Imidazole-containing Cd Metal-Organic Framework with Selective Adsorption Properties

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Abstract: Metal-organic framework material [Cd(tib)(dnbpdc) (H₂O)]·2DMF·2H₂O (**1**) [tib = 1,3,5-tris(1-imidazolyl)benzene, H₂dnbpdc = 2,2'-dinitro-4,4'-biphenyldicarboxylic acid] was synthesized and characterized by Thermogravimetric analyses (TGA), Powder X-ray diffraction (PXRD) analyses and Bruker D8 Advance X-ray diffractometer. The results showed that **1** was a 1D chain structure to be joined together by hydrogen bonds to generate a 3D supramolecular structure. CO₂ and N₂ adsorption behavior of the material was studied. It is significative that **1** can selective sorption of CO₂.

1 Introduction

In the past decades, remarkable attention have been concentrated on the design and synthesis of functional metal-organic frameworks (MOFs) materials due to their rich and varied structures as well as potential application, such as gas storage and separation, magnetism,, heterogeneous catalysis, photoluminescence and so on. [1-10]. Building MOFs with expected properties is an important task. However, it is still a challenge to investigate factors influencing the structural building of MOFs because varied factors can affect the structure and property of MOFs [11, 12]. Such factors mainly include the selection of organic linkers, metal ions, reaction temperature. Among these factors, the organic linker is very crucial for formation of MOFs with various structures and properties. Therefore, proper organic linkers are significant in building the functional MOF materials. To our knowledge, 2,2'-dinitro-4,4'-biphenyldicarboxylic acid (H₂dnbpdc) may act as a good bridging ligand due to its various coordination modes and rigid multicarboxylic groups [13, 14].

In our previous studies, a rigid tridentate ligand 1,3,5-tris(1-imidazolyl)benzene (tib) with specific structure and interesting properties has been used in construction of MOFs [15-20]. Thus, it is meaningfull with imidazole-containing ligand tib and dicarboxylic acid H₂dnbpdc to construct MOFs with novel structures and properties. In this work, one new Cd metal-organic framework [Cd(tib)(dnbpdc) (H₂O)]·2DMF·2H₂O (**1**) [tib = 1,3,5-tris(1-imidazolyl)benzene, H₂dnbpdc = 2,2'-dinitro-4,4'-biphenyldicarboxylic acid] was synthesized and characterized. Structural characterization revealed that **1** was a 1D chain structure to be joined together by hydrogen bonds to generate a 3D supramolecular structure. Gas adsorption property of the complex was

studied. It is interesting that **1** shows selective and hysteretic sorption of CO₂ over N₂.

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 tib was prepared according to the procedures reported previously [21]. Elemental analyses for C, H and N were performed on a FLASH EA 1112 elemental analyzer. Thermogravimetric analyses (TGA) were carried out on a Mettler-Toledo (TGA/DSC1) 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 TENSOR 27 spectrophotometer with KBr pellets. Powder X-ray diffraction (PXRD) analyses were performed on a Bruker D8 Advance X-ray diffractometer with Cu K α (λ = 1.5418 Å) radiation. Sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument.

2.2 X-ray crystallography

Crystallographic data of **1** was collected on a Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) using the ω -scan technique. The diffraction data were integrated using the SAINT program [22], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program [23]. The structures were solved by direct methods with SHELXS-2014 and all the non-hydrogen atoms were

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refined anisotropically on F^2 by the full-matrix least-squares technique with the SHELXL-2014 [24, 25]. All the hydrogen atoms, except for those of water molecules, were generated geometrically and refined isotropically using the riding model. The hydrogen atoms of the coordinated water molecules were found from the Fourier map directly, while those of free water molecules were not found.

2.3 Synthesis of complex 1

A mixture of tib (13.8 mg, 0.05 mmol), $H_2dnbpdc$ (16.5 mg, 0.05 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol) in DMF/ H_2O (8 mL, v/v, 2:1) was sealed in a 18 mL glass vial and heated at 90 °C for 72 h, and then slowly cooled to room temperature. Light yellow block shaped crystals of **1** were obtained in 75% yield (based on $H_2dnbpdc$). Anal. Calcd for **1** ($C_{35}H_{38}N_{10}O_{13}Cd$): C, 45.74; H, 4.17; N, 15.24%. Found: C, 46.01; H, 4.39; N, 15.07%. IR (KBr pellet, cm^{-1}): 3396 (m), 1664 (s), 1614 (s), 1527 (s), 1400 (s), 1345 (s), 1253(m), 1073 (m), 1013 (m), 928 (m), 828 (m), 788 (m), 654 (w), 420 (w).

