

Synthesis, crystal structure and adsorption properties of a novel Fe(III) porous coordination polymer containing 1, 4-naphthalenedicarboxylate ligand

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Abstract: A novel porous coordination polymer, iron naphthalenedicarboxylate $\text{Fe}(\text{OH})(1,4\text{-NDC}) \cdot 2\text{H}_2\text{O}$ is hydrothermally synthesized by the reaction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1, 4-naphthalenedicarboxylic acid (1, 4- H_2NDC) at 150 °C. The compound crystallizes in a tetragonal space group $\text{P4}_2/\text{nmc}$; $a = 2.144\,7(4)$ nm, $c = 0.688\,49(14)$ nm, $V = 3.166\,9(11)$ nm³, $Z = 8$, $R = 0.084\,5$, $wR = 0.182\,9$. The crystal structure exhibits a three-dimensional framework which is composed of infinite chains of corner-sharing octahedral $\text{Fe}(\text{OH})_2\text{O}_4$ with 1, 4-NDC ligands forming two types of channels with square-shaped cross-sections. The large channels present a cross-section of $0.76\text{ nm} \times 0.76\text{ nm}$, while the small channels are about $0.30\text{ nm} \times 0.30\text{ nm}$. No structural transformation occurs after removing the guest water molecules, while a robust structure generates with permanent porosity. The adsorption measurements show that the anhydrous sample of the compound can adsorb CO_2 into its pores. The adsorption isotherms for methanol, acetone, tetrahydrofuran and benzene are also measured.

Key words: porous coordination polymer; selective adsorption; 1, 4-naphthalenedicarboxylic acid

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Design and synthesis of metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have been developed into one of the most attractive topics due to the fascinating structural diversity and potential applications in catalysis^[1], gas adsorption^[2], selective separation^[3], and gas storage^[4-5]. Up to date, through the wide choice of metals and deliberately designed ligands, a great number of magnetic, electrical, optical, and catalytic properties have already been incorporated into such materials. In recent years, not only crystallographic studies but also dynamic aspects of framework and adsorption properties have been highlighted by several compounds representing special frameworks^[6], in which the storage of important gases and vapors, such as methane, hydrogen, acetylene, ethanol, carbon dioxide and benzene molecules has been achieved, which enhances the application of these frameworks in the field of energy and environment^[7]. PCPs can be easily con-

structed by self-assembly of metal ions (or metal clusters) and organic linkers. The polycarboxylates have been widely used in the construction of PCPs because of their different possibilities of linkage with the inorganic cations (chelating, single bond, etc.). A large number of infinite one-, two- and three-dimensional carboxylate polymers with novel structure and unique properties have been synthesized.

It is well known that 1, 4- H_2NDC is a useful ligand in constructing various functional PCPs. In this work, we use 1, 4- H_2NDC and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to construct one type of intriguing polymeric structure $\text{Fe}(\text{OH})(1,4\text{-NDC}) \cdot 2\text{H}_2\text{O}$ (named as compound 1). Its architecture exhibits a three-dimensional framework made by infinite chains of corner-sharing octahedral $\text{Fe}(\text{OH})_2\text{O}_4$ with 1, 4-NDC ligands, forming two types of square-shaped channels. The large channels present a cross-section of $0.76\text{ nm} \times 0.76\text{ nm}$, while the small channels are about $0.30\text{ nm} \times 0.30\text{ nm}$. The adsorption measurements show that the anhydrous sample of compound 1 can adsorb CO_2 into its pores. The adsorption isotherms for vapors, such as methanol, acetone, tetrahydrofuran and benzene, are also measured.

1 Experiment

All the reagents are of analytical grade and obtained from commercial sources without further purification.

1.1 Synthesis of $[\text{Fe}(\text{OH})(1,4\text{-NDC})] \cdot 2\text{H}_2\text{O}$

The mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.0 mmol, 0.278 2 g), 1, 4- H_2NDC (1.0 mmol, 0.216 2 g) and H_2O (20 mL) was placed in a 25 mL Teflon autoclave, and then heated at 150 °C for 3 d. The reaction mixture was allowed to cool to room temperature naturally. After filtering off and washing with distilled water, red styliform crystal of compound 1 was obtained in pure phase (yield: 80%). Analysis calculated for compound 1 ($\text{C}_{12}\text{H}_{11}\text{FeO}_7$): C, 44.58; H, 3.40. Found: C, 44.74; H, 3.22.

