

# Construction of two new coordination polymers based on semirigid tripodal carboxylic acid



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## ABSTRACT

Two new complexes,  $\{[\text{Cd}_3(\text{cpia})_2(\text{bix})_3 \cdot (\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (**1**) and  $\{[\text{Co}(\text{Hcpia})(\text{tib})] \cdot \text{H}_2\text{O} \cdot \text{DMF}\}_n$  (**2**), have been synthesized by the solvothermal reaction of semirigid tripodal carboxylate 5-(4'-carboxylphenoxy) isophthalic acid ( $\text{H}_3\text{cpia}$ ) with imidazolyl-based auxiliary ligands: 4-bis(imidazol-1-ylmethyl) benzene (bix) and 1,3,5-tris(1-imidazolyl) benzene (tib). Complex **1** reveals a 4-fold interpenetrated three-dimensional framework, which is generated by joining the right- and left-  $[\text{Cd}(\text{bix})_n]$  helical chains with  $\text{cpia}^{3-}$  ions. Complex **2** reveals an ABAB stacked mode, constructed by the stacking of two-dimensional (2D) bilayer network. In addition, the luminescent property and UV–Vis absorption in the solid state of complexes **1** and **2** have been studied.

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## 1. Introduction

The designed construction of crystalline materials from various molecular building blocks have attracted extensive attention due to their intriguing aesthetic structures and topological features [1–4], as well as their various of applications in photochemistry [5,6], molecular magnetism [7,8], heterogeneous catalysis [9,10], and molecular sorption [11,12]. Recently years some reports have demonstrated that some influencing factors such as organic ligands [13], solvent systems [14], metal ions [15], and counterions [16] can play crucial roles on the structures of metal–organic frameworks (MOFs), thereby affecting the properties of the as-prepared products. However, among the above factors, the organic ligands can be recognized as a more significant impact on the desirable MOFs because of the different spacer lengths, flexibility, steric hindrance effects, and so on. Thus, systematic studies of diversified organic ligands leading to different structures and properties are important and interest.

Among polycarboxylate linkers, semirigid tripodal carboxylates have attracted great interest [17]. Researches show that these linkers have excellent coordination ability and can free rotate in a certain extent to meet the requirement of coordination geometries of metal ions in the assembly process. However, to best of our knowledge, reports about a semirigid tripodal carboxylic ligand, such as 5-(4'-carboxylphenoxy) isophthalic acid ( $\text{H}_3\text{cpia}$ ), are still quite

rare [18]. Based on the careful observations of the geometries of ligands and their coordinated behaviors, it is reasonable to believe that the mixed-ligands of  $\text{H}_3\text{cpia}$  and other auxiliary ligands can generate unique architectures and topologies. Therefore, 1,4-bis(imidazol-1-yl-methyl) benzene (bix), 1,3,5-tris(1-imidazolyl) benzene (tib) (Scheme 1) were selected to solvothermally synthesize two intriguing coordination polymers:  $\{[\text{Cd}_3(\text{cpia})_2(\text{bix})_3 \cdot (\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Co}(\text{Hcpia})(\text{tib})] \cdot \text{H}_2\text{O} \cdot \text{DMF}\}_n$  (**2**). These complexes were characterized by infrared spectra (IR) spectra, X-ray powder diffraction (PXRD) and X-ray crystallography. In addition, their luminescences and UV–Vis spectrum were discussed in detail.

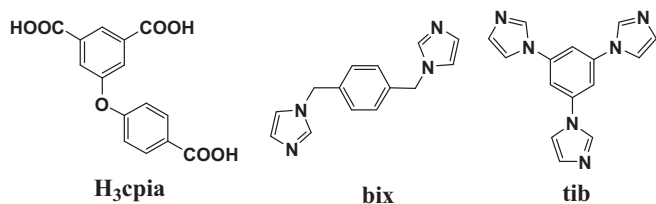
## 2. Experimental

### 2.1. General remarks

Reagents and solvents employed were commercially available and used as received. IR absorption spectra of the complexes were recorded in the range of 400–4000  $\text{cm}^{-1}$  on a Nicolet (Impact 410) spectrometer with KBr pellets. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using  $\text{Cu K}\alpha$  radiation (0.15418 nm), in which the X-ray tube was operated at 40 kV and 40 mA. Luminescent spectra were recorded with a SHIMADZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10  $\text{K min}^{-1}$  under  $\text{N}_2$  atmosphere.

