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Dicarboxylate anion-dependent assembly of Co(II) and Ni(II) coordination polymers with 1,2-bis(4-pyridyl)ethane

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Abstract

Using mixed ligands and hydrothermal reactions, five new coordination polymers, $[Co(o\text{-}CCA)(bpe)(H_2O)]_n \cdot 0.25nCH_3OH$ (**1**), $[Ni(o\text{-}CCA)(bpe)(H_2O)]_n \cdot 0.5nH_2O$ (**2**), $[M(p\text{-}CCA)(bpe)_{1.5}(H_2O)]_n \cdot nH_2O$ (M = Co, (**3**); Ni, (**4**)) and $[Co(o\text{-}BDC)(bpe)(H_2O)]_n \cdot nH_2O$ (**5**) (H_2CCA = carboxycinnamic acid; bpe = 1,2-bis(4-pyridyl)ethane; $o\text{-}H_2BDC$ = 1,2-benzenedicarboxylic acid) were obtained. Complexes **1**–**4** possess complicated 3D metal-organic frameworks, but different position of functional dicarboxylate groups results in different architecture, forming diversity of structures. **1** and **2**, **3** and **4** are isomorphous, respectively, in which solvent molecules are clatharated. When *o*-BDC instead of CCA was used, complex **5** was obtained, which is of (4,4) 2D grid-like layers with cavities. Thermal stabilities of complexes **1**–**4** were discussed.

Keywords: Carboxycinnamic acid; Co(II) and Ni(II) complexes; Benzenedicarboxylic acid; Mixed ligand; Coordination polymer

1. Introduction

Metal-organic coordination polymers have received increasing interest in recent decades, not only because of their intriguing variety of architectures and topologies, but also because of their potential applications in catalysis [1], molecular separation [2], gas storage [3] and sensors [4]. In constructing coordination polymers, multifunctional ligands such as a variety of polyacids, 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethane are used as linkers, forming extended networks having grid [5], honeycomb [6], brick wall [7] and other geometries [8]. The assembly of metal ions and ligands in coordination polymers can be regarded as a programmed system in which the stereo and interactive information stored in the ligands is read by the metal ions through the algorithm defined by their coordination geometry [9]. Hence, the selection or design of a suitable ligand is crucial to the construction of coordination polymers. Carboxycinnamic acid (H_2CCA) has common characteristics of exo-dicarboxylic acids: (a) it has two carboxyl groups that may be completely or partially deprotonated, resulting in rich coordination modes. (b) It can act not only as hydrogen bond acceptor, but also as hydrogen bond donor, depending on the number of deprotonated carboxyl groups. Moreover, H_2CCA possesses two asymmetric carboxylate groups, acrylate and formate groups, and the former one is flexible and can rotate to some degree. However, the coordination chemistry of H_2CCA is seldom reported. Kurmoo et al. reported one cobalt(II) complex of *p*-carboxycinnamic acid ($p\text{-}H_2CCA$) $[Co(p\text{-}CCA)(H_2O)_2]_n$ consisting of square-grid layers [10]. And Cao et al. reported four cadmium(II) complexes of *o*-carboxycinnamic acid ($o\text{-}H_2CCA$) [11]. By introducing different auxiliary ligands, the four complexes are assembled from single-stranded helical chains, double-stranded zigzag chains to 2D layers. Benzenedicarboxylic acid (H_2BDC) is one of the best rigid ligands used to construct coordination polymers [12]. In order to study how the asymmetric and the symmetric dicarboxylate groups impact the dimension and structure

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of the complexes, we selected *p*-H_2CCA, *o*-H_2CCA, *p*-H_2BDC and *o*-H_2BDC, together with 1,2-bis(4-pyridyl)ethane (bpe) as linkers, to assemble coordination polymers. Under hydrothermal conditions, we obtained six coordination polymers, $[Co(o\text{-}CCA)(bpe)(H_2O)]_n \cdot 0.25nCH_3OH$ (**1**), $[Ni(o\text{-}CCA)(bpe)(H_2O)]_n \cdot 0.5nH_2O$ (**2**), $[M(p\text{-}CCA)(bpe)_{1.5}(H_2O)]_n \cdot nH_2O$ (M = Co, (**3**); Ni, (**4**)), $[Co(o\text{-}BDC)(bpe)(H_2O)]_n \cdot nH_2O$ (**5**) and $[Co(p\text{-}BDC)(bpe)]_n$ (**6**). Complex **6** is the same to that reported by Fu et al. [13], therefore, we report the syntheses and characterizations of five new complexes **1**–**5**.

2. Experimental

2.1. Materials and apparatus

All reagents were used as received without further purification. The C, H, N microanalyses were carried out with a Vario EL elemental analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique.

2.2. Synthesis

2.2.1. Synthesis of $[Co(o\text{-}CCA)(bpe)(H_2O)]_n \cdot 0.25nCH_3OH$ (1)

A mixture of *o*-H_2CCA (0.02 g, 0.1 mmol), $CoCl_2 \cdot 6H_2O$ (0.024 g, 0.1 mmol), bpe (0.018 g, 0.1 mmol), CH_3OH (5 mL) and deionized water (5 mL) was sealed in a Teflon-lined stainless vessel (25 mL), and heated at 140 °C for 72 h, then cooled slowly to room temperature. Yield: 0.037 g (80.4%). *Anal.* Calc. for $C_{22.25}H_{21}N_2O_{5.25}Co$: C, 58.13; H, 4.57; N, 6.10. Found: C, 58.31; H, 4.81; N, 6.14%. IR data (KBr pellet, cm^{-1}): 3442s, 3065m, 1637m, 1616s, 1571m, 1546s, 1419s, 1394s, 1285w, 1224w, 1071w, 1022w, 973w, 821w, 772m, 758m.

