



From interpenetration to non-interpenetration: A series of self-assemblies predominated by reaction conditions



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ABSTRACT

Four Cd/Zn coordination frameworks, namely, $[\text{Cd}(\text{TPBA-4})(\text{NO}_3)_2] \cdot 2\text{DMF} \cdot 1.22\text{H}_2\text{O}$ (**1**), $[\text{Cd}(\text{TPBA-4})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$ (**2**), $[\text{Cd}(\text{TPBA-4})(\text{NO}_3)_2] \cdot 2.2\text{Me}_2\text{CO} \cdot 0.32\text{H}_2\text{O}$ (**3**), and $[\text{Zn}(\text{TPBA-4})(\text{NO}_3)_2] \cdot 1.5\text{Me}_2\text{CO}$ (**4**) were synthesized by the reaction of *N,N',N''*-tris(pyrid-4-ylmethyl)-1,3,5-benzenetricarboxamide (TPBA-4) with the corresponding d^{10} metal salts. X-ray diffraction analysis revealed that complex **1** was of two-fold interpenetrated 2D network with interlocked cage-like motif. The structure of **2** is three-fold interpenetrated 2D honeycomb network. On the other hand, the **3** and **4** are isomorphous and isostructural, and have different 2D networks compared to **1** and **2**. Thus the series of complexes have the same metal atoms and ligands but different structures. In complex **1**, **2**, **3**, and **4**, the flexible TPBA-4 ligands are versatile and adopt different conformations according to different reaction conditions, which predominates the final structures of these complexes. The physical properties of these complexes were also investigated.

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1. Introduction

Design and synthesis of metal organic frameworks (MOFs) has drawn great attentions from scientists resulted from not only their interesting structural diversities, but also their potential applications including adsorption, magnetism and catalysis, in which the tripodal ligands is one of the most used organic linker [1,2]. By now, chemists have reported various MOFs (metalloclages or capsules, infinite one-dimensional (1D) chain, two-dimensional (2D) honeycomb networks, and three-dimensional (3D) architectures) by reactions of tripodal ligands with transition metal salts [3,4]. In most conditions, the final structures of MOFs can be dominated by many factors, including synthetic conditions, solvent properties, the nature of organic ligands and etc. With different syntheses procedures, MOFs with various structures or morphologies can be expected [5,6]. On the other side, flexible tripodal ligands with methylene groups can adopt various conformations to meet the coordination need of MOFs, resulting interesting structural diversities through different synthetic process, including interpenetrating, polythreading, self-threading, and etc [7]. Meanwhile,

although the interpenetrations of MOFs are well documented [8], examples of interlocked cages through the formation of the quadruple aromatic stacking were rarely reported [9].

Furthermore, MOFs constructed by ligands containing carboxamide $[-\text{C}(\text{O})\text{NH}-]$ group have been widely studied [10]. Due to the good abilities of carboxamide group in the formation of hydrogen bonds, related MOFs are widely explored in research fields concerning water clusters, gas storage, molecular recognition, catalysis etc [11]. For extending this approach, a tripodal ligand *N,N',N''*-tris(pyrid-4-ylmethyl)-1,3,5-benzenetricarboxamide (TPBA-4) has been synthesized. One twofold interpenetrated complex $[\text{Cd}(\text{TPBA-4})(\text{NO}_3)_2] \cdot 2\text{DMF} \cdot 1.22\text{H}_2\text{O}$ (**1**), one threefold interpenetrated complex $[\text{Cd}(\text{TPBA-4})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$ (**2**), and two other MOFs, namely, $[\text{Cd}(\text{TPBA-4})(\text{NO}_3)_2] \cdot 2.2\text{Me}_2\text{CO} \cdot 0.32\text{H}_2\text{O}$ (**3**) and $[\text{Zn}(\text{TPBA-4})(\text{NO}_3)_2] \cdot 1.5\text{Me}_2\text{CO}$ (**4**) were obtained by assembly reactions between TPBA-4 and nitrates with different solvent systems. In this paper we report the preparation, crystal structures, and physical properties of these complexes.

