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A key route to designing huge eight-fold interpenetrated coordination networks with ths-type topology: Synthesis, structures, and topological characteristics

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ABSTRACT

Solvothermal reactions of Cd(II) or Mn(II) ions with 4'-(4-carboxylphenyl)-2,2':6',2"-terpyridine acid (Hcpt) and thiophene-2,5-dicarboxylic acid (H_2tpd) resulted in the formation of two isostructrual coordination networks $\{[M_2(cpt)_2(tpd)]\cdot 3.5H_2O\}_n$ (M=Cd, **1**; M=Mn, **2**). These complexes have been characterized by single-crystal X-ray diffraction analyses, infrared spectra (IR), elemental analyses, and powder X-ray diffraction (PXRD). Complexes **1** and **2**, formed by the cpt^- and tpd^{2-} bidentate connectors, have a 3D framework with a 3-connected, uninodal 10^3-**ths** topology possessing an unusual eight-fold [4*2] interpenetration mode. In addition, the **ths** cage has a long intracage M···M distance. In contrast, only a 1D coordination network $\{[CdCl(cpt)]\cdot 3.75H_2O\}_n$ (**3**) was obtained under similar conditions while in the absence of the H_2tpd ligand. Compound **3** is propagated only by the [CdCl(cpt)] unit, which illustrated that the incorporation of the cpt^- and Cl^- ligands to form a 1D network. The distinct ancillary anions (tpd^{2-} or Cl^-) play a critical role in determining the coordination features and the network connectivity of metal ions. This work presents a successful route to preparing rare eight-fold [4*2] interpenetrated networks.

1. Introduction

Many advances have been made regarding the synthesis of coordination polymers (CPs), because of their potential applications [1–8] and topologically diverse architectures [9–12]. So far, a number of rigid CPs have been prepared by the use of a good geometry match between the metal centers and the appropriate ligands under suitable synthesis conditions [13–15]. Many three-dimensional frameworks with either large channels or chirality, possessing the three-connected nets, have been widely studied [16–22]. However, a rational route to controlling framework dimensionality remains a great challenge in crystal engineering [23–25], especially, the governing principles in the degree of interpenetration are less ascertained and remain elusive [23,26,27].

Compared with the extensive research dealing with bridging carboxylic acids, the properties of elongated bridging pyridyl carboxylic acids in metal–organic frameworks (MOFs) remain largely unexplored [28,29]. In this regard, the bulky 4'-(4-carboxylphenyl)-2,2':6'2"-terpyridine acid (Hcpt), possessing a bulky head and a special tail, is an effective building block with chelating effect and geometrical rigidity. Considering the fact that interpenetration is one of the key issues in the design of coordination networks, we envisaged that an elongated rigid ligand with a bulky and unique tail, along with a tuning bischelating ligand would be an excellent combination for achieving this goal. Herein, we report on the design of eight-fold [4*2] interpenetrated frameworks. This work is of interest for several reasons: (i) a **ths**-type network with an eight-fold [4*2] interpenetration mode is very rare (Fig. 1), (ii) the combination of an elongated bulky bridging ligand with the thiophene-2,5-dicarboxylate (tpd^{2-}) ligand was found to be the key to the successful design of an eight-fold interpenetrated coordination network, (iii) the **ths**-cage has unusual long intracage M···M distances of $59.65\times 23.00\times 23.00$ Å^3 (Fig. 2), and this is of fundamental interest.

2. Experimental

2.1. General

All reagents were purchased commercially and used as-received without further purification. Organic compound 4'-(4-carboxylphenyl)-2,2':6',2"-terpyridine acid (Hcpt) was prepared

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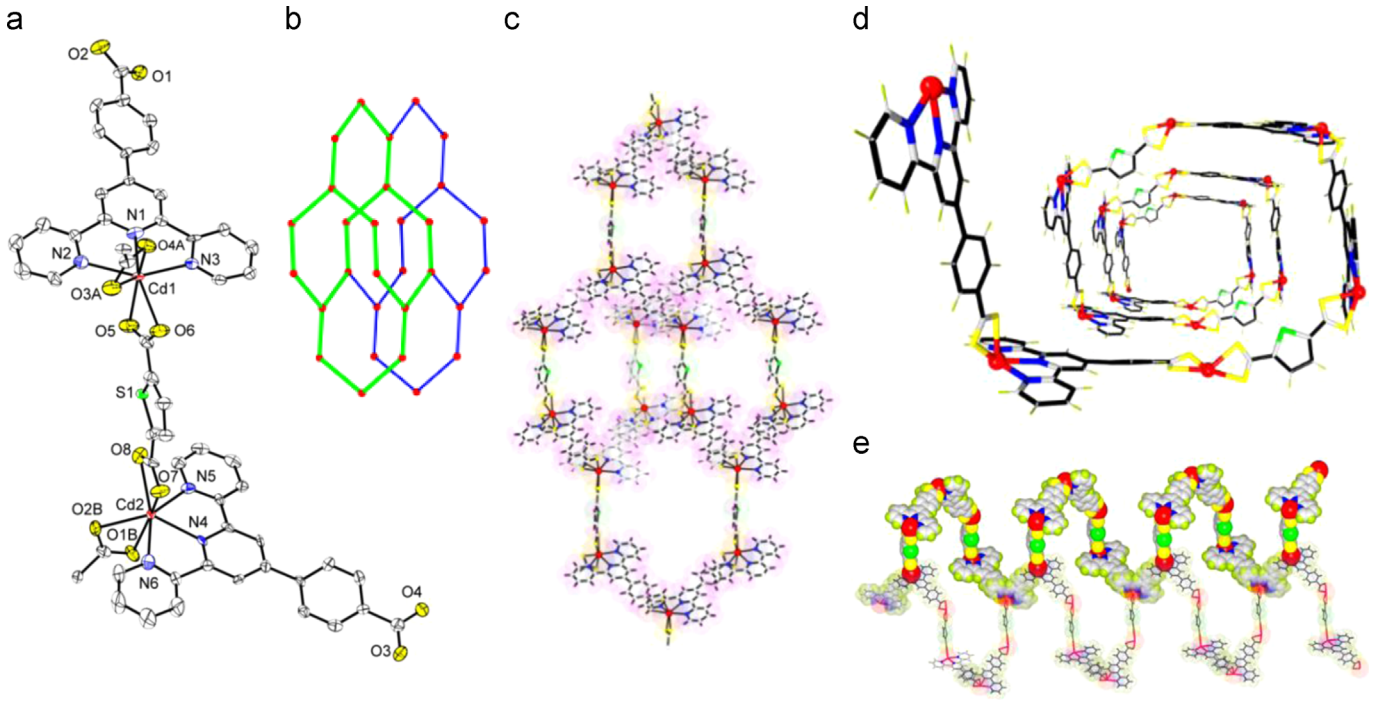