2.2.2. Synthesis of $[Ni(o\text{-}CCA)(bpe)(H_2O)]_n \cdot 0.5nH_2O$ (2)

A mixture of *o*-H_2CCA (0.02 g, 0.1 mmol), $NiCl_2 \cdot 6H_2O$ (0.024 g, 0.1 mmol), bpe (0.018 g, 0.1 mmol), NaOH aqueous solution (0.3 mL, 0.65 mol L^{-1}) and deionized water (5 mL) was sealed in a Teflon-lined stainless vessel (25 mL), and heated at 140 °C for 72 h, then cooled slowly to room temperature. Columnar crystals were obtained, washed with water and ethanol, and dried in air. Yield: 0.026 g (56.5%). *Anal.* Calc. for $C_{22}H_{21}N_2O_{5.5}Ni$: C, 57.38; H, 4.56; N, 6.09. Found: C, 57.52; H, 4.85; N, 5.94%. IR data (KBr pellet, cm^{-1}): 3454m, 3068m, 1637m, 1618s, 1571m, 1543s, 1411s, 1394s, 1285w, 1225w, 1071w, 973m, 821m, 772m, 759m.

2.2.3. Synthesis of $[Co(p\text{-}CCA)(bpe)_{1.5}(H_2O)]_n \cdot nH_2O$ (3)

The synthesis of complex **3** followed the similar procedure as for complex **2** except using *p*-H_2CCA instead of *o*-H_2CCA. Yield: 0.025 g (44.5%). *Anal.* Calc. for $C_{28}H_{28}N_3O_6Co$: C, 59.84; H, 4.99; N, 7.48. Found: C, 59.58; H, 5.17; N, 7.50%. IR data (KBr pellet, cm^{-1}): 3441s, 2930m, 1616s, 1559m, 1425m, 1376s, 1224m, 1070w, 1020m, 982w, 816m, 791m, 605w, 551m.

2.2.4. Synthesis of $[Ni(p\text{-}CCA)(bpe)_{1.5}(H_2O)]_n \cdot nH_2O$ (4)

The synthesis of complex **4** followed the similar procedure as for complex **3**. Yield: 0.026 g (46.3%). *Anal.* Calc. for $C_{28}H_{28}N_3O_6Ni$: C, 59.87; H, 5.35; N, 7.48. Found: C, 59.56; H, 5.06; N, 7.42%. IR data (KBr pellet, cm^{-1}):

Table 1
Crystal data and structure refinement parameters for **1**–**5**

	1	2	3	4	5
Chemical formula	$C_{22.25}H_{21}N_2O_{5.25}Co$	$C_{22}H_{21}N_2O_{5.50}Ni$	$C_{28}H_{28}N_3O_6Co$	$C_{28}H_{28}N_3O_6Ni$	$C_{20}H_{20}N_2O_6Co$
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Pccn*	*Pccn*	*C*2/*c*	*C*2/*c*	*P*2$_1$/*n*
a (Å)	19.511(3)	19.459(2)	21.397(5)	21.314(8)	13.627(2)
b (Å)	13.258(2)	13.166(1)	14.159(3)	14.144(5)	8.809(1)
c (Å)	16.241(3)	16.118(1)	20.368(5)	20.383(7)	15.457(2)
α (°)	90	90	90	90	90
β (°)	90	90	120.154(4)	120.298(5)	90.720(2)
γ (°)	90	90	90	90	90
V (Å^3)	4201.3(1)	4129.6(6)	5336(2)	5305(3)	1855.6(4)
Z	8	8	8	8	4
F(000)	1900	1912	2336	2344	916
D_{calc} (mg m^{-3})	1.452	1.480	1.398	1.405	1.587
Formula weight	459.34	460.12	561.46	561.24	443.31
T (°C)	293(2)	293(2)	293(2)	293(2)	293(2)
θ Range (°)	1.86–26.40	1.87–25.01	1.83–25.01	1.82–25.01	1.98–26.32
Absorption coefficient (mm^{-1})	0.855	0.979	0.690	0.779	0.967
Goodness-of-fit on F^2	0.995	1.093	1.029	1.146	1.026
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0468$, $wR_2 = 0.1093$	$R_1 = 0.0413$, $wR_2 = 0.1052$	$R_1 = 0.0699$, $wR_2 = 0.1391$	$R_1 = 0.0644$, $wR_2 = 0.1564$	$R_1 = 0.0341$, $wR_2 = 0.0799$

3456s, 2972m, 1616s, 1560m, 1425m, 1377s, 1232m, 1070w, 1022m, 981w, 817m, 791m, 605w, 551m.

2.2.5. Synthesis of $[Co(o\text{-}BDC)(bpe)(H_2O)]_n \cdot nH_2O$ (**5**)

The synthesis of complex **5** followed the similar procedure as for complex **2** except using o-H_2BDC instead of o-H_2CCA. Yield: 0.023 g (51.9%). *Anal.* Calc. for $C_{20}H_{20}N_2O_6Co$: C, 54.14; H, 4.51; N, 6.32. Found: C, 54.12; H, 4.55; N, 6.37%. IR data (KBr pellet, cm^{-1}): 3406m, 3068w, 2926w, 2856w, 1640m, 1610m, 1578s, 1539s, 1438m, 1385s, 1227w, 1072w, 829m, 768m, 717m, 693m.

