



Structure, topology and property of metal-organic frameworks with pyridine-3,5-bis(phenyl-4-carboxylate) and varied metal centers



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ABSTRACT

Four new metal-organic frameworks $\{[\text{Zn}(\text{L})\cdot 2.6\text{H}_2\text{O}]_n$ (**1**), $[\text{Cd}(\text{L})(\text{H}_2\text{O})(\text{DMA})]_n$ (**2**), $[\text{Co}_3(\text{L})_2(\text{HCOO})_2(\text{H}_2\text{O})_2]_n$ (**3**) and $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})\cdot \text{DMF}]_n$ (**4**) [H_2L = pyridine-3, 5-bis(phenyl-4-carboxylic acid), DMA = N,N-dimethylacetamide, DMF = N,N-dimethylformamide] have been synthesized and characterized by single crystal and powder X-ray diffractions, IR and thermogravimetric analyses. **1** is a three-dimensional (3D) framework with $\{4^6\cdot 6^4\}$ topology, while **2** is a 3D framework formed by parallel/parallel inclined interpenetration of two-dimensional (2D) networks with $\{6^3\}$ topology. **3** processes a 3D framework structure with point symbol of $\{4\cdot 8^2\}_2\{4^2\cdot 8^{12}\cdot 10\}$, and **4** shows bilayer structure with $\{4^3\cdot 6^3\}$ topology, which is further assembled into a 3D supramolecular architecture by hydrogen bonding interactions. Gas adsorption property of **1**, **2** and **4**, photoluminescence of **1** and **2** as well as magnetic property of **4** were investigated.

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1. Introduction

As an emerging class of porous materials, metal-organic frameworks (MOFs) have gained much attention in recent years because of their intriguing structural diversity and potential application in gas adsorption, separation and storage, catalysis, magnetism and photoluminescence [1–9]. MOFs have advantages over the conventional inorganic porous materials. For example, the structures and functionalities of MOFs can be systematically modulated via modification of component units [10–12]. However, to achieve the targeted MOFs with desired structures and properties is still a challenge, because structural uncertainty of MOFs is an inherent characteristic of assembly process. The structural character of ligands, coordination nature of metal centers, reaction conditions such as pH value, temperature, solvent and even the molar ratio of reactants can influence the formation of MOFs [13–15].

Taking into account the above-mentioned factors, without a doubt, the predesigned organic ligands play a deciding role in the construction of desirable MOFs. Selecting a suitable organic ligand with certain features like flexibility, appropriate angles and binding

sites, is crucial to the construction of MOFs. To our knowledge, carboxylate and pyridyl-containing ligands are often used, because the carboxylate group can have variable coordination modes and strong coordination abilities, and the pyridyl-containing ligands have been demonstrated to be powerful in construction of MOFs with novel structures and topologies [16,17]. Comparing with ligands only containing carboxylate or pyridyl group, the reports on pyridyl-carboxylate ligands are less to now. In this work, we choose a rigid pyridyl-carboxylate ligand, namely pyridine-3,5-bis(phenyl-4-carboxylic acid) (H_2L), to construct MOFs [18–20]. H_2L is a longer and more variable ligand to some extent compared with the well used 3,5-pyridine dicarboxylic acid and it not only has two carboxylate groups with variable coordination modes to construct interesting MOFs, but also involves the pyridyl N-donor to link metal ions or replace solvent molecules to form highly-connected frameworks. These characters may lead to form MOFs with unique structures and topologies [21,22].

Based on the reported and our recent work on transition metal MOFs [23–25], we synthesized four new frameworks, $\{[\text{Zn}(\text{L})\cdot 2.6\text{H}_2\text{O}]_n$ (**1**), $[\text{Cd}(\text{L})(\text{H}_2\text{O})(\text{DMA})]_n$ (**2**), $[\text{Co}_3(\text{L})_2(\text{HCOO})_2(\text{H}_2\text{O})_2]_n$ (**3**) and $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})\cdot \text{DMF}]_n$ (**4**) (DMA = N,N-dimethylacetamide, DMF = N,N-dimethylformamide). Among them, **1**, **2**, **3** are three-dimensional (3D) frameworks with different topologies, while **4** is a bilayer, which is further connected by hydrogen bonding interactions to form a 3D supramolecular architecture. Furthermore,

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gas adsorption, photoluminescence and magnetic properties of the complexes were investigated.