1.2 X-ray crystallographic measurements

A red single crystal with dimension of $0.10\text{ mm} \times 0.10\text{ mm} \times 0.20\text{ mm}$ was employed for data collection at 293 K on a Bruker Smart Apex II CCD single crystal diffractometer with graphite monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$) in a φ - ω scan mode. A total of 29 559 reflections and 1 906 unique ones were collected in the range of $3.00^\circ \leq \theta \leq 27.48^\circ$ with $R_{\text{int}} = 0.14$, of which the observed 1 906 reflections with $I > 2\sigma(I)$ were used in the succeeding structural calculations. The raw data frames were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using the SAINT pro-

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gram. Structure solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages^[8], respectively. The non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters. The H atoms were placed in the riding model. The unit cell volume included a large region of disordered solvent (water) which could not be modeled as discrete atomic sites. The intensity contribution of the disordered water molecules were calculated with PLATON/SQUEEZE and subtracted from the full data set. The final formula was deduced from the SQUEEZE results combined with elemental analysis and TGA data. The ratio of complex to water was found to be 1:2. The new data set, with the solvent contribution removed, was used in the final refinement.

1.3 Gas and vapor adsorption measurements

The adsorption isotherm measurements for nitrogen, argon at 77 K, carbon dioxide at 195 K, and methanol, acetone, tetrahydrofuran and benzene at 298 K were carried out using a volumetric adsorption instrument BELSORP18 from Bel Japan Inc.

2 Results and Discussion

2.1 X-ray single-crystal structure of compound 1

The crystal belongs to a tetragonal space group $P4_2/nmc$: $a = 2.144\,7(4)$ nm, $c = 0.688\,49(14)$ nm, and $V = 3.166\,9(11)$ nm³. The structure of compound 1 consists of a three-dimensional framework built up from the connection of infinite chains of corner-sharing octahedral $\text{Fe}(\text{OH})_2\text{O}_4$ with 1,4-NDC ligands. The bulky naphthalene rings of organic ligand are projected onto the pore surface, resulting in the forming of two kinds of pore apertures with a square shape. The Fe^{3+} is coordinated to four oxygen atoms from four carboxylic groups and two hydroxyl groups located in *trans* position (see Fig. 1). Bond valence calculations, which generate a value of 1.29, confirm the occurrence of a hydroxide anion on axial oxygen which is required for the electroneutrality balance of the structure. The $\text{Fe}(\text{OH})_2\text{O}_4$ units are linked to each other through two opposite hydroxyl groups and an infinite chain running along the c axis is generated. The infinite Fe-OH-Fe chains are interconnected by the 1,4-NDC groups, creating two types of square-shaped channels parallel to the c axis. Each channel is delimited by four walls of naphthyl units and four chains of iron octahedra. The four walls surrounding a small channel have all the C5

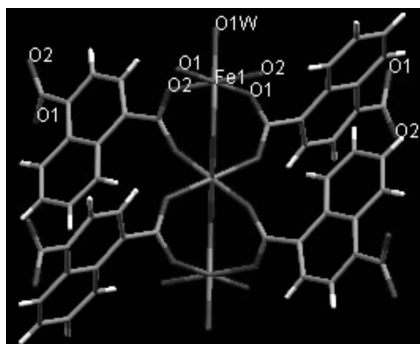


Fig. 1 Coordination environment of the iron(III) in compound 1

and C6 atoms of the naphthyl groups projecting into that channel. The four walls surrounding the other channels can accommodate guest water molecules, and are called large channels (see Fig. 2). Based on the crystallographic data and the van der Waals radii of atoms, the size of the large channels is about $0.76\text{ nm} \times 0.76\text{ nm}$, while that of the small channels is about $0.30\text{ nm} \times 0.30\text{ nm}$.

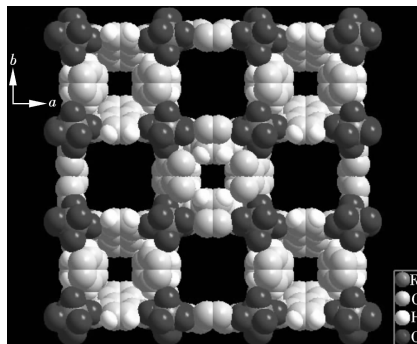


Fig. 2 Structural diagram of compound 1 along c axis direction

2.2 Thermal behavior of compound 1

The guest water molecules inside the channels can be removed at an elevated temperature without collapsing the host framework as confirmed by TGA (see Fig. 3) and X-ray diffraction studies (see Fig. 4). The thermogravimetric trace, performed under N_2 atmosphere at $5\text{ }^\circ\text{C}/\text{min}$, shows that the first weight loss starting at about $50\text{ }^\circ\text{C}$ is assigned to the removal of water molecules. 10.5% weight loss corresponds to two water molecules per chemical formula (calculated: 11.1%). The powder X-ray diffraction pattern of the anhydrous sample of compound 1 does not show substantial changes.