2.3. X-ray diffraction determination

Diffraction intensities for the six complexes were collected at 293 K on a Bruker SMART 1000 CCD diffractometer employing graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL 97 program [14]. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were initially located in a difference Fourier map. The O–H distances were then fixed at 0.85 Å and $U_{iso}(H)$ of the hydrogen atoms of H_2O was 1.5 times of $U_{eq}(O)$ in the next refinement. The crystallographic data for complexes **1**–**5** are listed in Table 1, and selected bond lengths (Å) and bond angles (°) in Tables 2 and 3.

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

1			
Co(1)–O(1)	2.053(3)	Co(1)–O(5)	2.156(3)
Co(1)–O(3)#1	2.149(3)	Co(1)–N(1)	2.158(4)
Co(1)–O(4)#1	2.169(3)	Co(1)–N(2)	2.106(4)
O(1)–Co(1)–O(3)#1	103.6(1)	O(5)–Co(1)–O(4)#1	87.1(1)
O(1)–Co(1)–O(4)#1	164.1(1)	O(5)–Co(1)–N(1)	175.9(1)
O(1)–Co(1)–O(5)	89.6(1)	N(1)–Co(1)–O(4)#1	96.0(1)
O(1)–Co(1)–N(1)	88.2(1)	N(2)–Co(1)–O(3)#1	157.9(1)
O(1)–Co(1)–N(2)	98.9(1)	N(2)–Co(1)–O(4)#1	96.7(1)
O(3)#1–Co(1)–O(4)#1	61.0(1)	N(2)–Co(1)–O(5)	90.1(1)
O(3)#1–Co(1)–O(5)	91.1(1)	N(2)–Co(1)–N(1)	86.9(2)
O(3)#1–Co(1)–N(1)	92.7(1)		
2			
Ni(1)–O(1)	2.045(2)	Ni(1)–O(5)	2.100(2)
Ni(1)–O(3)#1	2.129(2)	Ni(1)–N(1)	2.109(3)
Ni(1)–O(4)#1	2.108(2)	Ni(1)–N(2)	2.061(3)
O(1)–Ni(1)–O(3)#1	101.3(1)	O(5)–Ni(1)–O(4)#1	87.1(1)
O(1)–Ni(1)–O(4)#1	163.3(1)	O(5)–Ni(1)–N(1)	177.3(1)
O(1)–Ni(1)–O(5)	90.5(1)	N(1)–Ni(1)–O(3)#1	92.8(1)
O(1)–Ni(1)–N(1)	87.4(1)	N(2)–Ni(1)–O(3)#1	160.9(1)
O(1)–Ni(1)–N(2)	97.9(1)	N(2)–Ni(1)–O(4)#1	98.7(1)
O(4)#1–Ni(1)–O(3)#1	62.2(1)	N(2)–Ni(1)–O(5)	90.8(1)
O(4)#1–Ni(1)–N(1)	95.4(1)	N(2)–Ni(1)–N(1)	87.7(1)
O(5)–Ni(1)–O(3)#1	89.3(1)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $y+1/2$, $-z+1/2$.

Table 3
Selected bond lengths (Å) and angles (°) for complexes **3**, **4** and **5**

3			
Co(1)–O(1)	2.140(4)	Co(1)–N(1)	2.124(4)
Co(1)–O(3)	2.113(4)	Co(1)–N(2)#1	2.149(4)
Co(1)–O(5)	2.072(4)	Co(1)–N(3)	2.140(4)
O(1)–Co(1)–N(2)#1	84.6(2)	O(5)–Co(1)–N(2)#1	95.1(2)
O(3)–Co(1)–O(1)	175.9(2)	O(5)–Co(1)–N(3)	176.6(2)
O(3)–Co(1)–N(1)	88.8(2)	N(1)–Co(1)–N(3)	88.8(2)
O(3)–Co(1)–N(2)#1	97.4(2)	N(1)–Co(1)–O(1)	89.5(2)
O(3)–Co(1)–N(3)	89.2(2)	N(3)–Co(1)–O(1)	94.4(2)
O(5)–Co(1)–O(1)	88.9(2)	N(1)–Co(1)–N(2)#1	171.9(2)
O(5)–Co(1)–O(3)	87.4(1)	N(3)–Co(1)–N(2)#1	86.1(2)
O(5)–Co(1)–N(1)	90.4(2)		
4			
Ni(1)–O(1)	2.127(3)	Ni(1)–N(1)	2.089(4)
Ni(1)–O(3)	2.111(3)	Ni(1)–N(2)#1	2.116(4)
Ni(1)–O(5)	2.056(4)	Ni(1)–N(3)	2.111(4)
O(1)–Ni(1)–N(2)#1	85.1(1)	O(5)–Ni(1)–N(2)#1	95.0(2)
O(3)–Ni(1)–O(1)	176.3(1)	O(5)–Ni(1)–N(3)	176.4(1)
O(3)–Ni(1)–N(1)	88.0(2)	N(1)–Ni(1)–O(1)	89.9(2)
O(3)–Ni(1)–N(2)#1	97.2(2)	N(1)–Ni(1)–N(2)#1	173.0(2)
O(3)–Ni(1)–N(3)	89.2(2)	N(1)–Ni(1)–N(3)	89.1(2)
O(5)–Ni(1)–O(1)	89.6(1)	N(3)–Ni(1)–O(1)	93.8(2)
O(5)–Ni(1)–O(3)	87.4(1)	N(3)–Ni(1)–N(2)#1	86.4(2)
O(5)–Ni(1)–N(1)	89.8(2)		
5			
Co(1)–O(1)	2.055(2)	Co(1)–O(5)	2.156(2)
Co(1)–O(3)	2.152(2)	Co(1)–N(1)	2.161(2)
Co(1)–O(4)#1	2.066(2)	Co(1)–N(2)#2	2.151(2)
O(1)–Co(1)–O(3)	89.35(6)	O(4)#1–Co(1)–O(5)	97.06(7)
O(1)–Co(1)–O(4)#1	172.2(6)	O(4)#1–Co(1)–N(1)	89.90(7)
O(1)–Co(1)–O(5)	89.33(7)	O(4)#1–Co(1)–N(2)#2	86.71(7)
O(1)–Co(1)–N(1)	94.97(7)	O(5)–Co(1)–N(1)	87.11(7)
O(1)–Co(1)–N(2)#2	88.56(7)	N(2)#2–Co(1)–O(3)	90.18(7)
O(3)–Co(1)–O(5)	177.6(7)	N(2)#2–Co(1)–O(5)	91.82(7)
O(3)–Co(1)–N(1)	90.98(7)	N(2)#2–Co(1)–N(1)	176.3(8)
O(4)#1–Co(1)–O(3)	84.41(6)		

