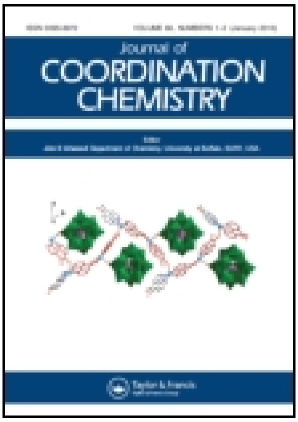

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Two cobalt coordination polymers based on an asymmetric dicarboxylate: structural diversity tuned by auxiliary ligands

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Two cobalt coordination polymers based on an asymmetric dicarboxylate: structural diversity tuned by auxiliary ligands

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Two 1-D cobalt coordination polymers, $[Co(mbtx)(hpht)(H_2O)]_n$ (**1**) and $[Co(mbix)(hpht)]_n$ (**2**) (mbtx = 1,3-bis(1,2,4-triazol-1-ylmethyl)benzene, mbix = 1,3-bis(imidazol-1-ylmethyl)benzene, H_2hpht = homophthalic acid), were synthesized by hydrothermal reactions and characterized by elemental analyzes, IR spectroscopy, thermogravimetry, and single-crystal X-ray diffraction. Complex **1** is a 1-D heterostranded double-helical chain as a result of bridging hpht and mbtx, and the 1-D chains are further self-assembled into a 2-D layer structure through hydrogen bonds. Complex **2** shows a 1-D molecular ladder structure, linked through C–H···π interactions to give a 2-D layer structure, which is further linked through C–H···O hydrogen bonds to form a 3-D framework. The mbtx adopts *cis*-conformation in **1**, while for **2**, mbix has *trans*-conformation. Factors causing the differences between **1** and **2** are discussed.

Keywords: Coordination polymer; Crystal structure; Auxiliary ligand; Structural diversity

1. Introduction

Crystal engineering based on metal-organic frameworks (MOFs) attracts interest with elegant framework topologies and potential applications in molecular magnetism, catalysis, gas sorption, fluorescence sensing, and optoelectronic devices [1–3]. Though it is a great challenge for directional synthesis of such materials due to lack of understanding in formation mechanisms, rational design of desirable MOFs can be realized by judicious choice of the metal centers and organic linkers, as well as synthetic routes. Geometric orientation, binding mode, coordination preferences at specific metal ions of linkers and self-assembly of subunits can act synergistically to provide access to a diversity of structural topologies [3]. MOFs constructed from aromatic rigid polycarboxylates, such as 1,5-benzenedicarboxylate, 1,3-5-benzenetricarboxylate, and 1,2,4,5-benzenetetracarboxylate, have been extensively studied because of diversity coordination modes and sensitivity to pH values of the

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carboxylates. However, unsymmetrical and flexible benzene carboxylic acids have rarely been used; structures constructed from these ligands remain less developed and compared with rigid ligands, using flexible ones to construct coordination polymers promotes formation of helical or looped structures.

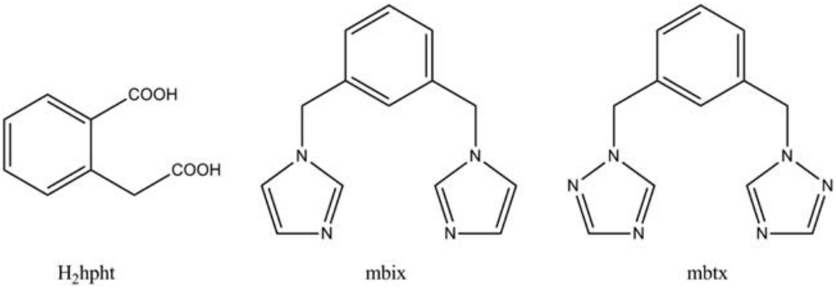
Unsymmetrical homophthalic acid (H_2hpht) has a flexible ethylic carboxylate, which may not be coplanar with benzene. Owing to its flexibility, H_2hpht has various conformations as well as coordination modes, making it difficult to control the final structure. Metal complexes with 0-, 1-, 2-, and 3-D structures constructed from H_2hpht have been reported [4–8].