3 Results and discussion

3.1 Crystal structure description

The results of X-ray crystallographic analysis show that **1** crystallizes in the triclinic $P\bar{1}$ space group. As shown in Fig. 3a, each Cd(II) is six-coordinated by three imidazole nitrogen, two carboxylate oxygen atoms and one coordinated water molecule. In **1**, each tib ligand links three Cd(II) atoms using its three imidazole groups to form an infinite 1D chain (Fig. 2). It is noteworthy that $dnbpdc^{2-}$ acts as terminal ligand alternately coordinating at the up and down positions of the 1D chain (Fig. 2) in monodentate linkage mode. Furthermore, there are $C-H \cdots O$ hydrogen bonding interactions between the neighbor 1D chains to generate 2D layer structure of **1** (Fig. 3) and 3D supramolecular framework of **1** (Fig. 4).

Fig. 1. Coordination environment of Cd(II) in **1**. Hydrogen atoms and free solvent molecules are omitted for clarity.

Fig. 2. 1D chain structure of **1**.

Fig. 3. 2D layer structure of **1** with hydrogen bonds indicated by dashed lines.

Fig. 4. 3D supramolecular structure of **1** with hydrogen bonds indicated by dashed lines.

3.2 Powder X-ray diffraction (PXRD) and Thermogravimetric analysis (TGA)

The pure phase of the synthesized **1** was confirmed by powder X-ray diffraction (PXRD) measurements and the results are shown in Fig. 5. Each PXRD pattern of the as-synthesized sample is consistent with the simulated one indicating the phase purity of the bulk samples.

Complex **1** is air stable and their thermal stability was investigated in the temperature range of 30-800 °C by TG measurements (Fig. 6). The TG curve of **1** displays a weight loss of 19.5% between 90-310 °C, which corresponds to the loss of water and DMF molecules (calc. 19.8 wt.%), and further weight loss was

observed at about 360 °C, owing to the collapse of the framework of **1**.

Fig. 5. PXRD pattern of **1**.

Fig. 6. TGA curve of **1**.

3.3 Gas and vapor adsorption properties.

The porosity and high stability of the frameworks prompted us to examine their gas sorption behavior. The sorption performances of the activated samples **1'** for N₂ at 77 K, CO₂ at 195 K were discussed here. The activated sample **1'** was prepared by immersing the as-synthesized sample **1** in acetone for 3 days to remove the nonvolatile solvates, the solvent was decanted every 8 h, and fresh acetone was added. The activated sample **1'** was obtained by heating the solvent-exchanged sample at 423 K under a dynamic high vacuum for 10 h.

As shown in Fig. 7 and Fig. 8, the sorption isotherms for **1'** suggest that almost no adsorption of N₂ at 77 K. The final value of CO₂ adsorption at 195 K is 32.2 cm³·g⁻¹ at P = 0.99 atm corresponding to about 1.5 CO₂ molecules per formula unit for **1'**. The hysteresis and incomplete desorption suggests the strong interactions between the adsorbate and adsorbent [26], which includes the hydrogen bond interactions between the guest molecules and framework, as well as the guest molecules and the guest molecules. Given the above analysis results, we can see that complex **1** can select adsorption of CO₂ molecules.

Fig. 7. N₂ at 77 K sorption isotherms for **1'**. (Filled shape, adsorption; open shape, desorption).

Fig. 8. CO₂ at 195 K sorption isotherms for **1'** (Filled shape, adsorption; open shape, desorption).

Conclusions

In conclusion, one new Cd (II)-based MOF with mixed ligands had been synthesized. By using dicarboxylate as the auxiliary ligand, we had obtained one 1D chain structure. Furthermore, N₂ and CO₂ adsorption behavior of **1** was investigated and the results indicated that the frameworks showed the ability to selectively adsorb CO₂, suggesting a possible application in selective gas adsorption and separation.

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