Symmetry transformations used to generate equivalent atoms: (#1) $-x+1/2$, $y+1/2$, $-z+1/2$ for **3** and **4**, (#1) $-x+5/2$, $y+1/2$, $-z+1/2$; (#2) $x+1$, y, z for **5**.

3. Results and discussion

3.1. Description of the structures

Complexes **1** and **2**, **3** and **4** are two isomorphous pairs except that in complexes **1** and **2**, the clathrated guest molecules are different (CH_3OH for complex **1** and H_2O for complex **2**). And because of the different radii of the Co(II) and Ni(II) ions, there are corresponding differences in the distances of M–O and M–N (M = Ni or Co) in the two paired complexes, however only the structures of **1**, **3** and **5** will be described in detail.

3.1.1. $[Co(o\text{-}CCA)(bpe)(H_2O)]_n \cdot 0.25nCH_3OH$ (**1**)

The coordination environment of Co(II) ion in complex **1** is shown in Fig. 1. Each Co(II) ion is six-coordinated by three oxygen atoms (O(1), O(3A), O(4A)) of two o-CCA anions, one oxygen atom (O(5)) of water molecule and two nitrogen atoms (N(1), N(2)) of two bpe ligands,

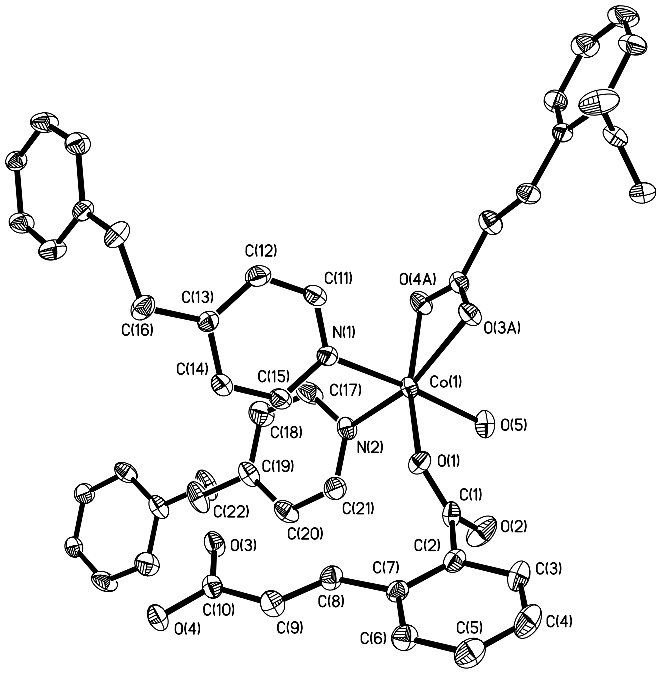


Fig. 1. Coordination environment of Co(II) ion in complex **1** with 30% thermal ellipsoids, all hydrogen atoms and crystal water molecules are omitted for clarity.