Co(II) is able to coordinate simultaneously in solution to both oxygen- and nitrogen-containing ligands. Cobalt coordination polymers containing both aromatic carboxylate and N-heterocyclic ligands have been reported [9,10]. Flexible bis(N-containing heterocyclic ring) ligands with certain spacers, for example, 1,2-bis(4-pyridyl)ethane (bpe), 1,4-bis(imidazol-1-ylmethyl)benzene (pbix), and 1,4-bis-(1,2,4-triazol-1-ylmethyl)benzene (pbtx), can freely rotate to meet the requirement of coordination geometries of metal ions in the assembly process and have been found to be useful in the construction of MOFs [11–17]. However, the research on MOFs constructed from 1,3-bis(imidazol-1-ylmethyl)benzene (mbix) or 1,3-bis (1,2,4-triazol-1-ylmethyl)benzene (mbtx) are rarely reported [18–24], with different atoms in the 1-position to nitrogen. To prepare novel structures, understanding of coordination of flexible aromatic polycarboxylates and investigating the effect of different N-containing heterocyclic rings to assemble MOFs, we use mbtx or mbix as mixed ligands with H_2hpht and isolated two new 1-D cobalt coordination polymers, $[Co(mbtx)(hpht)(H_2O)]_n$ (**1**) and $[Co(mbix)(hpht)]_n$ (**2**) (mbtx = 1,3-bis(1,2,4-triazol-1-ylmethyl)benzene, mbix = 1,3-bis(imidazol-1-ylmethyl)benzene, H_2hpht = homophthalic acid) (scheme 1). Infrared spectra, crystal structures and thermogravimetric properties were investigated.

2. Experimental

2.1. *Materials*

Commercially available reagents were used as received. The ligands mbix and mbtx were prepared according to reported procedures [25,26].



Scheme 1. Schematic drawings of ligands.

2.2. *Synthesis of complexes*

2.2.1. Synthesis of [Co(mbtx)(hpht)(H_2O)]$_n$ (1). A mixture of $CoCl_2 \cdot 2H_2O$ (0.0237 g, 0.1 mmol), homophthalic acid (0.0180 g, 0.1 mmol), mbtx (0.0240 g, 0.1 mmol) and LiOH (0.0082 g, 0.2 mmol) was placed in a Teflon-lined stainless steel vessel. The mixture was sealed and heated at 100 °C for 4 days, and then the reaction system was cooled to room temperature. Pink crystals were obtained in 60% yield (based on Co). Elemental analysis (%): Calcd for ($C_{21}H_{20}CoN_6O_5$): C, 50.92; H, 4.07; N, 16.97. Found: C, 50.91; H, 4.09; N, 16.96. IR spectrum (cm^{-1}): 536w, 586w, 647 m, 676 m, 736 m, 775w, 836w, 860w, 892w, 916w, 950w, 1027w, 1091w, 1130 m, 1174w, 1199w, 1203w, 1207 m, 1280 m, 1317w, 1405s, 1523w, 1564s, 3123w, 3126w, 3411s.

2.2.2. Synthesis of [Co(mbix)(hpht)]$_n$ (2). A mixture of $CoCl_2 \cdot 2H_2O$ (0.0236 g, 0.1 mmol), homophthalic acid (0.0179 g, 0.1 mmol), mbix (0.0238 g, 0.1 mmol) and Na_2CO_3 (0.0212 g, 0.1 mmol) was placed in a Teflon-lined stainless steel vessel. The mixture was sealed and heated at 100 °C for 4 days, and then the reaction system was cooled to room temperature. Pink crystals were obtained in 53% yield (based on Co). Elemental analysis (%): Calcd for ($C_{23}H_{20}CoN_4O_4$): C, 58.11; H, 4.24; N, 11.79. Found: C, 58.10; H, 4.25; N, 11.80. IR spectrum (cm^{-1}): IR spectrum (cm^{-1}): 449w, 474w, 501 m, 565 m, 651 m, 671w, 678w, 719w, 748w, 773w, 800 m, 836 m, 862 m, 950 m, 1028w, 1091s, 1153w, 1174w, 1199w, 1243 m, 1272 m, 1363s, 1394s, 1432w, 1452w, 1521 m, 1585s, 1621s, 2898w, 2939w, 2968w, 2985w, 3035w, 3104s, 3428s.

