Design and Synthesis of New 1D and 2D R-isophthalic Acid-based Coordination Polymers (R = Hydrogen or Bromine)

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Abstract: Three new R-isophthalic acid-based (R = H or Br) coordination polymers have been designed and synthesized. By changing the N-containing ligand in the system, we are able to tune the dimensionality of coordination polymers from one-dimension (1D) to two-dimensions (2D) with the same basic building unit. Also, different metal ions can be incorporated into the same structures. Compound **1** [Cu(bipa)(py)$_2$]·0.5(H$_2$O) (H$_2$bipa = 5-bromoisophthalic acid; py = pyridine) and compound **2** [Co(bipa)(py)$_2$] are 1D chain structures. Compound **3** [Cu$_8$(ipa)$_8$(bpe)$_8$]·2(bpe)·4(H$_2$O) (bpe=1,2-bis(4-pyridyl)ethane) is a 2D layered structure.

Keywords: 1D and 2D polymers · Coordination polymers · Isophthalic acid · N Ligands · Solvothermal reaction

Introduction

Recently, coordination polymers (CPs), also referred to as metal organic frameworks (MOFs), have attracted great attention owing to their potential for use in a variety of applications such as gas adsorption and separation,[1] chemical sensing,[2] catalysis,[3] magnetics[4] and optical devices.[5] Based on their dimensionality, coordination polymers may be classified as one dimensional (1D), two dimensional (2D) and three dimensional (3D) structures. Even though 3D structures are most intensely studied, 1D and 2D structures also have their own interests. For example, 1D coordination polymers have been found to have interesting magnetic, electrical, mechanical and optical properties.[6] For flexible 2D structures, a unique gate phenomenon is observed in which inter-layer distances change as a result of adsorption/ desorption of gases.[7] Thus rational design and control of the dimensionality of coordination polymers is important in order to achieve desired properties.

Coordination polymers are constructed by incorporating metal cations, anionic and/or neutral linkers. In order to obtain targeted dimensionality of a coordination polymer, it is essential to select appropriate linkers. Polycarboxylic acids represent one type of the most commonly used anionic linkers for the construction of coordination polymers. Many of them have been employed to synthesize coordination polymers with different topologies.[8] While various studies have been reported on isophthalic acid-based coordination polymers in the past several years, none of them center on a systematic approach in controlling the dimensionality of the structures.[9,10] In this work, we demonstrate such an approach to control the dimensionality of R-isophthalic acid-based (R = H or Br) coordination polymers by using different N-containing neutral linkers. We successfully synthesized three new structures, of which two are 1D chain-like structures and the third one is a 2D layered structure. All three compounds have similar coordination environment, wherein R-isophthalic acid coordinates to the metal centers to form a 1D chain, and two neutral linkers coordinate to each metal center vertically. When pyridine is used, it serves as terminal ligand resulting in 1D chains as in the case of compound **1** or [Cu(bipa)(py)$_2$]·0.5(H$_2$O) and compound **2** or [Co(bipa)(py)$_2$]. On the other hand, if 1,2-bis(4-pyridyl)-ethane is used, it functions as pillar ligand and connects two adjacent chains together to give rise to a 2D layered structure, as in the case of compound **3** or [Cu$_8$(ipa)$_8$(bpe)$_8$]·2(bpe) ·4(H$_2$O).

Materials and Methods

Materials

Copper(II) nitrate trihydrate (99%) and 5-bromoisophthalic acid (96%) were used as obtained from Acros organics. Cobalt(II) nitrate hexahydrate (97.7%) was used as purchased from Alfa Aesar. 1,2-bis(4-pyridyl)-ethane (97%) and pyridine (99.9%) were used as purchased from Fisher Scientific.

