Synthesis, structure and selective adsorption property of Zn metal-organic framework

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Abstract. Zn metal-organic framework material $[Zn_2(tib)(HBTB)_2(H_2O)] \cdot 2H_2O$ (1) [tib = 1,3,5-tris(1imidazolyl)benzene, $H_3BTB = 4,4',4''$ -benzene-1,3,5-triyl-tribenzoic 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 2D network to be joined together by hydrogen bonds to generate a 3D supramolecular structure. Gas, vapor adsorption behavior of the material was studied. It is meaningful that 1 can selective sorption of CO₂ and MeOH.

1 Introduction

The rational design and synthesis of functional metalorganic frameworks (MOFs) materials have caused remarkable attention in the past decades due to their rich and varied structures as well as potential application, such as gas storage and separation, ion exchange, heterogeneous catalysis, drug delivery and luminescence [1-10]. However, It still remains challenging by controlsynthesizing and predicting structures of the functional MOFs because of many factors which can affect the structure and property of MOFs [11,12]. Among these factors, the selection of organic linkers is very crucial for formation of MOFs with definite framework structure and desired property. Therefore, proper organic bridging linkers are significant in building the desired MOFs materials. To our knowledge, 4,4',4"-benzene-1,3,5-triyltribenzoic acid (H₃BTB) may act as a good bridging ligand due to its various coordination modes and rigid multicarboxylic groups [13-16].

In our previous studies, a rigid tridentate ligand 1,3,5tris(1-imidazolyl)benzene (tib) with specific structure and interesting properties has been used in construction of MOFs [17-22]. Thus, it is meaningfull for using mixed N-donor ligands tib and multicarboxylic acid H₃BTB to construct MOFs with novel structures and properties. In this work, one new Zn metal-organic framework $[Zn_2(tib)(HBTB)_2(H_2O)] \cdot 2H_2O$ (1) [tib =1,3,5-tris(1-imidazolyl)benzene, $H_3BTB = 4,4',4''$ benzene-1,3,5-triyl-tribenzoic acid] was synthesized and characterized. Structural characterization revealed that 1 was a 2D network to be joined together by hydrogen bonds to generate a 3D supramolecular structure. Gas, vapor 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 [23]. 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 using 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 ($\lambda = 0.71073$ Å) using the ω -scan technique. The diffraction data were integrated using the SAINT program [24], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program [25]. The structures were solved by direct methods using SHELXS-2014 and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix leastsquares technique with the SHELXL-2014 [26,27]. All the hydrogen atoms, except for those of water molecules,

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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 Preparation of complex 1

Complex 1 was synthesized by tib (13.8 mg, 0.05 mmol) H₃BTB (22.0 mg, 0.05 mmol) and Zn(NO₃)₂·6H₂O (30.0 mg,0.1 mmol) in H₂O (8 mL) in a 18 mL glass vial and heated at 160 °C for 72 h. After cooling to room temperature, colorless block crystals of 1 were obtained with a yield of 75% based on tib. Anal. Calcd for 1 (C₆₉H₅₀N₆O₁₅Zn₂): C, 62.13; H, 3.78; N, 6.30%. Found: C, 62.07; H, 3.85; N, 6.25%. IR (KBr pellet, cm⁻¹): 3449 (m), 1689 (s), 1662 (s), 1620 (s), 1511 (m), 1401 (s), 1240 (m), 1177 (m), 1075 (s), 1015 (s), 946 (m), 854 (m), 774 (s), 683 (m), 646 (m), 482 (m).

3 Results and discussion

3.1 Crystal structure description

The results of X-ray crystallographic analysis show that 1 crystallizes in the triclinic P-1 space group. As illustrated in Fig. 1, the asymmetric unit of 1 contains two crystallographically independent Zn atoms, Zn1 is six-coordinated with distorted octahedral geometry by two imidazole N atoms (N1, N5A) from two different tib and four carboxylate O ones (O1, O2, O7, O8) from two distinct HBTB²⁻, with Zn1-N bond distance from 2.019(3) Å to 2.023(4) Å and the Zn1-O one from 1.962(3) Å to 1.982(3) Å. Furthermore, the coordination angles around Zn1 are in the scope of 97.54(13)°-121.79(15)°. While Zn2 is five-coordinated by one imidazole N atom (N3B) from tib ligand, three carboxylate O atoms (O3, O11C, O12C) from different HBTB²⁻ and one terminal water molecule (O1W). The bond length and coordination angles around Zn2 are in normal category.



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

In 1, one tib joins three Zn(II) atoms to construct a 1D chain (Fig. 2). Meanwhile, partly deprotonated HBTB²ligand adopts (κ^1)-(κ^2)- μ_2 -HBTB or (κ^2)-(κ^2)- μ_2 -HBTB coordination mode to connect two Zn(II) atoms to also form a 1D chain structure. The combination of 1D Zn-tib chain and 1D Zn-HBTB chain generates the final 2D network structure of **1** (Fig. 3). Eventually, Hydrogen bonding C(10)-H(10A)...O1W and C(3)-H(3)...O11 bridge the layers to form a 3D supramolecular structure of **1** (Fig. 4).



Fig. 2. 1D chain structure of Zn-tib in 1 along b axis.



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

3.2 Gas and vapor adsorption properties.

The porosity and high stability of the frameworks prompted us to examine their gas/vapor sorption behavior. The sorption performances of the activated samples 1' for N₂ at 77 K, CO₂ at 195 K, CH₃OH and CH₃CH₂OH at 298 K were discussed here. The activated sample 1' was got by directly heating the fresh assynthesized samples at 160 °C for 10 h under high vacuum. The PXRD pattern of activated samples implied their good crystallinity (Fig. 5). The results showed that 1 had good stability and the desolvated samples 1' maintained the framework structures without destroying.



Fig. 5. PXRD pattern of 1 and the activated sample.

As shown in Fig. 6 and Fig. 7, the sorption isotherms for **1'** suggest that almost no adsorption of N₂ at 77 K and CH₃CH₂OH at 298 K. The final value of CO₂ adsorption at 195 K is 32.14 cm³·g⁻¹ at P = 0.99 atm corresponding to about 1.9 CO₂ molecules per formula unit for **1'**. As for CH₃OH adsorption of **1'** at 298 K (Fig. 7), the final values of 47.3 cm³·g⁻¹ (71.8 mg·g⁻¹) at P = 0.99 atm are corresponding to 2.8 CH₃OH molecules per formula unit for **1'**. The hysteresis and incomplete desorption suggests the strong interactions between the adsorbate and adsorbent [28], which includes the hydrogen bond interactions between the guest molecules and framework, as well as the guest molecules and the guest molecules.



Fig. 6. N₂ at 77 K and CO₂ at 195 K sorption isotherms for 1'. (Filled shape, adsorption; open shape, desorption).





Given all the above analysis results, we can see that complex 1 can select adsorption of CO_2 molecules.

4 Conclusions

In conclusion, one new Zn (II)-based MOF with mixed ligands had been synthesized. By using tricarboxylate as the auxiliary ligand, we had obtianed one 2D network. Furthermore, gas, vapor adsorption behavior of **1** was investigated and the results indicated that the

frameworks showed the ability to selectively adsorb CO₂ and MeOH, suggesting a possible application in selective gas/vapour adsorption and separation.

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