2.3. *Physical measurements and X-ray structural determination*

Elemental analyzes for C, H, and N were performed on an Elementar Vario EL-III elemental analyzer. FT-IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Nicolet Avatar-360 spectrometer. Thermogravimetric analyzes were carried out on a Netzsch STA-409PC analyzer from room temperature to 1000 °C under nitrogen flow at a heating rate of 10 °C/min. X-ray powder diffraction (XRPD) data were collected on a Shimazu XRD-6000 diffractometer at 40 kV, 30 mA for Cu Kα radiation ($\lambda = 1.5406$ Å), with a scan speed of 2° min^{-1} and a step size of 0.02° in 2θ. The calculated XRPD pattern was produced using the Mercury program and single-crystal reflection data.

X-ray diffraction data were collected on a Bruker Smart Apex II CCD equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with SHELXS-97 [27] and refined with SHELXL-97 [28] by full-matrix least-squares techniques on F^2. All nonhydrogen atoms were refined anisotropically and hydrogens anisotropically [29,30]. Hydrogens except for those of water were generated geometrically. The details of the crystal parameters, data collection and refinement for the compounds are summarized in table 1.

3. Results and discussion

3.1. *IR spectroscopy*

Complexes **1** and **2** show intense peaks at 3400 cm^{-1} belonging to O–H stretching band of carboxylate and/or water. The characteristic bands of carboxylate group in the two

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{21}H_{20}CoN_6O_5$	$C_{23}H_{20}CoN_4O_4$
Formula weight	495.36	475.36
Temperature	298(2) K	298(2) K
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a (Å)	14.727(8)	9.3819(8)
b (Å)	8.897(5)	10.6285(11)
c (Å)	16.937(9)	11.8350(12)
α (°)	90.00	78.197(2)
β (°)	100.262(8)	78.773(2)
γ (°)	90.00	64.8030(10)
V (Å^3)	2184.0(2)	1037.62(17)
Z	4	2
D_c (g·cm^{-3})	1.507	1.521
Absorption coefficient (mm)	0.832	0.866
θ range (°)	2.44–25.00	2.50–24.99
Limiting indices	$-17 \leqslant h \leqslant 17$, $-10 \leqslant k \leqslant 10$, $-11 \leqslant l \leqslant 20$	$-10 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-11 \leqslant l \leqslant 14$
F(000)	1020	490
Reflections collected	10,149	5144
Unique reflections	3848[R(int) = 0.0977]	3579[R(int) = 0.0382]
Reflections observed [$I > 2\sigma(I)$]	2137	2678
Data/restraints/parameters	3848/0/298	3579/0/289
Goodness-of-fit on F^2	1.469	1.047
R_1, wR_2 [$I > 2\sigma(I)$]	0.0774, 0.1576[a]	0.0536, 0.1299[b]
R_1, wR_2 (all data)	0.1434, 0.1892	0.0755, 0.1479
Largest diff. peak/hole (e Å^{-3})	0.719/−1.035	0.677/−0.715

[a] $w = 1/[\sigma^2(F_o^2) + (0.0000P)^2]$.
[b] $w = 1/[\sigma^2(F_o^2) + (0.0669P)^2 + (0.2926)P]$, where $P + (F_o^2 + 2F_c^2)/3$.

complexes are at 1564 and 1585 cm^{-1}, respectively, for antisymmetric stretching and 1405 and 1394 cm^{-1}, respectively, for symmetric stretching. The absence of the expected bands at 1685–1715 cm^{-1} for protonated carboxylate illustrates the complete deprotonation during the self-assembly process. Sharper and weaker bands within the 1400–450 cm^{-1} region may correspond to benzene/N-containing ring bending modes.

3.2. *Crystal structure*

Selected geometric parameters for **1** and **2** are given in table 2 and hydrogen bond data are listed in table 3.

3.2.1. The structure of [Co(mbtx)(hpht)(H_2O)]$_n$ (1). Crystallographic analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/c$. As shown in figure 1, the asymmetric unit contains one Co(II), one mbtx, one coordinated water and one completely deprotonated hpht. The Co is in a distorted octahedral coordination sphere where the basal plane is occupied by four oxygens, three from two hpht anions and one from coordinated water; the axes are occupied by two nitrogens from symmetry-related mbtx molecules. The Co–O bond distances are 2.064(3)–2.133(4) Å and the Co–N bond lengths are 2.135(6) and 2.150(6) Å.

