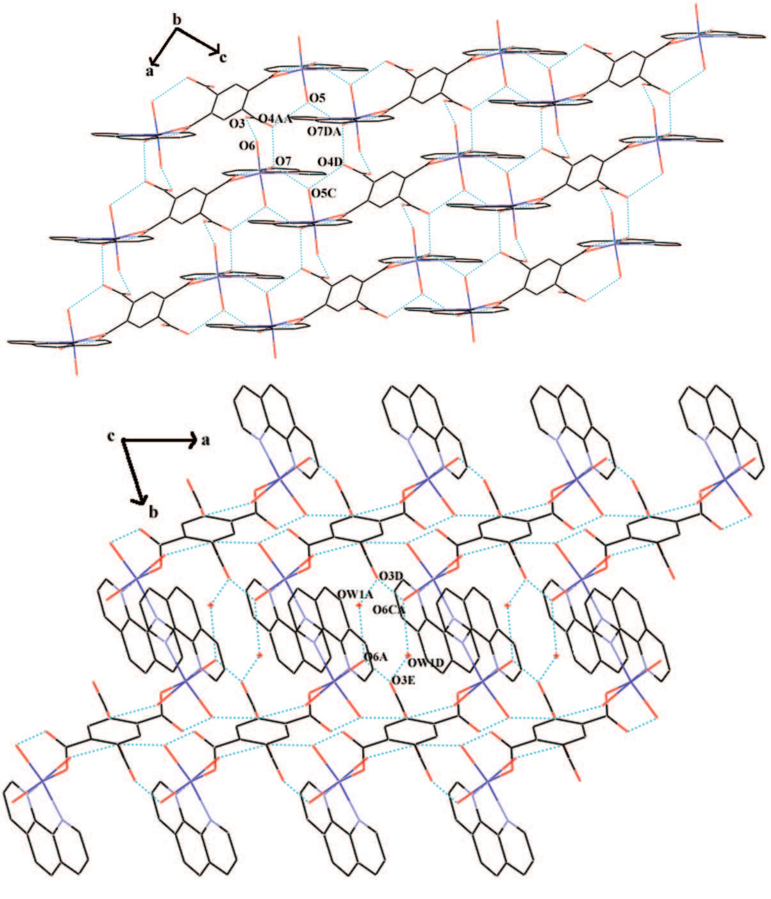

Figure 3. View of two types of the hexagonal-shape strong intermolecular hydrogen-bonding interactions in **1**.

In the packing arrangement of **2** (figure 4b), the adjacent 2-D layers are parallel; a 3-D framework is formed via π–π interactions between aromatic groups of phen ligands. The distance between the aromatic groups is about 3.39 Å.

3.3. *Thermal analysis*

TGA curve of compound **1** exhibits three weight loss stages. The first weight loss starts at *c*. 88–140°C to give a total weight loss of 4.37%, corresponding to the release of crystallographic water (4.13%). The second weight loss starts at 170–220°C 13.10%, corresponding to the release of coordinated water molecules (12.39%). The third weight loss starts at *c*. 280–500°C, corresponding to the decomposition of organic ligands 63.35% (*c*. 69.96%). TGA curve of compound **2** exhibits two weight-loss stages. The first weight loss is 8.10% (Calcd 7.38%) in the range of 190–230°C, corresponding to the release of coordinated water molecules. The second weight loss is 75.24% (Calcd 79.35%) in the temperature range of 380–430°C, corresponding to the release of phen and 1,2,4-btc ligands.

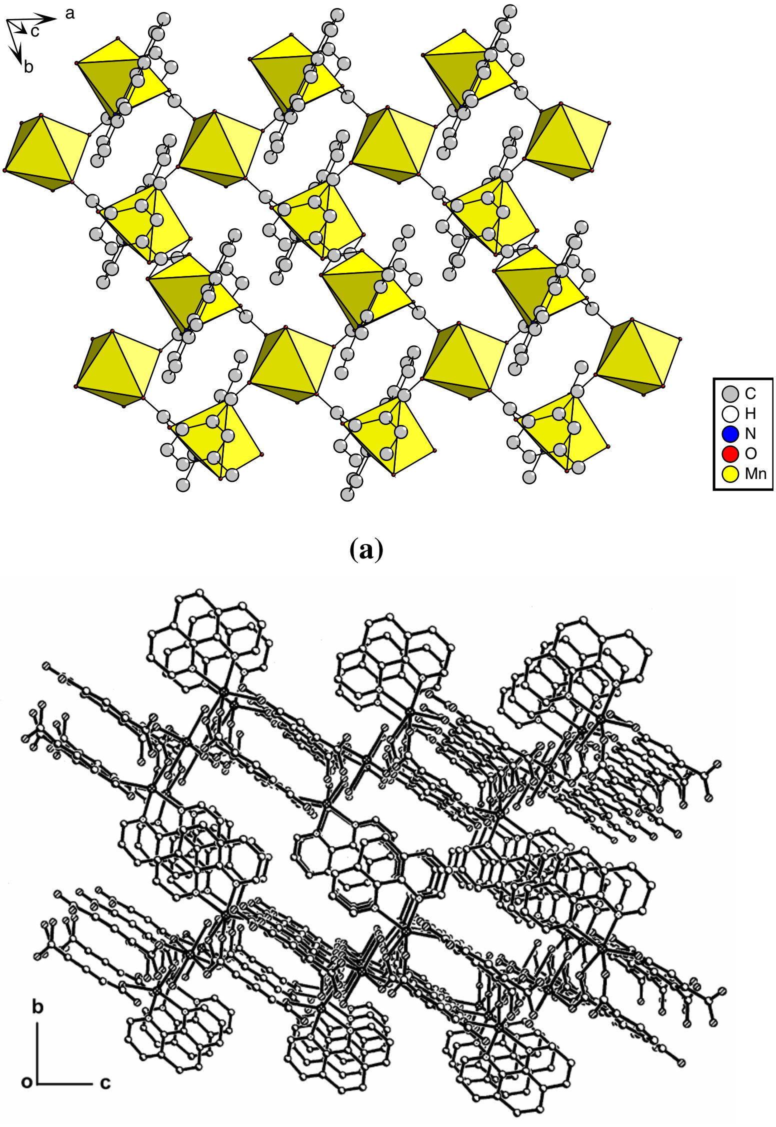

Figure 4. (a) Polyhedral representation of the 2D (4, 6) network of **2**. (b) View of the three-dimensional structure of **2**, showing strong π–π stacking interactions.

4. Conclusions

In this article, the synthesis of 2-D coordination polymers of **1** and **2** not only proves the capability of hydrothermal reactions in preparing novel metal–organic polymers with mixed organic ligands, but also confirms that such coordination polymers may be designed and synthesized according to the inherent stereo and interactive information stored in the organic ligands and metal ions. Atomic coordinates, thermal parameters, bond lengths and angles are available from the authors on request.

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