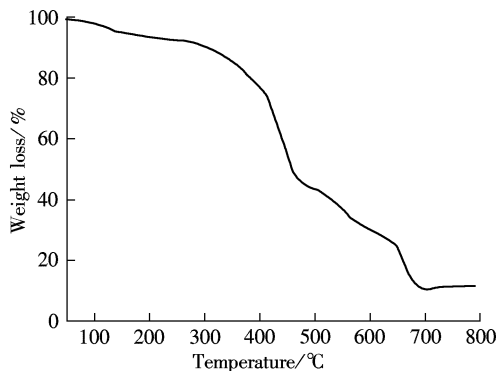


Fig. 3 Thermogravimetric analysis of compound 1

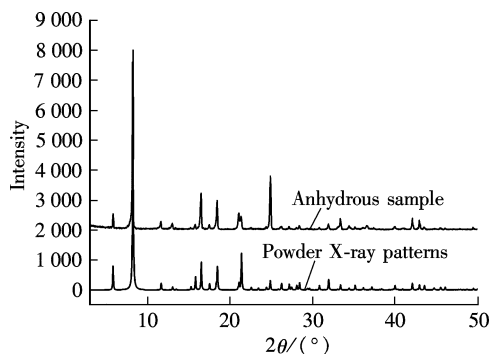


Fig. 4 Powder X-ray patterns and anhydrous sample of compound 1

This result suggests that the pore dimension and geometry of the anhydrous sample of compound 1 are similar to those of sample 1, but in the anhydrous sample the structure is porous and it contains an array of independent and empty channels.

2.3 Adsorption properties of compound 1

To elucidate the permanent porosity and the nature of pores of compound 1, adsorption isotherms of various guests were performed. The sample was subjected to water evacuation at 150 °C for 12 h and 0.133 Pa, giving rise to the anhydrous sample.

The adsorption isotherms of N₂ and Ar at 77 K show that only surface adsorption occurs, indicating that N₂ and Ar molecules do not diffuse into the channels at low temperature even if the pore diameter is suitable for N₂ and Ar to pass through (see Fig. 5). This behavior has already been described in MOFs with pore sizes less than 1 nm^[9–10]. The CO₂ (surface area is 0.179 nm²; kinetic diameter is 0.33 nm^[11]) adsorption isotherm at 195 K is described by a Type-I curve^[12] demonstrating the microporosity of the framework. The saturation capacity of CO₂ is up to 105 cm³/g, corresponding to 1.34 moles CO₂ per mole of naphthalene moiety. The surface area accessible to carbon dioxide is evaluated as 479 m²/g by the Langmuir equation. Vapors, such as methanol and acetone, are also adsorbed efficiently, showing Langmuir type- I curves (see Fig. 6). The saturation capacity for methanol and acetone are 97 and 53 cm³/g, respectively, indicating that 4.5 and

2.6 molecules per unit cell are stored. Taking into account the volumes of the molecules of 0.067 2 and 0.122 nm³ for methanol and acetone, respectively, we calculate an occupied value of 0.300 nm³ per unit cell. In the case of benzene and tetrahydrofuran, the lower loading of 1.1 and 1.2 molecules per unit cell at $P/P_0 = 0.95$ suggests a looser interaction of the benzene and tetrahydrofuran molecules with the framework.

3 Conclusion

In summary, we have successfully synthesized and characterized a three-dimensional framework made by infinite chains of corner-sharing octahedral Fe(OH)₂O₄ with 1, 4-naphthanedicarboxylate ligands. The structure shows parallel and independent nanochannels of two different cross-sections. The adsorption measurements show that the anhydrous sample of compound 1 can adsorb CO₂ into its pores.