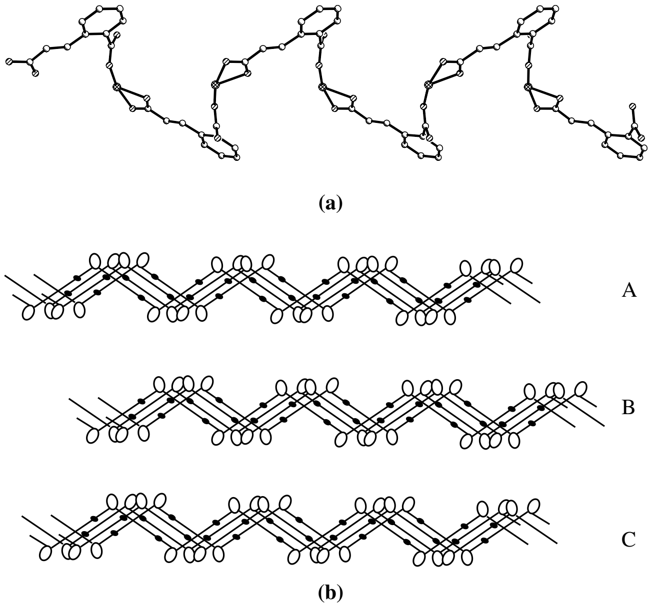
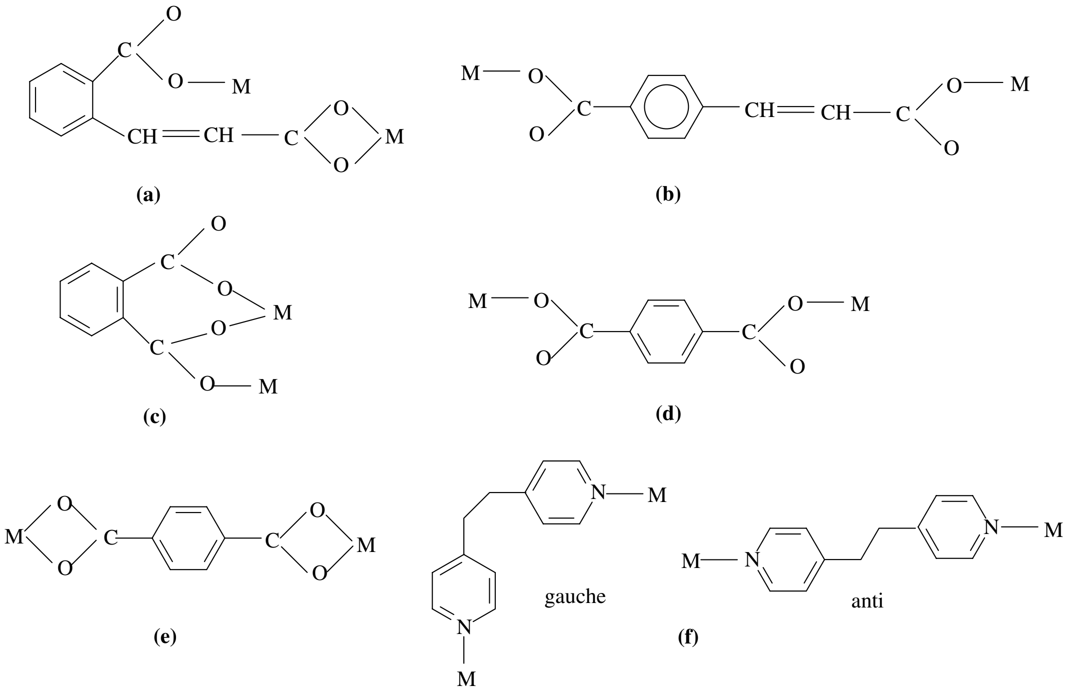


Fig. 2. (a) 1D zigzag chain constructed by *o*-CCA linking Co(II) ions and (b) the simplified representation of the 2D layers in complex **1** viewed along the *c* axis.

leading to a distorted octahedron. There is one kind of crystallographically independent *o*-CCA anion, acting as a tridentate ligand (see Scheme 1a). The formate group of the *o*-CCA anion adopts a monodentate mode, while the acrylate adopts a chelating-bidentate mode, and thus the *o*-CCA anion bridges two Co(II) ions, and the Co···Co distance is 7.181 Å (7.157 Å for Ni). All Co(II) ions are linked by *o*-CCA anions into 1D infinite zigzag chains, as shown in Fig. 2(a). Along the *c* axis, the chains are parallel to each other, forming 2D layers (see Fig. 2(b) A, B, C).

In complex **1**, bpe molecules adopt two conformations, anti and gauche forms (see Scheme 1f). They all act as bidentate ligands, bridging Co(II) ions into wave-like chains, as shown in Fig. 3. All these chains are parallel to



Scheme 1. The coordination modes of the ligands in complexes **1**–**6**.

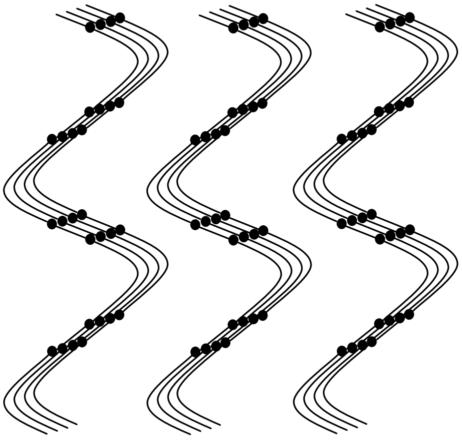


Fig. 3. The simplified representation of wave-like chains constructed by bpe linking Co(II) ions in complex **1** viewed along the *b* axis.

each other, forming 2D layers (see Fig. 3 A, B, C). The chains shown in Figs. 2 and 3 intersect at Co(II) ions and thus form a 3D metal-organic framework, in which free methanol molecules are clathrated (see Fig. 4, crystal water molecules in complex **2**). Hydrogen bonds are observed between the coordination water molecules and the uncoordinated carboxylate oxygen atoms ($H\cdots O = 1.831$ Å, $O\cdots O = 2.662$ Å, $\angle OHO = 164.2°$), and between the free methanol molecules and the uncoordinated carboxylate oxygen atoms ($H\cdots O = 1.895$ Å, $O\cdots O = 2.738$ Å, $\angle OHO = 170.8°$), which brings further stability for the structure.