Synthesis

Compound 1 [Cu(bipa)(py)$_2$]·0.5(H$_2$O)

Solvothermal reaction of 24.5 mg of H$_2$bipa (0.1 mmol), 24.16 mg of Cu(NO$_3$)$_2$·3H$_2$O (0.1 mmol), 60 µL pyridine (py) and 5 ml DI water was carried out in a 23 mL acid digestion bomb. The bomb was closed and heated at 100 °C for 1 day. After cooling down to room temperature, the products were filtered and washed with distilled water and DMF in order to remove excess starting materials followed by drying in air. Blue column-like crystals were collected after the isolation procedure.

Compound 2 [Co(bipa)(py)$_2$]

Solvothermal reaction of a mixture containing 24.5 mg of H$_2$bipa (0.1 mmol), 29.15 mg of Co(NO$_3$)$_2$·6H$_2$O (0.1 mmol), 115 µL pyridine (py) and 5 ml DI water was conducted at 100 °C in a 23 mL acid digestion bomb for 1 day. Purple thin column-like crystals were isolated after the reaction.

Compound 3 [Cu$_8$(ipa)$_8$(bpe)$_8$]·2(bpe)·4(H$_2$O)

Solvothermal reaction of 12.3 mg of H$_2$ipa (0.1 mmol), 18.4 mg of Bpe (0.1 mmol), 24.16 mg of Cu(NO$_3$)$_2$·3H$_2$O (0.1 mmol), and 5 ml DI water was performed at 80 °C in a 23 mL acid digestion bomb for 1 day afforded light green thin plate-like crystals.

Structure Characterization

Single crystal X-ray diffraction of samples was performed on a Bruker Smart APEX CCD diffractometer with graphite

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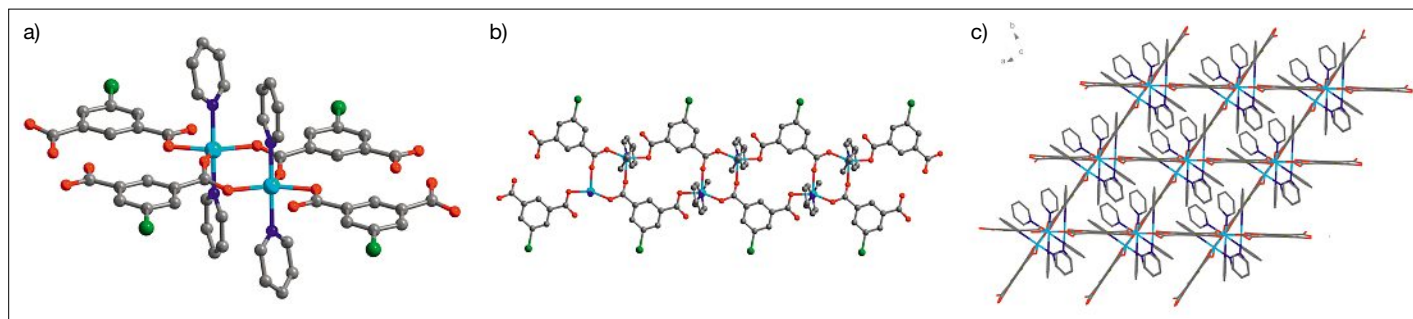[‡]These authors contributed equally

Fig. 1. (a) The trigonal bipyramidal coordination geometry of copper atoms in **1**. The sky blue atoms are Cu; green, blue, red and gray atoms represent Br, N, O, and C, respectively. (b) The 1D chain in **1**. Hydrogen atoms are omitted for clarity. The guest water molecules are removed from the structure. (c) The view of **1** down the *c* axis. Chains are shown as the stick model. For clarity, guest/solvent molecules are removed from the structure.

monochromatized MoK$_\alpha$ radiation. The structure analyses were carried out using SHELX97 or SHELXTL software packages. An A alert is generated for compound **3** because of the large amount of solvent disorder in the structure, which could not be modeled. Thus SQUEEZE instruction in PLATON was used to omit the unresolved disorder.[11] The powder X-ray diffraction analyses were performed on a Rigaku D/M-2200T automated diffraction system (Ultima$^+$) with graphite monochromated CuK$_\alpha$ radiation (λ = 1.54178 Å). Measurements were made in a 2θ range of 5–50°. The data were collected at room temperature with a step size of 0.01° and a counting time of 8–10 s/step at the operating power of 46 kV/40 mA.