The hpht anion links two Co(II) with a separation of 5.426(3) Å, in which the two carboxylates chelate a Co(II), and the ethylic carboxylate coordinates one neighboring

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

Complex 1			
Co(1)–O(2)	2.064(4)	Co(1)–O(3)	2.106(4)
Co(1)–O(4)#1	2.118(4)	Co(1)–O(1W)	2.133(4)
Co(1)–N(6)#2	2.135(6)	Co(1)–N(3)	2.150(6)
O(2)–Co(1)–O(3)	100.54(16)	O(2)–Co(1)–O(4)#1	176.43(19)
O(3)–Co(1)–O(4)#1	78.24(16)	O(2)–Co(1)–O(1W)	88.28(16)
O(3)–Co(1)–O(1W)	171.10(16)	O(4)#1–Co(1)–O(1W)	93.02(15)
O(2)–Co(1)–N(6)#2	95.0(2)	O(3)–Co(1)–N(6)#2	92.32(19)
O(4)#1–Co(1)–N(6)#2	88.39(19)	O(1W)–Co(1)–N(6)#2	85.67(18)
O(2)–Co(1)–N(3)	86.6(2)	O(3)–Co(1)–N(3)	91.49(19)
O(4)#1–Co(1)–N(3)	90.1(2)	O(1W)–Co(1)–N(3)	90.21(18)
N(6)#2–Co(1)–N(3)	175.5(2)		
Complex 2			
Co(1)–O(3)#1	1.952(3)	Co(1)–O(1)	1.971(3)
Co(1)–N(4)#2	2.005(3)	Co(1)–N(2)	2.006(3)
O(3)#1–Co(1)–O(1)	98.78(12)	O(3)#1–Co(1)–N(4)#2	103.99(13)
O(1)–Co(1)–N(4)#2	117.39(12)	O(3)#1–Co(1)–N(2)	110.29(12)
O(1)–Co(1)–N(2)	108.95(12)	N(4)#2–Co(1)–N(2)	115.77(13)

Note: Symmetry codes for **1**: $\#1 = -x+1, y-1/2, -z+1/2$; $\#2 = -x+1, y+1/2, -z+1/2$. for **2**: $\#1 = -x+1, -y+2, -z+1$; $\#2 = x, y+1, z-1$.

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1** and **2**.

D–H···A	d(D-H)	d(H···A)	d(D···A)	∠DHA
Complex 1				
O(1W)–H(1W A)···O(3)#1	0.85	2.39	2.830(6)	112.7
O(1W)–H(1WA)···O(4)#2	0.85	2.28	3.114(6)	166.9
O(1W)–H(1WB)···O(1)#3	0.85	1.96	2.795(6)	166.3
C(8)–H(8A)···O2	0.97	2.50	3.106(8)	120.1
C(11)–H(11)···O1#3	0.93	2.52	3.389(9)	155.9
C(21)–H(21)···O1#3	0.95	2.30	3.136(9)	146.7
Complex 2				
C(16)–H(16B)···O(4)#1	0.97	2.41	3.233(6)	141.9
C(17)–H(17)···O(1)#2	0.93	2.58	3.507(5)	172.6
C(18)–H(18)···O(2)#3	0.93	2.57	3.501(5)	175.2
C(19)–H(19)···O(4)#1	0.93	2.52	3.197(6)	115.5
C(22)–H(22)···O(2)#4	0.93	2.51	3.384(5)	121.8

Note: Symmetry transformation used to generate equivalent atoms for **1**: $\#1 = -x+1, y-1/2, -z+1/2$; $\#2 = x, y-1, z$; $\#3 = -x+1, -y+1, -z+1$. for **2**: $\#1 = -+x, y, z$; $\#2 = 1-x, 2-y, 1-z$; $\#3 = -x, 3-y, 1-z$; $\#4 = -x, 2-y, 1-z$.

Co(II) with a bridging coordination. The mbtx is *cis* conformation (the two triazole rings are on the same sides of the phenyl plane) to connect two Co ions with a separation of 14.198(1) Å. The dihedral angle between triazole planes is 45.9°, and the dihedral angles between the triazole and benzene rings are 73.7° and 86.0°, respectively. The N1–C16–C10 and N4–C19–C12 angles (N1 and N4 separately from the two triazole groups, C16 and C19 from the CH_2 groups between the phenyl ring and triazole ring, C10 and C12 from the phenyl ring) are 115.5 and 109.4°.