3.1.2. $[Co(p\text{-}CCA)(bpe)_{1.5}(H_2O)]_n \cdot nH_2O$ (3)

Complex **3** possesses a 3D metal-organic framework with clathrated free water molecules. There is only one metal environment in complex **3**, as shown in Fig. 5. The coordination geometry around each Co(II) ion, comprising N_3O_3 from two *p*-CCA anions, one water molecule and three bpe molecules, can be described as a distorted octahedron. The oxygen atom (O5) of water molecule and the nitrogen atom (N3) of bpe ligand occupy the axial position. There is one kind of crystallographically independent *p*-CCA anion, acting as a bidentate ligand (see Scheme 1b). Both carboxylate groups of *p*-CCA anion adopt a monodentate mode, bridging two Co(II) ions, and the $Co\cdots Co$ distance is 7.657 Å (7.641 Å for Ni). In complex **3**, *p*-CCA anions are disordered and the occupancy is 0.5. All Co(II) ions are linked by *p*-CCA anions into 1D straight infinite chains, as shown in Fig. 6(a). The chains are parallel to each other, forming 2D layers, as shown in Fig. 6(b) A, B, C and D.

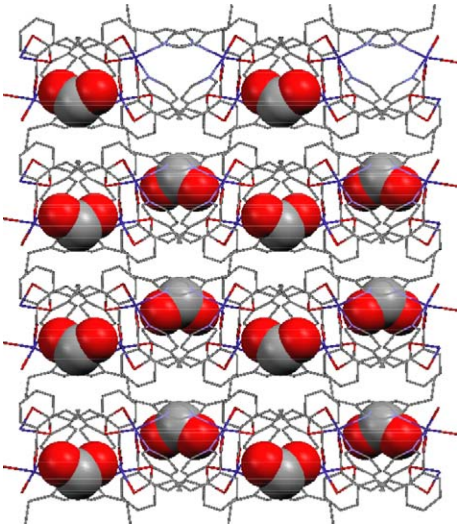


Fig. 4. The 3D network of complex **1** viewed along the *a* axis (the space filling diagram represents the clathrated methanol molecules).

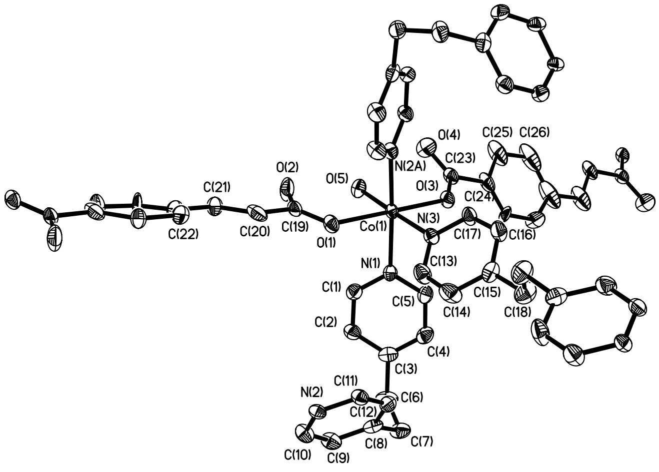
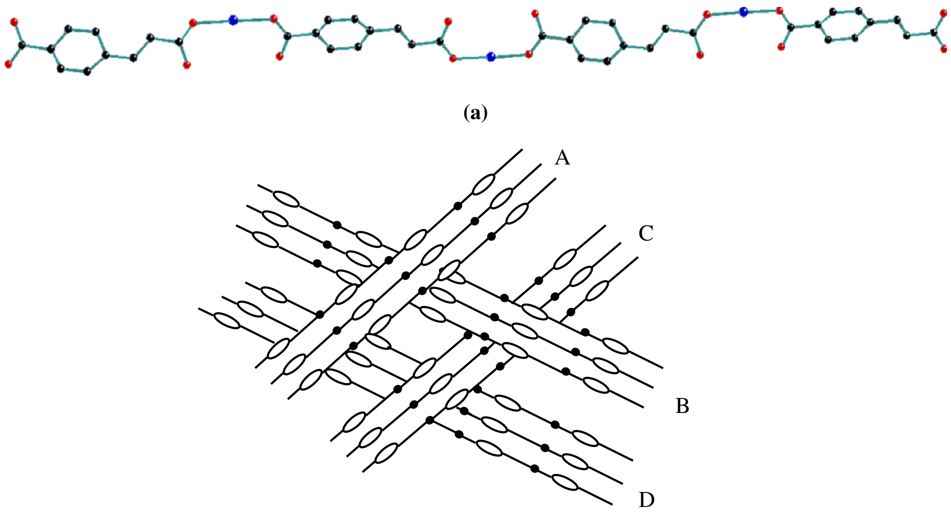


Fig. 5. Coordination environment of Co(II) ion in complex **3** with 30% thermal ellipsoids, all hydrogen atoms and crystal water molecule are omitted for clarity.

In complex **3**, bpe ligands adopt two conformations, and act as bidentate ligands, too. All Co(II) ions are bridged by bpe ligands to form 2D brick-wall-like grids, as shown in Fig. 7. The chains shown in Fig. 6 and grids shown in Fig. 7 intersect at Co(II) ions, and thus form a 3D complicated metal-organic framework. And free water molecules are clathrated. There are hydrogen bonds between the coordinated/free water molecules and the uncoordinated carboxylate oxygen atoms ($H\cdots O = 1.887$–2.767 Å, $O\cdots O = 2.583$–2.892 Å, $\angle OHO = 128.5°$–$138.0°$), which stabilizes the structure.