Results and Discussion

Single-crystal X-ray analysis revealed that **1** crystallizes in the monoclinic space group *C*2/*c*. Each copper atom connects to three oxygen atoms from three bipa ligands and two nitrogen atoms from two py molecules to achieve a trigonal bipyramidal coordination geometry (Fig. 1a). One of the two carboxylate groups from each bipa bridges to the two copper atoms while the other carboxylate group bonds to one copper atom through one oxygen atom. Pyridine ligands are terminal and occupy the apical positions at each copper atom. As shown in Fig. 1b, the two five-coordinated Cu atoms form a secondary building unit (SBU), which alternates with bipa to form a 1D chain. Fig. 1c shows the view of the chains down the *c* axis. These chains are running along two directions [110] and [1-10] and thus are perpendicular to each other. The uncoordinated carboxylate oxygen atoms engage in hydrogen bonding with the inter-chain water molecules. The crystal data of **1** are summarized in Table 1.

The Cu–O bond lengths range from 1.9646(17) to 2.2085(19) Å (with an average value of 2.062 Å). The closest distance between the two neighboring Cu

is 4.509 Å. The O-Cu-O bond angles are 93.51(7)/109.53(7)/156.48(8)°, different from a 120° angle in an ideal bipyramid, while the N-Cu-N bond angles [173.09(9)°] are close to linear.

Since both structure **1** and **2** are 1D structures with similar coordination environment, the bond lengths and angles are compared in Table 2. The two compounds have similar bond lengths. In contrast to a

bipyramidal coordination sphere in **1**, cobalt in **2** has an octahedral coordination.

When cobalt was used as a metal ion source, a similar structure was obtained. Single-crystal X-ray diffraction analysis revealed that [Co(bipa)(py)$_2$] (**2**) crystallizes in a monoclinic space group *C*2/c. It is also a 1D chain structure with a coordination environment slightly different from **1** (Fig. 2a). Each Co is coordinated equa-

Table 1. Crystallographic data for compounds **1**, **2** and **3**.

	[Cu(bipa)py] (**1**)	[Co(bipa)py] (**2**)	[Cu$_8$(ipa)$_8$(bpe)$_8$] (**3**)
Formula	C$_{18}$H$_{14}$BrCuN$_2$O$_{4.50}$	C$_{18}$H$_{13}$BrCoN$_2$O$_4$	C$_{91}$H$_{74}$Cu$_4$N$_{10}$O$_{16}$
Formula weight [g/mol]	473.76	460.14	1817.81
Space group	*C*2/c	*C*2/c	*P*-1
Crystal system	Monoclinic	Monoclinic	Triclinic
a [Å]	18.514(2)	25.4916(14)	13.284(2)
b [Å]	8.7406(10)	10.1425(6)	16.042(2)
c [Å]	22.973(3)	27.0478(15)	20.257(3)
α [°]	90	90	103.398(2)
β [°]	109.632(2)	93.455(1)	90.050(2)
γ [°]	90	90	93.631(3)
V [Å^3]	3501.4(7)	6980.5(7)	4190.4(10)
Z	8	16	2
Crystal color, habit	Blue, column-like	Purple, column-like	Light green, plate-like
D$_{calc}$ [g/cm^{-3}]	1.797	1.751	1.48
T [K]	293(2)	293(2)	293(2)
Diffractometer	CCD	CCD	CCD
λ [Å]	0.71073	0.71073	0.71073
R factor, I > 2σ(I)^a	0.0415	0.022	0.0891
R factor, all data^a	0.0628	0.0259	0.1255
wR factor, I > 2σ(I)^b	0.0956	0.0537	0.02284
wR factor, all ^{b}	0.1046	0.0556	0.2468

^{a}R(F) = Σ ||F$_o$| − | F$_c$||/ S | F$_o$|; ^{b}Rw(F^2) = { Σ [w(F$_o^2$ − F$_c^2$)^2]/ Σ [w(F$_o^2$)^2]}$^{1/2}$

Table 2. The bond distances and bond angles in **1** and **2**.