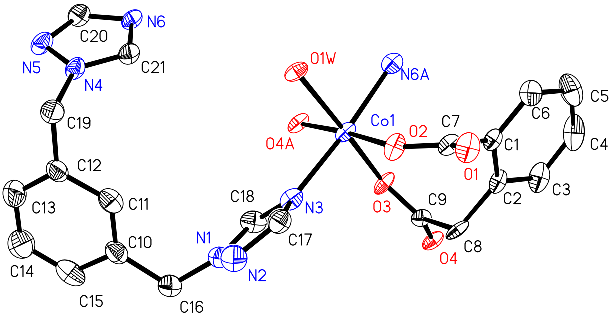


Figure 1. ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probability.

As illustrated in figure 2, each hpht and mbtx links two Co's to give a 1-D helical chain along the *b*-axis. Since both mbtx and hpht are flexible ligands, it is not difficult to possess the same screw pitch in the molecular self-assembly process. As a result, two different helical chains form the heterostranded double-helical structures. Although many double-, triple- and higher-order stranded helical structures have been reported, a heterostranded double-helical structure is really rare [31–33]. For each infinite helical chain, the screw pitch contains two units of Co-ligands and neighboring 1-D helical chains are further linked by one O–H···O and two C–H···O hydrogen bonds to give a 2-D layer structure (figure 3) [34,35]. In these hydrogen bonds, acceptors come from uncoordinated oxygens of carboxylates in hpht (table 3). Each 2-D layer structure has van der Waal's interactions forming the 3D framework (figure S1).

3.2.2. The structure of [Co(mbix)(hpht)]$_n$ (2). Single-crystal X-ray diffraction analysis reveals that **2** crystallizes in triclinic space group *P*-1. As illustrated in figure 4, the asymmetric contains one crystallographically distinct Co(II), one mbix and one completely deprotonated hpht. The Co is in a distorted tetrahedral coordination sphere, coordinated by two nitrogens of two distinct mbix, with Co–N bond lengths of 2.005(3) and 2.006(3) Å, and by two oxygens, one of which belongs to the rigid –COOH of hpht anion and the other is from the flexible $-CH_2COO^-$ group of a different hpht. All Co–O bond separations are 1.952(3)–1.971(3) Å.

The mbix has *trans*-conformation (the two imidazole rings are on opposite sides of the phenyl plane) coordination to connect two Co(II) cations with a separation of 14.198(1) Å, resulting in formation of a 1-D polymeric chain. The dihedral angle between imidazole planes is 44.70°, and dihedral angles between the imidazole and benzene rings are 85.3° and 88.0°, respectively. The N1–C16–C10 and N3–C21–C12 angles (N1 and N3 separately from two triazole groups, C16 and C21 from CH_2 groups between the phenyl ring and triazole ring, C10 and C12 from the phenyl ring) are 112.7° and 112.2°. In **2**, the distance between H24 of imidazole and the centroid of the benzene ring in the same mbtx molecular is 3.50 Å, with the corresponding angle of C24–H24···centroid 106.4° (table 4) indicating weak C–H···π interaction, stabilizing the 1-D polymeric chain [35].

The hpht anion coordinates Co(II) to construct the 1-D molecular ladder, with bridging coordination (figure 5). Separation of two adjacent Co(II) cations bridged by hpht anions is 4.820(1) Å. The distance between H24 and the centroid of the benzene ring of hpht in neighboring 1-D molecular ladder is 3.38 Å, with the corresponding C24–H24···centroid