3.1.3. $[Co(o\text{-}BDC)(bpe)(H_2O)]_n \cdot nH_2O$ (5)

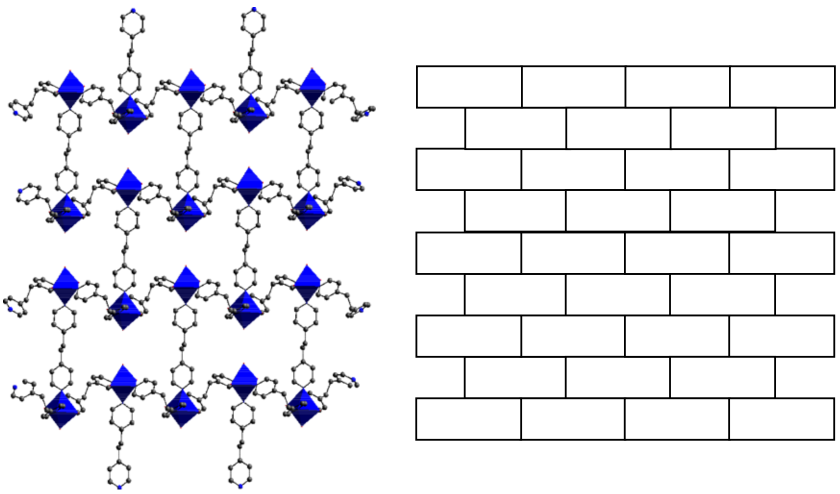
There is only one kind of metal environment in complex **5** (see Fig. 8). Each Co(II) ion is coordinated by three oxygen atoms (O(1), O(3), O(4A)) of two *o*-BDC anions, one oxygen atom (O(5)) of coordinated water molecule and two nitrogen atoms (N(1), N(2A)) of two bpe ligands. The coordination geometry can be described as a distorted octahedron. In complex **5**, *o*-BDC anion adopts a tridentate mode, as shown in Scheme 1c. One carboxylate group adopts a bridging-bidentate mode, and the other adopts a monodentate mode, thus linking two Co(II) ions, in which the $Co\cdots Co$ distance is 5.290 Å. All bpe ligands are in



(a)

(b)

Fig. 6. (a) 1D chain constructed by *p*-CCA linking Co(II) ions and (b) the simplified representation of the 2D layers in complex **3**.



(a) (b)

Fig. 7. (a) The brick-wall-like grids constructed by bpe linking Co(II) ions in complex **3** and (b) the brick-wall scheme of Co(II)-bpe linking assembly in complex **3**.

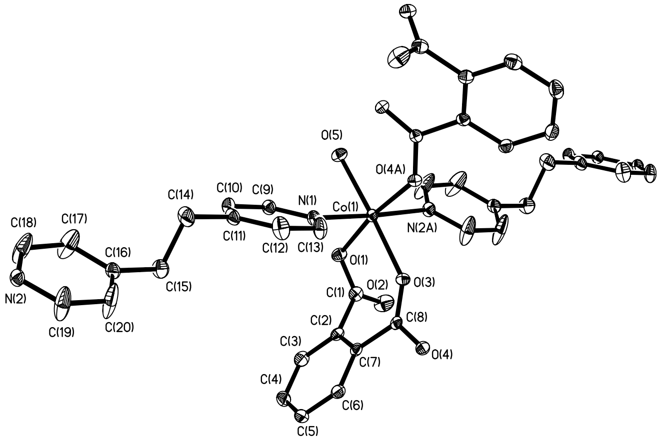


Fig. 8. The coordination environment of Co(II) ion in complex **5** with 30% thermal probability, all hydrogen atoms are omitted for clarity.

anti-form and act as bidentate ligands. Both *o*-BDC anions and bpe ligands link Co(II) ions into (4,4) 2D grid-like layers with cavity of 13.627×5.290 Å. These layers are stacked parallel along the *c* axis exhibiting the ABABAB sequence (see Fig. 9(a)). Crystal water molecules are located between the layers, as shown in Fig. 9(b). There are hydrogen bonds between the coordinated/crystal water molecules and carboxylate oxygen atoms ($\mathrm{H}\cdots\mathrm{O} = 2.110$–$2.311$ Å, $\mathrm{O}\cdots\mathrm{O} =$ 2.880–2.972 Å, $\angle\mathrm{OHO} = 134.4°$–$163.2°$), and between the coordinated water molecules and crystal water molecules ($\mathrm{H}\cdots\mathrm{O} = 2.121$ Å, $\mathrm{O}\cdots\mathrm{O} = 2.924$ Å, $\angle\mathrm{OHO} = 156.7°$).

3.1.4. Comparison of the structures

From the above descriptions, it is obvious that the geometry of ligands has a significant effect on the formation and

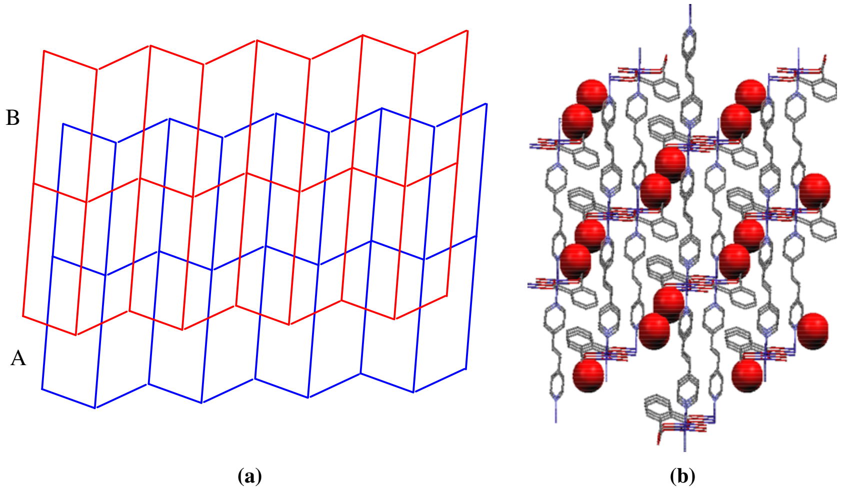


Fig. 9. (a) The simplified representation of 2D layers of complex **5** and (b) the 3D network of complex **5** viewed along the *b* axis (the red balls represent crystal water molecules). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