Bond length [Å]		[Cu(bipa)py] (**1**)	[Co(bipa)py] (**2**)
	Metal–O1	2.023(2)	2.018(14)
	Metal–O2	\	2.005(15)
	Metal–O3	2.209(19)	2.137(14)
	Metal–O4	1.965(17)	2.225(14)
	Metal–N1	2.020(2)	2.158(19)
	Metal–N2	2.023(2)	2.143(18)
Bond angle (deg)	O1-Metal-O2	\	113.92(6)
	O1-Metal-O3	93.51(7)	156.91(6)
	O1-Metal-O4	156.48(8)	96.83(5)
	O3-Metal-O4	109.53(7)	60.39(5)
	N1-Metal-N2	173.09(9)	173.4(7)

Bpe occupies the two apical positions of each metal ion. The neighboring Cu metals are connected through ipa ligands to form a 1D chain (Fig. 3b), with a shortest Cu···Cu distance of 4.075 Å. The adjacent chains are interconnected through bpe to give rise to a 2D layered structure (Fig. 3c). The overall crystal structure is formed by stacking the layers on top of each other, as shown in Fig. 3d. Water and bpe molecules filled in the space within the layers were removed from the structure for clarity. Fig. 3d also shows the 1D channels porous structure. The solvent accessible volume is 23% after removing guest water molecules. The crystal data of **3** are summarized in Table **1**.

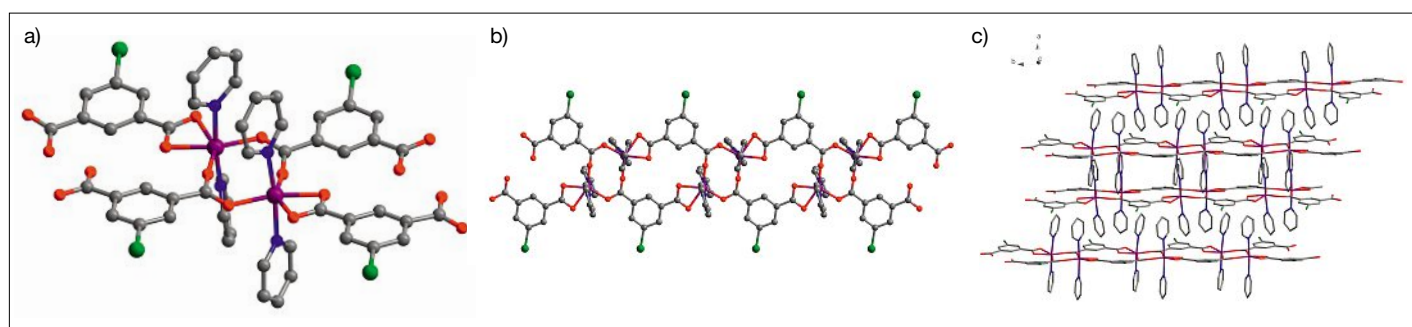A comparison based on the single crystal data of the three new coordination poly-

Fig. 2. (a) The pseudo-octahedra coordination geometry of cobalt atoms in **2**. The dark purple atoms are Co; green, blue, red and gray atoms represent Br, N, O, and C, respectively. (b) The 1D chain in **2**. Hydrogen atoms are omitted for clarity. **(c)** The view of **2** down the *c* axis. Four chains are shown as the stick model.

torially by three carboxylate groups from three bipa, two of them *via* bridging mode and the other one *via* chelating mode. Two Co atoms form a SBU. Py molecules occupy the two apical positions of each metal ion. The neighboring Co$_2$ SBUs are connected through bmip ligands to form a 1D chain (Fig. 2b) in the [010] direction. Fig. 2c shows the view of chains down the *c* axis. Chains have only one direction and pack with different distances in between each other. The crystal data of **2** are summarized in Table 1.