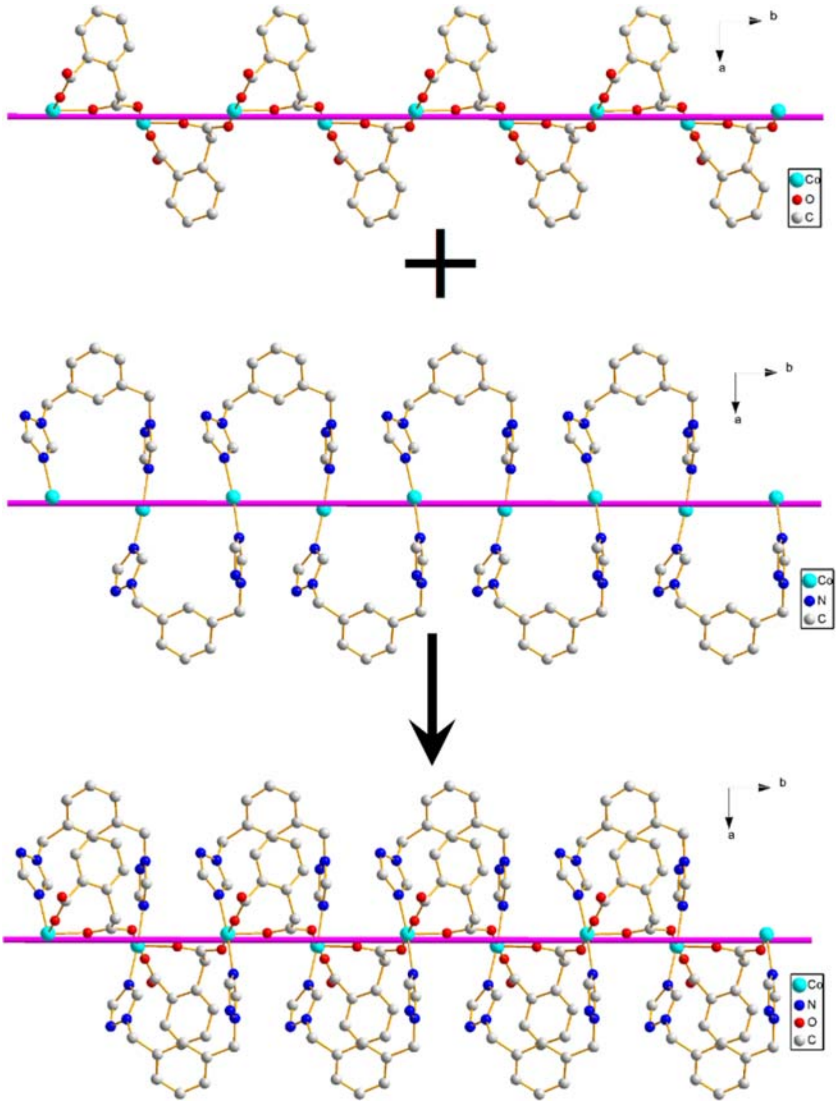


Figure 2. Two different helical chains interwind to heterostranded double-helical structure in **1**.

angle of 156.4° implying C–H···π interactions between two adjacent 1-D molecular ladders. Through these interactions, adjacent 1-D molecular ladders are stacked to give a 2-D layer structure (figure 6).

The 3D supramolecular framework of **2** illustrated in figure S2 has four C–H···O hydrogen bonds between two uncoordinated oxygens in hpht and the imidazole C–H as well as methylene C–H of mbix in an adjacent 2-D layer, with C···O distances 3.197(6)–3.501(5) Å. Such hydrogen bonds further link the 2-D layers to provide a 3D framework (figure S2).

Although the syntheses of **1** and **2** are almost the same, the crystal structures are different. Differences may be due to C24 on the 2-position of imidazole, which is in the