Fig. 1. Structures and framework topology of **1**: (a) ORTEP diagram showing the asymmetrical unit by thermal ellipsoids with a 50% probability level; (b) schematic view of a **ths** topological network; (c) superimposed space-filling representation of the **ths**-type cage, having the intracage Cd···Cd distances with $59.65 \times 23.00 \times 23.00$ Å^3; (d) top view of a helix with [Cd(cpt)(tpd)] unit; (e) side view of a helix; Cd red, O yellow, C gray, N blue, S green, and H lime. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

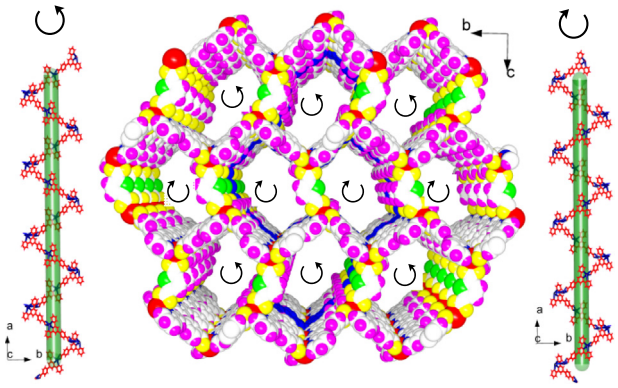

Fig. 2. View of chiral channels of a single **ths**-type net of **1**, which are formed of right- and left-handed helical chains with the [Cd(cpt)(tpd)] unit.

according to literature methods [30]. Thermogravimetric analyses (TGA) were performed under nitrogen with a Perkin-Elmer TGA-7 TG analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets on a Perkin-Elmer Paragon 1000 spectrometer. Elemental analyses were determined using a Perkin-Elmer 2400 CHN elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Siemens D-5000 diffractometer at 40 kV, 30 mA for Cu$K\alpha$ ($\lambda = 1.5406$ Å), with a step size of 0.02° in θ and a scan speed of 1 s per step. The photoluminescence spectra for the solid compounds were recorded on a Hitachi F4500 spectrometer.

2.2. Synthesis of compounds *1* and *2*

A mixture of $CdCl_2 \cdot 2.5H_2O$ (24.0 mg, 0.10 mmol), Hcpt (18.3 mg, 0.05 mmol), H_2tpd (12.1 mg, 0.05 mmol), H_2O (10 mL) was sealed in a 23-mL Teflon-lined stainless steel Parr acid digestion bomb, heated at 160 °C for 72 h, and then allowed to cool to room temperature for 60 h. Brown rod-shaped crystals of **1** were isolated on a filter and washed with deionized water and ethanol, and dried in air. Yield 27.2% (15.8 mg, 0.0136 mmol, based on Cd^{II}). Elem. Anal. (%) Calcd. for $Cd_2C_{50}H_{37}N_6O_{11.5}S$: C, 51.65; H, 3.21; N, 7.23. Found: C, 51.11; H, 3.09; N, 7.32. Compound **2** was synthesized under similar reaction conditions using the same molar ratios of reactants, except that $MnCl_2 \cdot 4H_2O$ (21.7 mg, 0.10 mmol) was used instead of $CdCl_2 \cdot 2.5H_2O$. Red rod-shaped crystals of **2** were isolated on a filter and washed with deionized water and ethanol, and dried in air. Elem. Anal. (%) Calcd. for $Mn_2C_{50}H_{35.5}N_6O_{10.75}S$: C, 58.06; H, 3.46; N, 8.13. Found: C, 58.10; H, 3.43; N, 8.22.

2.3. Synthesis of compound *3*

Compound **3** was synthesized under similar reaction conditions using the same molar ratios of reactants for **1**, except that H_2tpd ligand was not added. Yellowish-brown rod-shaped crystals of **3** were isolated on a filter and washed with deionized water and ethanol, and dried in air. Yield 26% (7.1 mg, 0.013 mmol, based on the Hcpt ligand). Elem. Anal. (%) Calcd. for $CdC_{22}H_{21.5}N_3O_{5.75}Cl$: C, 47.67; H, 3.82; N 7.58. Found: C, 47.53; H, 3.43; N, 7.53.

2.4. Single-crystal X-ray diffraction

A suitable single crystal of compound **1** with dimensions of $0.28 \times 0.25 \times 0.20$ mm^3 was mounted on the tip of a glass fiber and placed onto the goniometer head for indexing and intensity data collection using a Nonius Kappa CCD diffractometer with a graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were collected at 296(2) K. All the structures were solved using direct methods. All the hydrogen atoms of the ligands were placed in calculated positions with isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were