By replacing the monofunctional ligand pyridine with a bifunctional N,N'-donor ligand we expect that the 1D chains can be further connected to form extended networks of 2D layered structures. Compound [Cu$_8$(ipa)$_8$(bpe)$_8$]·2(bpe)·4(H$_2$O) (**3**) was synthesized by this approach using bpe.

The crystal structure of **3** is a 2D network containing five-coordinated copper metal centers. Each Cu ion is five-coordinated to three carboxylate groups of three ipa molecules in the equatorial positions. One of the carboxylate groups from ipa connects to two copper atoms in bridging mode, while the other carboxylate group connects to one copper atom only (Fig. 3a). The two Cu atoms form a dimeric SBU.
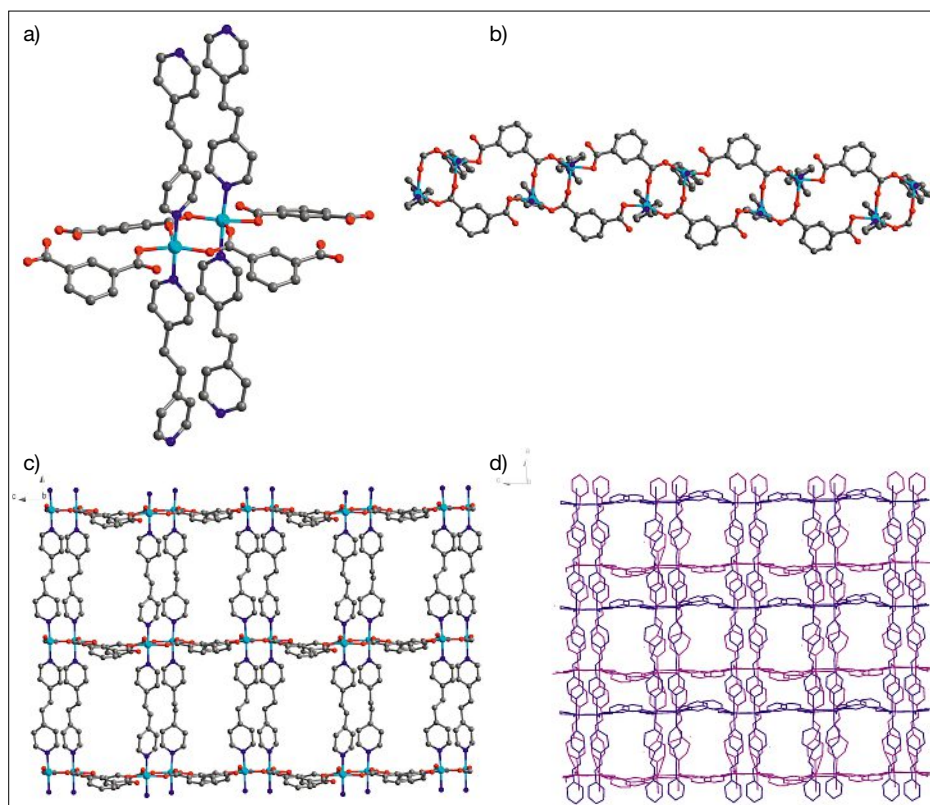