2. Experimental

2.1. Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Ligand H₂L was prepared according to the procedure reported in the literature [18–20]. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C Elemental Analyzer at the analysis center of Nanjing University. Thermogravimetric analyses (TGA) were carried out on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C min⁻¹. FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ on a Bruker Vector 22 FT-IR spectrophotometer using KBr pellets. Power X-ray diffraction (PXRD) patterns were obtained on Bruker D8 Advance diffractometer using Cu-K α (λ = 1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA. Photoluminescence properties for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. Magnetic measurements were performed on a Quantum Design MPMS-SQUID-VSM magnetometer between 1.8 and 300 K. Sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument.

2.2. Synthesis of {[Zn(L)]·2.6H₂O}_n (**1**)

A mixture of Zn(NO₃)₂·6H₂O (14.9 mg, 0.05 mmol) and H₂L (4.8 mg, 0.015 mmol) was stirred in DMF/ethanol/H₂O mixed solvent (8 ml, v/v/v: 5/2/1). The resultant solution was sealed in a 15 mL bottle and heated at 90 °C for three days. After cooling to room temperature, colorless block-shaped crystals of **1** were obtained in 41% yield. Anal. Calcd for C₁₉H_{16.2}NO_{6.6}Zn: C, 53.13; H, 3.80; N, 3.26%. Found: C, 53.02; H, 3.78; N, 3.17%. IR (KBr): ν (cm⁻¹) 3448 (s), 1673 (m), 1623 (s), 1535 (s), 1551 (m), 1465 (w), 1394 (s), 1166 (m), 1093 (m), 1012 (m), 939 (w), 865 (w), 786 (s), 707 (s), 676 (m), 609 (w).

2.3. Synthesis of [Cd(L)(H₂O)(DMA)]_n (**2**)

To a 15 mL bottle, Cd(NO₃)₂·4H₂O (15.4 mg, 0.05 mmol), H₂L (4.8 mg, 0.015 mmol) and DMA/ethanol/H₂O (8 ml, v/v/v: 5/2/1) were loaded. The bottle was sealed and heated at 90 °C for three days. Then colorless block-shaped crystals of **2** were obtained and dried in air. Yield: 46%. Anal. Calcd for C₂₃H₂₂N₂O₆Cd: C, 51.65; H, 4.15; N, 5.24%. Found: C, 51.90; H, 4.09; N, 5.16%. IR (KBr): ν (cm⁻¹) 3390 (s), 1599 (s), 1552 (s), 1469 (w), 1396 (m), 1255 (w), 1177 (m), 1088 (s), 862 (s), 781(s), 705 (m), 676 (s), 626 (s).

2.4. Synthesis of [Co₃(L)₂(HCOO)₂(H₂O)₂]_n (**3**)

Complex **3** was obtained by the same procedure used for preparation of **1** except that Zn(NO₃)₂·6H₂O was replaced by Co(NO₃)₂·6H₂O. Pink block crystals of **3** were obtained in 35% yield. Anal. Calcd for C₄₀H₂₈N₂O₁₄Co₃: C, 51.25; H, 3.01; N, 2.99%. Found: C, 51.30; H, 2.98; N, 2.94%. IR (KBr): ν (cm⁻¹) 3476 (m), 1610 (s), 1538(m), 1414 (s), 1457 (m), 1175 (m), 1021 (m), 910 (m), 862 (m), 776 (s), 705 (w), 669 (m).