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Scheme 1.  $H_3cpia$  and imidazole ligands.

## 2.2. Syntheses of the complexes

### 2.2.1. $\{[Cd_3(cpia)_2(bix)_3(H_2O)_2] \cdot H_2O\}_n$ (**1**)

A mixture of  $Cd(NO_3)_2 \cdot 4H_2O$  (0.2 mmol),  $bix$  (0.15 mmol) and  $H_3cpia$  (0.1 mmol) was dissolved in 10 mL of DMF/ $H_2O$  (1:1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 100 °C for 2 days. Colorless-plank crystals were obtained in 53% yield, which were washed with mother liquid, and dried under ambient condition. *Anal. Calc.* for  $C_{72}H_{62}N_{12}O_{17}Cd_3$ : C, 50.73; H, 3.67; N, 9.86. Found: C, 50.88; H, 3.51; N, 9.76%. IR (KBr,  $cm^{-1}$ ): 3401(w), 3135(w), 3058(w), 1672(m), 1610(s), 1562(s), 1452(m), 1365(s), 1246(s), 1170(m), 1109(m), 971(w), 776(m), 731(m), 656(m) (Fig. S1).

### 2.2.2. $\{[Co(Hcpia)(tib)] \cdot H_2O \cdot DMF\}_n$ (**2**)

Compound **2** was prepared by a procedure similar to that for the preparation of compound **1** by using  $Co(NO_3)_2 \cdot 6H_2O$  (0.2 mmol),  $tib$  (0.1 mmol), and  $H_3cpia$  (0.1 mmol) in 9 mL DMF/ $H_2O$  (1:2, v/v). Purple crystals were obtained in 46% yield. *Anal. Calc.* for  $C_{33}H_{29}N_7O_9Co$ : C, 55.45; H, 4.02; N, 13.49. Found: C, 55.93; H, 3.92; N, 13.94%. IR (KBr,  $cm^{-1}$ ): 3401(w), 3126(w), 3058(w), 2923(w), 1671(s), 1614(s), 1507(s), 1455(m), 1383(s), 1250(s), 1164(m), 1013 (m), 971(w), 971(w), 773(w), 724(m), 656(m) (Fig. S2).

## 3. X-ray crystallography

Single crystals of **1** and **2** were prepared by the methods described in the synthetic procedure. X-ray crystallographic data of **1** and **2** were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures of complexes **1** and **2** were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on  $F_o^2$  values [19]. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The distribution of peaks in the channels of **1** and **2** was chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining solvents was removed by the SQUEEZE routine in PLATON [20]. The number of solvent molecules were obtained by element analyses and TGA. The relevant crystallographic data are presented in Table 1, while the selected bond lengths and angles are given in the Supporting information (Table S1).

## 4. Results and discussion

### 4.1. Structural description of $\{[Cd_3(cpia)_2(bix)_3(H_2O)_2] \cdot H_2O\}_n$ (**1**)

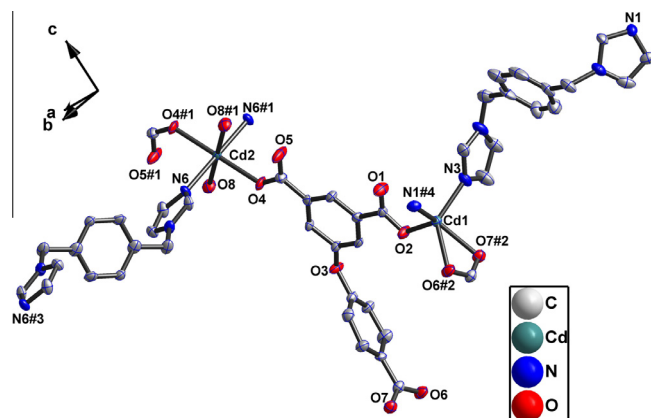
Complex **1** crystallized in monoclinic crystal system of  $P2_1/n$  space group. The asymmetric unit contains one and a half independent Cd(II) cations, one  $cpia^{3-}$  anion, one and half  $bix$ , and one