Fig. 3. (a) The trigonal bipyramidal coordination geometry of copper atoms in **3**. The sky blue atoms are Cu; green, blue, red and gray atoms represent Br, N, O, and C, respectively. (b) The 1D chain in **3** projected along the [-1, 1, 0] direction. Hydrogen atoms are omitted for clarity. The guest water molecules are removed from the structure. (c) The view of **3** down the *c* axis. Chains are shown as the stick model. (d) The packing of the two layers. Different layers are shown in different color.
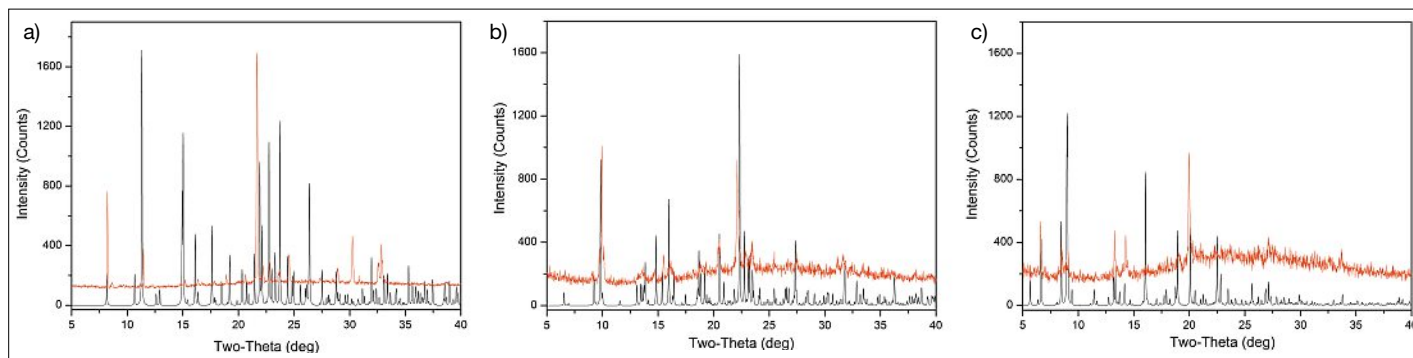
Fig. 4. PXRD patterns of (a) **1**, (b) **2** and (c) **3**. Black lines represent the simulated PXRD patterns and red lines represent the experimental PXRD patterns.

mers shows that their coordination building units are very similar. Compounds **1** and **2** have the same terminal pyridine and thus they both form one-dimensional chains. The difference between the two structures lies in the different metal centers. In compound **1** all three bipa coordinated to copper monodentately, while in compound **2** one of the three bipa ligands coordinated to cobalt in a bidentate mode. The Cu atoms in compounds **1** and **3** have exactly the same coordination geometry except that py in **1** is replaced by bpe in **3**. The incorporation of N-containing neutral ligands with mono- and di- functional groups leads to 1D chain and 2D layered structures, respectively.

The phase purity of all three compounds is analyzed by powder X-ray diffraction (PXRD) method. The experimental PXRD patterns of the samples are collected and compared to the simulated patterns calculated from single crystal structures (see Fig. 4). From the figure, it is clear that the two match well, indicating that pure phases of the three compounds have been obtained.

Conclusion

Two new 1D and one new 2D R-isophthalic acid-based (R = H or Br) coordination polymers have been successfully designed and synthesized *via* solvothermal reactions. Their crystal structures were determined by single crystal X-ray diffraction methods. In all three structures, metal cations are linked by R-isophthalic acid to form 1D chain. In the two 1D structures **1** and **2**, pyridine coordinates to the metal centers as the terminal ligand. Because of the different coordination habit of copper and cobalt, the two metal ions in the 1D structures have slightly different coordination modes: Cu is five-coordinated and Co is six-coordinated. In the 2D structure **3**, bpe coordinates to the metal centers as a bidentate ligand and bridges the 1D chains into a 2D layer structure. Thus, by tuning the N-containing neutral ligands and using

different metal centers, we have successfully obtained three coordination polymers with different dimensionalities.

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