2.5. Synthesis of {[Mn(L)(H₂O)]·DMF}_n (**4**)

Complex **4** was obtained by the same procedure used for preparation of complex **3** except that Co(NO₃)₂·6H₂O was replaced

by 0.05 ml Mn(NO₃)₂ (50 wt%). After cooling to room temperature, pink block-shaped crystals of **4** were obtained in 61% yield. Anal. Calcd. for C₂₂H₂₀N₂O₆Mn: C, 57.03; H, 4.35; N, 6.05%. Found: C, 56.95; H, 4.32; N, 6.11%. IR (KBr): ν (cm⁻¹) 3400 (s), 1659 (s), 1603 (m), 1534 (m), 1393 (s), 1097 (w), 1011 (w), 863 (s), 818 (w), 786 (s), 706 (m), 661 (m).

2.6. X-ray crystallography

Diffraction data of **1–4** were collected on a Bruker Smart Apex II CCD with graphite monochromated Mo K α radiation source (λ = 0.71073 Å) in ω scan mode at 293(2) K. The diffraction data were integrated by using the SAINT program [26], which was also used for the intensity corrections for the Lorentz and polarization effects. Semiempirical absorption corrections were applied using SADABS program [27]. All the structures were solved by direct methods using SHELXS-97 [28] and all the non-hydrogen atoms were refined on F^2 by full-matrix least-squares procedures with SHELXL-97 [29]. Hydrogen atoms, except those of water molecules, were generated geometrically and refined isotropically using the riding model. The hydrogen atoms of free water molecules in **1** were not found, while those of coordinated water molecules in **2**, **3** and **4** were found directly. Atoms O1W in **1** and C20, C21, C22, C23, N2 in **2** are disordered. The details of the crystal parameters, data collection and refinements for **1–4** are summarized in Table 1. Selected bond lengths and angles for **1–4** are collected in Table S1. The parameters of hydrogen bonding data for **2** and **4** are listed in Table S2.

3. Results and discussion

3.1. Structure description of {[Zn(L)]·2.6H₂O}_n (**1**)

Crystallographic analysis shows that the asymmetric unit of **1** contains half molecule of [Zn(L)]·2.6H₂O. As shown in Fig. 1a, the Zn(II) atom is five-coordinated with distorted trigonal bipyramid coordination geometry by four carboxylate oxygen atoms from four different L²⁻ and one nitrogen from the fifth L²⁻. The bond length of Zn1–O1, Zn1–O2 and Zn–N1 are 1.953(2) Å, 2.270(3) Å and 2.057(3) Å, respectively. In addition, the coordination angles around Zn1 span from 84.62(10) to 174.55(11) ° (Table S1).

In **1**, both carboxylate groups adopt bis-monodentate coordination mode (Scheme 1, mode I). Thus, the Zn(II) atoms are connected by carboxylate groups along *c* axis to generate an infinite one-dimensional (1D) chain (Fig. 1b) [30]. The Zn(II)–Zn(II) distance within the chain is 4.21 Å. The 1D chains are further connected by L²⁻ ligands to result in formation of a 3D framework with 1D channels (Fig. 1c). To get a better insight into the structure of **1**, topological approach is used for reducing multidimensional structure to simple node-and-linker reference net. By simplifying the L²⁻ ligand as 5-connector and Zn(II) as 5-connecting node, the 3D framework of **1** can be represented as a topology with the point symbol of {4⁶·6⁴} calculated by TOPOS software [31]. PLATON calculation suggests that the resulting effective free volume in **1**, after removal of free water molecules, is 27.5% [32].

3.2. Structure description of [Cd(L)(H₂O)(DMA)]_n (**2**)

When Cd(NO₃)₂·4H₂O was used under the same reaction conditions, just using Cd(NO₃)₂·4H₂O instead of Zn(NO₃)₂·6H₂O, the crystals are too small to measure their structures. When DMA was used to replace DMF, complex **2** was isolated. The asymmetric unit of **2** contains one Cd(II), one L²⁻ ligand, coordinated solvent of water and DMA molecules. As shown in Fig. 2a, Cd1 is seven-coordinated by four oxygen atoms from two different L²⁻ ligands,

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