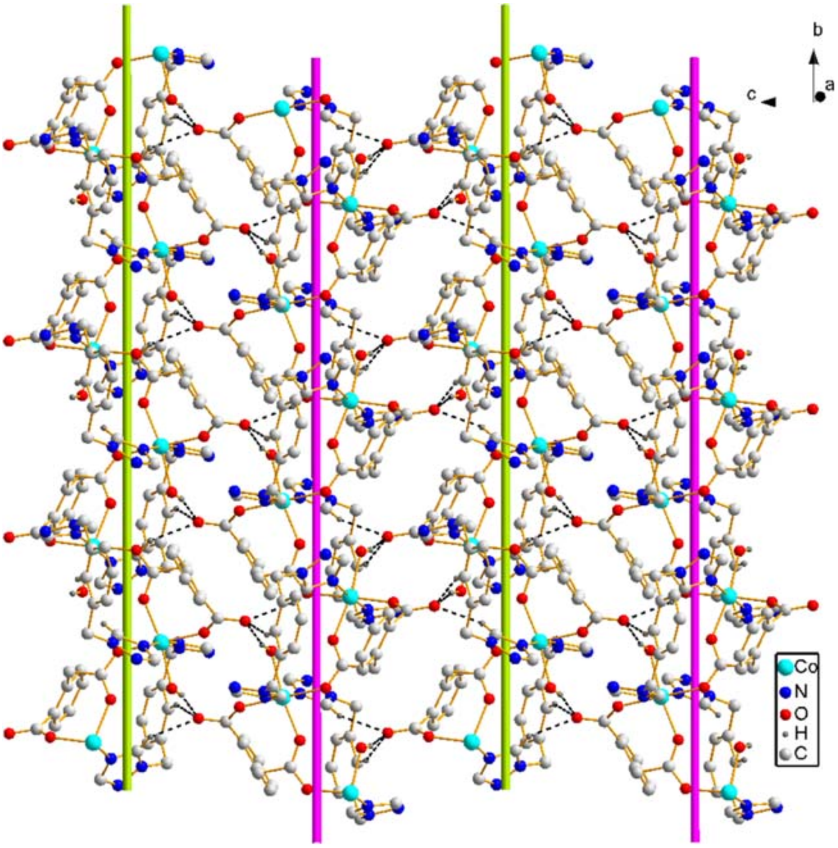


Figure 3. 2-D layer structure of **1** linked by adjacent 1-D helical chain through hydrogen bonds indicated by dashed lines; other hydrogens are omitted for clarity.

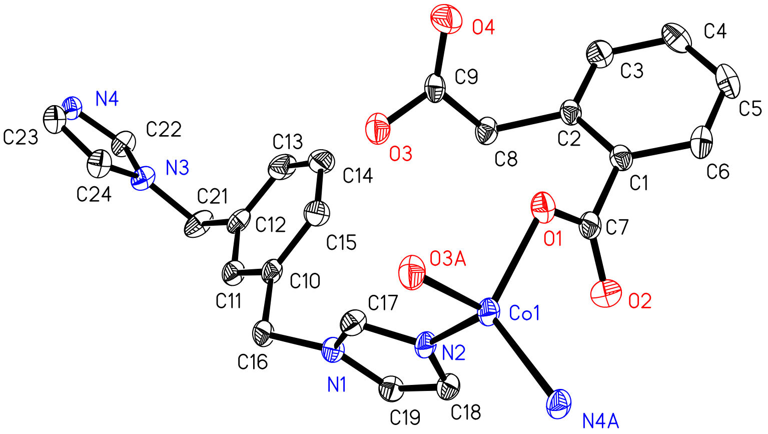


Figure 4. ORTEP drawing of **2** showing the labeling of atoms with thermal ellipsoids at 30% probability.

Table 4. Bond lengths (Å) and angles (°) of C–H· · ·π interactions in **1** and **2**.

	d(C–H)	d(H· · ·centroid)	∠C–H···centroid
Complex 1			
C4–H4· · ·centroid	0.93	3.44	105.8
Complex 2			
C24#1–H24#1· · ·centroid#2	0.93	3.50	106.4
C24#1–H24#1· · ·centroid#3	0.93	3.38	156.4

Note: Symmetry codes for **2**: $\#1 = 1 + x, y, z$; $\#2 = x, -2 + y, 1 + z$; $\#3 = x, -1 + y, 1 + z$.

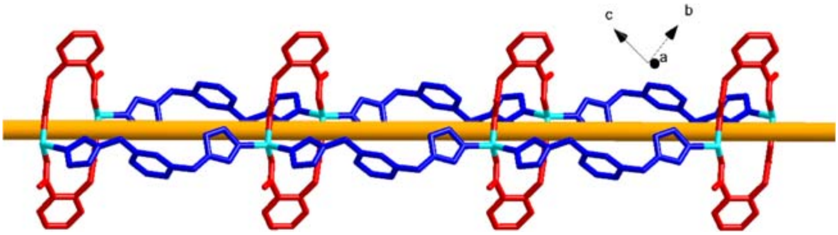


Figure 5. Perspective view of the 1-D ladder network of **2**.