structure of the complexes. Complexes **1**–**4** all possess 3D metal-organic frameworks, while complexes **5** is of (4,4) 2D grid-like layers with cavities, and complex **6** is of 3D cuboidal box-like structure [13]. This may be attributed to flexible CCA ligands in complexes **1**–**4** and rigid BDC ligands in complexes **5** and **6**, respectively. The combination of mixed flexible ligands such as CCA and bpe in the construction of coordination polymers may result in complicated structure, while mixed rigid and flexible ligands such as BDC and bpe may result in regular geometry. Other examples can be found in literatures, such as 3,4-pyridinedicarboxylate and bpe [15], 5-nitro-1,3-benzenedicarboxylate and bpe [16], *o*-H_2CCA and 4,4′-bipyridine [11], nitrilotriacetic acid and 4,4′-bipyridine [17], 4,4′-oxybis(benzoic acid) and 4,4′-bipyridine [18]. In order to construct regular geometry for coordination polymers, it is feasible to use mixed rigid and flexible ligands, rather than mixed flexible ligands.

Comparing the structures of complexes **1** and **3**, it can be concluded that the position of functional groups takes an important role in formation and architecture of the complexes. In *o*-CCA anions, the two carboxylate groups are in the adjacent position and there is an angle of nearly 60° between the two carboxylate groups; while in *p*-CCA anions, the two carboxylate groups are in opposite position. So the two carboxylate groups in *o*-CCA anion are much nearer than those in *p*-CCA anion, which induces different steric effect. In complex **1**, there are two bpe and two *o*-CCA anions around each Co(II) ion, while in complex **3** there are three bpe and two *p*-CCA anions. In order to complete the six-coordination of the Co(II) ion, the acrylate group of *o*-CCA anion adopts a chelating-bidentate mode in complex **1** (see Scheme 1a). That is the reason why *p*-CCA and *o*-CCA anions adopt different coordination modes. Similar situation is observed in complexes **5** and **6**. In complex **5**, *o*-BDC anions act as tridentate ligands (see Scheme 1c), while in complex **6**, *p*-BDC anions adopt bis(monodentate) mode and bis(chelating-bidentate) mode (see Scheme 1d and e) [13], which induces distinctive structures for complexes **5** and **6.**

Table 4
Thermogravimetric analyses data of complexes **1**–**4**

	1	**2**	**3**	**4**
The first weight loss temperature [°C]	91–161	126–206	105–173	126–185
Loss of weight: Found (Calc.) [%]	5.9(5.7)	5.8(5.9)	6.1(6.4)	6.2(6.4)
Further decomposition temperature [°C]	196–685	263–712	185–600	223–610
The residue	CoO	NiO	CoO	NiO

3.2. Thermal analyses

Thermogravimetric analyses of the complexes **1**–**4** were carried out to examine their thermal stabilities. The data of the thermogravimetric analyses for **1**–**4** are listed in Table 4. All guest molecules (methanol for **1** and water for **2**–**4**) and coordinating water molecules were lost at the first weight loss, indicating that the clathrated molecules are correlated with the formation and architecture of metal-organic frameworks in complexes **1**–**4**. Taking complex **1** as an example, the TG curve shows that the first weight loss of 5.9% from 91 °C to 161 °C corresponds to the loss of free methanol molecules and coordinating water molecules (calcd. 5.7%). Increasing temperature led to the further decomposition of complex **1** at 196 °C. The final pyrolysis was completed at 685 °C, giving the powder of CoO.

4. Conclusion

In summary, using hydrothermal reactions, we obtained five new coordination polymers $[Co(o\text{-CCA})(bpe)(H_2O)]_n$

$\cdot 0.25n\mathrm{CH_3OH}$ (**1**), $[\mathrm{Ni}(o\text{-CCA})(\mathrm{bpe})(\mathrm{H_2O})]_n \cdot 0.5n\mathrm{H_2O}$ (**2**), $[\mathrm{M}(p\text{-CCA})(\mathrm{bpe})_{1.5}(\mathrm{H_2O})]_n \cdot n\mathrm{H_2O}$ (M = Co, (**3**); Ni, (**4**) and $[\mathrm{Co}(o\text{-BDC})(\mathrm{bpe})(\mathrm{H_2O})]_n \cdot n\mathrm{H_2O}$ (**5**)). In complex **1**, bpe ligands link Co(II) ions into wave-like chains, while in complex **3**, Co(II) ions are bridged by bpe into brick-wall-like grids, which is mainly attributed to coordination characteristics of *o*-CCA anion and *p*-CCA anion, respectively. The position of functional dicarboxylate groups takes an important role in the architectures of metal-organic frameworks. Complexes **1**–**4** all possess 3D complicated and different metal-organic frameworks, while complex **5** is of (4,4) 2D grid-like layers with cavities. These results show that in order to construct regular geometry, it is feasible to use mixed rigid and flexible ligands rather than mixed flexible ligands.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 601065–601069 for **1**–**5**, respectively. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail:deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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