2. Experimental

All commercially available chemicals are of reagent grade and used as received without further purification. C, H and N analyses were made on a Perkin-Elmer 240C elemental analyzer at the

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analysis center of Nanjing University. The ligand TPBA-4 was prepared in one step with 40% yield according to the literature [11]. Infrared (IR) spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr discs. Thermal gravimetric analysis (TGA) was recorded on a Netzsch STA-409PC instrument with flowing N_2 at heating rate of 20 °C/min. Powder X-ray diffraction patterns were examined on a RigakuD/max-RA rotating anode X-ray diffractometer with graphite monochromatic $Cu-K\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation at room temperature.

2.1. Synthesis of $[Cd(TPBA-4)(NO_3)_2] \cdot 2DMF \cdot 1.22H_2O$ (**1**)

$Cd(NO_3)_2 \cdot 4H_2O$ (15.4 mg, 0.05 mmol) suspended in DMF (2 mL) was added dropwise at room temperature to a solution of TPBA-4 (24.0 mg, 0.05 mmol) in 2 mL DMF. The resulting pale yellow solution was then stirred for another 2 h and filtrated. The crystals suitable for X-ray structure analysis were prepared by slowly diffusing diethyl ether into the DMF solution in a test tube for one week. Yield: 50%. Anal. Calcd. (%) for $C_{33}H_{40.44}Cd_1N_{10}O_{12.22}$: C, 44.78; H, 4.61; N, 15.83. Found: C, 44.85; H, 4.65; N, 15.78. FT-IR (KBr pellet, cm^{-1}): 3604br, 3058 m, 1670s, 1640 m, 1551s, 1429 m, 1384s, 1297s, 1031 m, 795 m, 718 m.

2.2. Synthesis of $[Cd(TPBA-4)(NO_3)_2] \cdot H_2O$ (**2**)

The complex **2** was prepared by solvothermal method. A mixture containing $Cd(NO_3)_2 \cdot 4H_2O$ (23.1 mg, 0.075 mmol), TPBA-4 (36.0 mg, 0.075 mmol), 5 mL of methanol and 2 mL of benzyl alcohol was sealed in a stainless steel vessel, heated to 80 °C and kept for 3 days. After the mixture was cooled to room temperature over 12 h, colorless needle-like crystals of **2** were obtained in 46% yield. Anal. Calcd. (%) for $C_{27}H_{26}Cd_1N_8O_{10}$: C, 44.12; H, 3.57; N, 15.25. Found: C, 44.20; H, 3.50; N, 15.33. FT-IR (KBr pellet, cm^{-1}): 3562br, 3008 m, 1644 m, 1548s, 1424 m, 1384s, 1290s, 1023 m, 795 m, 719 m.

2.3. Synthesis of $[Cd(TPBA-4)(NO_3)_2] \cdot 2.2Me_2CO \cdot 0.32H_2O$ (**3**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (23.1 mg, 0.075 mmol) and TPBA-4 (36.0 mg, 0.075 mmol) in 5 mL of methanol and 2 mL of benzyl alcohol was sealed in a stainless steel vessel and placed in an oven, then directly heated to 80 °C and kept for 3 days. After the mixture was cooled to room temperature over 12 h, the crystalline products of **2** were filtered. The single crystals of **3** suitable for X-ray structure analysis were offered by slow diffusion of acetone into the clear filtrate in 20% yield based on Cd. Anal. Calcd. (%) for $C_{33.53}H_{37.71}Cd_1N_8O_{11.50}$: C, 47.42; H, 4.48; N, 13.20. Found: C, 47.55; H, 4.56; N, 13.15. FT-IR (KBr pellet, cm^{-1}): 3563br, 3055 m, 1710s, 1643 m, 1548 m, 1429 m, 1384s, 1290s, 1025 m, 799 m, 721 m.