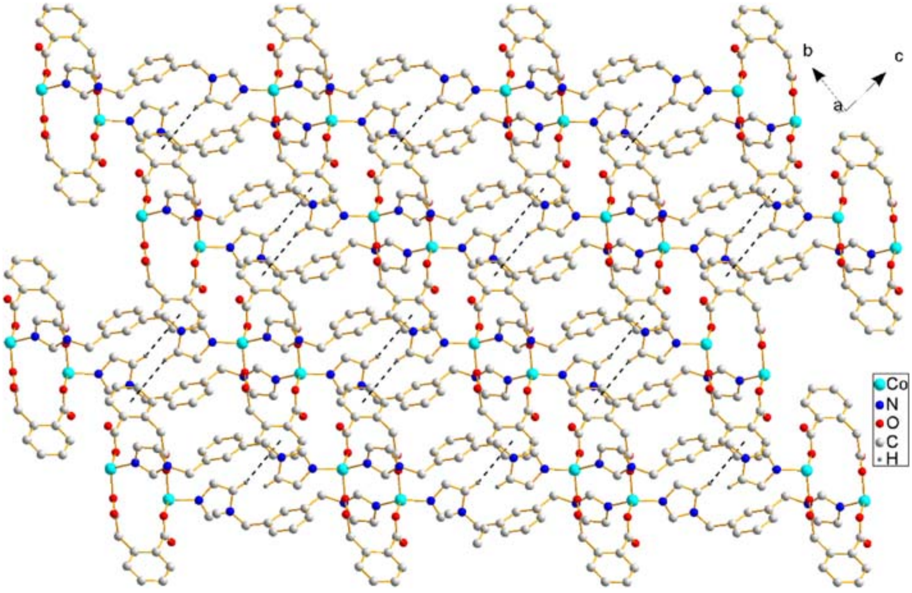


Figure 6. Front (a) and side (b) view of the 2-D layer structure linked by adjacent 1-D molecular ladders through C–H· · ·π interactions indicated by dashed lines in **2**; other hydrogens are omitted for clarity.

equivalent position with N5 of mbtx, forming C–H· · ·π interactions with the benzene ring in the corresponding mbix and benzene rings of hpht anions in adjacent 1-D molecular ladders, facilitating the *trans*-conformation of mbix and also stabilizing the stacking of these 1-D chains to form its high-dimensional structure.

Comparing with other coordination polymers of cobalt and aromatic rigid polycarboxylates [36,37], we consider the interesting different structures in the title complexes, such as molecular ladder, double-helical chain are mainly attributed to flexibility of hpht allowing coordination to cobalt with flexible modes.

3.3. *XRPD and thermogravimetric analysis*

The homogeneities of **1** and **2** are confirmed by XRPD analyzes (figure S3). Their peaks are consistent with those calculated from X-ray single-crystal diffraction data. The difference in intensities may be due to preferred orientation of the microcrystalline powder samples.

Thermogravimetric diagram (figure S4) of **1** indicates it is stable to 200 °C. The first weight loss occurred between 200 and 258 °C, attributed to loss of water, with weight loss of 3.3% in agreement with calculated (3.6%). Above 258 °C, successive weight-loss steps correspond to release of organic molecules and the collapse of the framework. The framework of **2** was of higher thermal stability, stable up to 304 °C. Then, successive weight loss corresponded to release of organic ligands and collapse of the framework.

4. Conclusion

$[Co(mbtx)(hpht)(H_2O)]_n$ (**1**) and $[Co(mbix)(hpht)]_n$ (**2**) were synthesized and their structures were determined by single-crystal X-ray diffraction. Complex **1** is a 1-D heterostranded double-helical chain resulting from bridging hpht and mbtx, and the 1-D chains are further self-assembled into a 2-D layer through hydrogen bonds. Complex **2** shows a 1-D molecular ladder linked through C–H· · ·π interactions to give a 2-D layer structure, further linked through C–H· · ·O hydrogen bonds to form the 3D framework. The structural diversities between **1** and **2** are caused by difference of btx and bix. The choice of auxiliary ligands is essential to form the expected structure. Developing systematic methodologies for synthesizing materials by using such flexible ligands can afford an opportunity to further enrich the structures and properties of coordination polymers and to provide more understanding for the directional synthesis of target complexes. Further systematic studies for the design and synthesis of such materials with H_2hpht and other auxiliary ligands are underway in our laboratory. This work may provide a strategy for preparing such MOFs with interesting structures.

Supplementary material

3D packing diagrams, XPRD patterns and TGA curves of **1** and **2**. X-ray crystallographic files in CIF format for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with deposition numbers CCDC 862175 and 862178. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223-336-033 or Email: deposit@ccdc.cam.ac.uk.

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