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

Complex	<b>1</b>	<b>2</b>
Formula	$C_{72}H_{62}N_{12}O_{17}Cd_3$	$C_{33}H_{29}N_7O_9Co$
Formula weight	1704.57	726.56
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
$a$ (Å)	11.5235(11)	12.6527(16)
$b$ (Å)	15.7807(15)	13.1757(17)
$c$ (Å)	22.220(2)	19.699(3)
$\alpha$ (°)	90	90
$\beta$ (°)	94.678(2)	103.051(2)
$\gamma$ (°)	90	90
$Z$	4027.2(7)	3199.2(8)
$V$ (Å <sup>3</sup> )	2	4
$D_{calc}$ ( $g\ cm^{-3}$ )	1.391	1.319
$\mu$ (Mo $K\alpha$ ) ( $mm^{-1}$ )	0.852	0.589
$F(000)$	1696	1300
Theta min–max (°)	1.9, 25.0	1.9, 25.0
Tot., uniq. data	19708, 7074	15577, 5622
$R_{int}$	0.113	0.057
Observed data [ $I > 2\sigma(I)$ ]	4605	3832
$R_1, wR_2$ ( $I > 2\sigma(I)$ )	0.0493, 0.1051	0.0561, 0.1384
$S$	0.90	1.03
Min. and max resd dens ( $e\ \text{\AA}^{-3}$ )	−0.90, 1.04	−0.52, 0.56

coordinated water molecule. As is shown in Fig. 1a, there are two types of coordination environments around the Cd(II) ions. Cd(II) lies in a distorted trigonal bipyramidal coordination environment of three oxygen atoms from two  $cpia^{3-}$  anions and two nitrogen atoms from two  $bix$ ; Cd(II) resides in an octahedral coordination sphere, which was defined by four oxygen atoms from two  $cpia^{3-}$  anions and two coordinated water molecules at the equatorial position, and two N atoms from two  $bix$  at the axial positions. The Cd–O lengths are in the range of 2.193(1)–2.393(9) Å, and Cd–N lengths are 2.196(1) and 2.294(9) Å, respectively.

In complex **1**, the neighboring Cd(II) ions are connected by  $cpia^{3-}$  to form an infinitely one-dimensional (1D) chain, which contains 24-membered  $[Cd_2(cpia)_2]$  metallocyclic ring with  $10.588 \times 11.611 \text{ \AA}^2$  in dimension (corresponding to the Cd···Cd distance and O···O separation, Fig. 1b). In two types *cis*- $bix$  ligands, the dihedral angles between adjacent imidazole rings and phenyl rings are  $71.791(4)^\circ$  and  $86.333(4)^\circ$ , respectively. One can join Cd(II) ions to form a helical chain, and the distance of Cd1···Cd1 is 14.071 Å. Another is linked by Cd(II) ions to generate a infinite 1D zigzag chain. The effective diameter of Cd2···Cd2 is 15.781 Å. These two kinds of 1D chains and  $cpia^{3-}$  further generate an infinite three-dimensional (3D) framework via sharing the Cd(II) ions



**Fig. 1a.** Coordination environment of the Cd(II) ion in **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 =  $3 - x, 1 - y, 1 - z$ ; #2 =  $2 - x, 1 - y, -z$ ; #3 =  $3 - x, 2 - y, 1 - z$ ; #4 =  $0.5 - x, 0.5 + y, 0.5 - z$ .

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