2.4. Synthesis of $[Zn(TPBA-4)(NO_3)_2] \cdot 1.5Me_2CO$ (**4**)

The complex was prepared by the same method described for complex **3** by using $Zn(NO_3)_2 \cdot 4H_2O$ (22.3 mg, 0.075 mmol) instead of $Cd(NO_3)_2 \cdot 4H_2O$. Yield: 30%. Anal. Calcd. (%) for $C_{31.50}H_{33}N_8O_{10.50}Zn_1$: C, 49.97; H, 4.40; N, 14.80. Found: C, 49.92; H, 4.50; N, 14.73. FT-IR (KBr pellet, cm^{-1}): 3564br, 3049w, 1711s, 1643s, 1550 m, 1426 m, 1384s, 1290s, 1025 m, 799 m, 721 m.

3. Crystallography

The collections of crystallographic data for the complexes **1** and **3** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated $Mo-K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The structure of **1** was solved by direct

methods with SHELX-97 [12], while the structure of **3** was solved by direct methods with SIR92 [13] and expanded using Fourier technique [12]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms except for those of water molecules were generated geometrically. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [14]. In complex **1**, the nitrate anions and DMF molecules are disordered: the N7, O71, O72, O73 are disordered into two positions with site occupancies of 0.664(11) and 0.336(11), respectively, while the C91, C92, C93 are disordered into two positions with site occupancies of 0.659(16), 0.341(16), respectively.

The data collections for complexes **2**, **4** were made on a Bruker Smart Apex CCD with graphite-monochromated $Mo-K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by direct methods using SHELX-97 [12] and refined by full-matrix least-squares methods anisotropically for non-hydrogen atoms. Calculations were performed on a personal computer with the Siemens SHELXTL program package [15]. Details of the crystal parameters, data collection and refinement are summarized in Table S1. Selected bond lengths and angles of these compounds with their estimated standard deviations are listed in Table S2.

4. Results and discussion

4.1. Crystal structure of **1**

The complex **1** was obtained by the self-assembly of $Cd(NO_3)_2 \cdot 4H_2O$ with ligand in DMF solution. Fig. 1 gives the coordination environment of complex **1**. The structure crystallizes in space group $R\bar{3}$, and all the cadmium atoms have identical coordination environments of slightly distorted penta-bipyramid with O_4N_3 binding set. The O atoms come from two different nitrate anions, while the N atoms come from three different ligands. In complex **1**, the Cd–O bond lengths are in the range of 2.277(10) to 2.496(5) Å with the O–Cd–O bond angles varying from 51.5(2)° to 175.9(4)°, while the Cd–N bond lengths range from 2.315(5) to 2.333(5) Å. The N–Cd–N and N–Cd–O bond angles are in the range of 84.1(3)° to 177.38(18)°, respectively (Table S2). On the other hand, each TPBA-4 ligand coordinates to three Cd atoms with “up” and “down” orientations. In complex **1**, all pyridyl N atoms and carbonyl O atoms are in the same side of the benzene ring plane with the distances ranging from 1.90 to 2.10 Å and 0.36 to 0.69 Å, respectively. As illustrated in Fig. 2, when ignoring the coordination effect of N51 atoms and nitrate anions, the TPBA-4 ligands containing N31 and N11 are arranged in the “face-to-face” orientation to form the M_3L_2 cage-like motifs (Fig. 2a) [16]. The equilateral

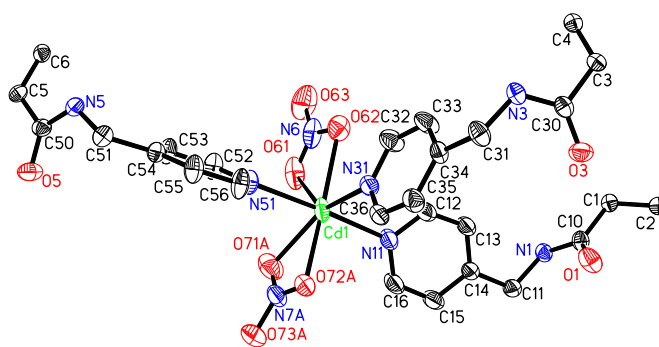


Fig. 1. The X-ray structure of cationic part of complex **1** with atom numbering scheme. The thermal ellipsoids were drawn at 30% probability. The solvent molecules and hydrogen atoms were omitted for clarity.

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