References

- [1] Lee J, Farha O K, Roberts J, et al. Metal-organic framework materials as catalysts[J]. *Chem Soc Rev*, 2009, **38**: 1450 – 1459.
- [2] Kitagawa S, Kitaura R, Noro S. Functional porous coordination polymers[J]. *Angew Chem Int Ed*, 2004, **43**(18): 2334 – 2375.
- [3] Li J R, Kuppler R J, Zhou H C. Selective gas adsorption and separation in metal-organic frameworks[J]. *Chem Soc Rev*, 2009, **38**: 1477 – 1504.
- [4] Rowsell J L C, Yaghi O M. Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks[J]. *J Am Chem Soc*, 2006, **128**(4): 1304 – 1315.
- [5] Murray L J, Dinca M, Long J R. Hydrogen storage in metal-organic frameworks[J]. *Chem Soc Rev*, 2009, **38**: 1294 – 1314.
- [6] Cussen E J, Claridge J B, Rosseinsky M J, et al. Flexible sorption and transformation behavior in a microporous metal-organic framework[J]. *J Am Chem Soc*, 2002, **124**(32): 9574 – 9581.
- [7] Czaja A U, Trukhan N, Muller U. Industrial applications of metal-organic frameworks[J]. *Chem Soc Rev*, 2009, **38**: 1284 – 1293.
- [8] Sheldrick G M. SHELXS-97 and SHELXL-97, Program for X-ray crystal structure solution and refinement [R]. Göttingen: Göttingen University, 1997.
- [9] Vaidhyanathan R, Bradshaw D, Rebilly J N, et al. A family of nanoporous materials based on an amino acid backbone [J]. *Angew Chem Int Ed*, 2006, **45**(39): 6495 – 6499.
- [10] Maji T K, Matsuda R, Kitagawa S. A flexible interpenetrating coordination framework with a bimodal porous functionality[J]. *Nat Mater*, 2007, **6**(2): 142 – 148.
- [11] Dybtsev D N, Chun H, Yoon S H, et al. Microporous manganese formate: a simple metal-organic porous material with high framework stability and highly selective gas sorption properties[J]. *J Am Chem Soc*, 2004, **126**(1): 32 – 33.
- [12] Sing K S W, Everett D H, Haul R A W, et al. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity[J]. *Pure Appl Chem*, 1985, **57**(4): 603 – 619.

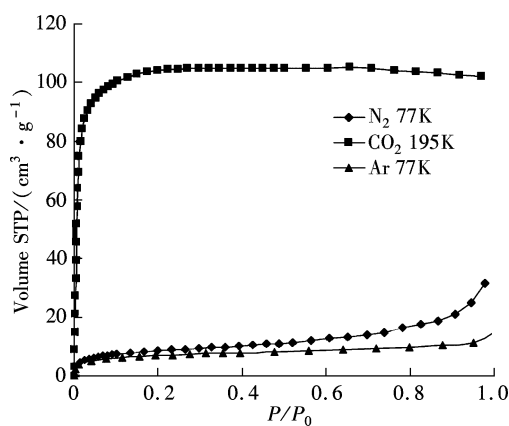


Fig. 5 Adsorption isotherms of anhydrous sample of compound 1 for CO₂, N₂ and Ar

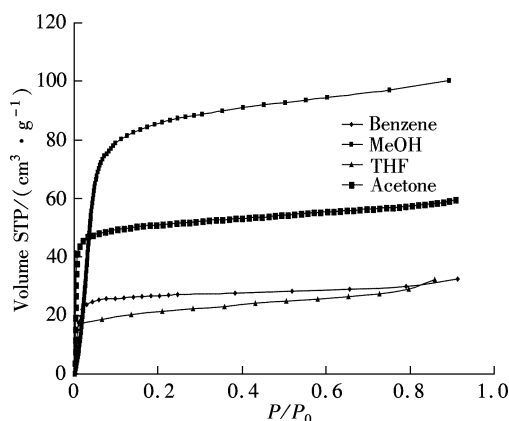


Fig. 6 Adsorption isotherms of anhydrous sample of compound 1 for MeOH, Acetone, Benzene and THF at 298 K

新型 1,4-萘二甲酸铁多孔配位聚合物的合成 和晶体结构及其吸附性质

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摘要:用水热法在 150 °C 下由 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 和 1,4-萘二甲酸 (1,4- H_2NDC) 合成了一个新型的配位聚合物 $\text{Fe}(\text{OH})(1,4\text{-NDC}) \cdot 2\text{H}_2\text{O}$. 单晶结构分析表明该化合物为四方晶系, 空间群为 $\text{P4}_2/\text{nmc}$, 晶胞参数 $a = 2.1447(4) \text{ nm}$, $c = 0.68849(14) \text{ nm}$, $V = 3.1669(11) \text{ nm}^3$, $Z = 8$, $R = 0.0845$, $wR = 0.1829$. 该化合物中含有羟基桥连的 Fe-O-Fe 无机链, 无机链通过 NDC 的连接形成了三维框架, 其中包含 2 种方形截面的孔道. 2 种孔道的尺寸分别为 $0.76 \text{ nm} \times 0.76 \text{ nm}$ 和 $0.30 \text{ nm} \times 0.30 \text{ nm}$. 化合物的结构没有随客体水分子的除去而发生改变, 因此形成了稳固的永久孔性结构. 吸附性质研究表明, 脱去水分子的该配位聚合物能够吸附 CO_2 . 对甲醇、丙酮、四氢呋喃和苯的吸附也进行了研究.

关键词:微孔配位聚合物; 选择性吸附; 1,4-萘二甲酸

中图分类号: O614.81⁺¹