Porous tetrahedral Zn(II)-tetrazolate framework with highly adsorption selectivity of CO_2 over N_2

Wu-wu Li [a, b, c], Ying Guo [b], Zun-ting Zhang [a, b, *]

[a] Key Laboratory of the Ministry of Education for Medicinal Resources and Natural Pharmaceutical Chemistry, Shaanxi Normal University, Xi'an 710062, China
[b] National Engineering Laboratory for Resource Development of Endangered Crude Drugs in Northwest of China and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China
[c] College of Chemistry & Chemical Engineering, Xianyang Normal University, Xianyang, 712000, China

ARTICLE INFO

ABSTRACT

Presented here is a new porous tetrahedral Zn(II)-tetrazolate framework, namely $[Zn_2(mtz)_3(OH)]_n \cdot n(DMF)$ (**1**, Hmtz = 5-methyl-1H-tetrazole, DMF = N,N'-dimethylformamide), has been successfully synthesized under solvothermal conditions. Single crystal X-ray structural analysis reveals that compound **1** features a three-dimensional (3D) porous framework with 4-connected dia-type topology. The 1D channels along the crystallograhical c axis are occupied by the lattice DMF molecules. The desolvated samples show highly adsorption selectivity of CO_2 over N_2.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Metal-organic frameworks (MOFs) as a new class of functional materials have great potential applications in the areas of luminescence, gas storage, catalysis, magnetism and so on [1–5]. Typically, MOFs are constructed by the self-assembly of metal ions with multidentate organic ligands *via* metal coordination bonds under approximate solvothermal conditions [6–8]. Up to now, it is still a great challenge in crystal engineering to obtain the predictable structures with potential properties. Therefore, selection of an approximate organic ligand can help us to direct the synthesis of the desired structures. Among various organic ligands, N-heterocyclic imidazole, triazole, tetrazole, and their derivatives have been investigated and proven to be a rational choice to synthesize MOFs with intriguing structural varieties and potential applications [9–13]. 5-methyl-1H-tetrazole (Hmtz) has four potential coordination sites, and can bridge metal ions on a plane. Among the reported tetrazole-based MOFs, tetrazole ligand often adopts a μ_2-

bridging mode, and the uncoordinated N-donor sites can effectively improve the MOFs' gas sorption and separation properties [14–16]. In viewing of that, in this work, we select 5-methyl-1H-tetrazole as the organic ligand to react with tetrahedral Zn(II) ions under solvothermal conditions. Successfully, we obtained a new porous tetrahedral Zn(II)-tetrazolate framework, namely $[Zn_2(mtz)_3(OH)]_n \cdot n(DMF)$ (**1** Hmtz = 5-methyl-1H-tetrazole, DMF = N,N'-dimethylformamide). Single crystal X-ray diffraction analyses indicate that compound 1 displays a 3D porous framework with 4-connected dia-type topology.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents employed in this work were commercially available and used without further purification. Elemental analyses (C, H and N) were determined with an elemental Vario EL III analyzer. Infrared spectrum using the KBr pellet was measured on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm^{-1}. Powder X-ray diffraction (PXRD) analyses were recorded on a PANalytical X'Pert Pro powder diffractometer with Cu/Kα radiation ($\lambda = 1.54056$ Å) with a step size

of 0.05°. Thermal analyses were carried out on a NETSCHZ STA−449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

2.2. Synthesis of $[Zn_2(mtz)_3(OH)]_n \cdot n(DMF)(1)$

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.058 g, 0.2 mmol), Hmtz (0.034 g, 0.4 mmol), DMF (3 mL) and H_2O (1 mL) was placed in a small vial at 110 °C for 72 h and then cooled to room temperature slowly. Colorless prism crystals were obtained in 42% yield based on $Zn(NO_3)_2 \cdot 6H_2O$. Anal. calcd. for $C_9H_{16}N_{13}O_2Zn_2$ (469.13): C, 23.02; H, 3.41; N, 33.25%. Found: C, 23.06; H, 3.45; N, 33.19%. IR (KBr pellet cm^{-1}): 3421(w), 1617 (s), 1584 (m), 1527 (s), 1371 (vs), 1315 (m), 1068 (s), 967 (w), 782 (m), 665(w).

2.3. X-ray crystallography

Suitable single crystal of **1** was carefully selected under an optical microscope and glued to thin glass fibers. Structural measurement was performed with a computer−controlled Oxford Xcalibur E diffractometer with graphite−monochromated Mo−Kα radiation ($\lambda = 0.71073$ Å) at T = 293(2) K. Absorption corrections were made using the SADABS program [17]. The structure was solved by direct methods and refined by full−matrix least−square methods on F^2 by using the SHELXL−97 program package [18]. All non−hydrogen atoms were refined anisotropically. The H atoms attached to their parent atoms of organic ligands were geometrically placed and refined using a riding model. Crystal data, as well as details of data collection and refinements of **1** are summarized in Table 1, selected bond lengths and angles are given in Table 2.

3. Results and discussions

3.1. Crystal structure of compound **1**

Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic $P2_1/c$ space group and features a 3D framework with 4-connected dia-type topology. The asymmetric unit of **1** contains two crystallographically independent Zn(II) ions, three μ_2-mtz$^-$ ligands, one μ_2-OH$^-$ ligand and one free DMF molecule. As shown in Fig. 1a, both Zn1 and Zn2 are tetrahedrally

Table 1
Crystal data and structure refinements for compound **1**.

	1
Formula	$C_9H_{16}N_{13}O_2Zn_2$
Fw (g/mol)	469.13
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.0236(8)
b (Å)	9.9851(6)
c (Å)	15.8600(9)
α(°)	90.00
β(°)	105.201(6)
γ(°)	90.00
Volume (Å^3)	1837.48(19)
Z	4
Density (cm^3/g)	1.696
Abs. coeff. (mm^{-1})	2.646
Total reflections	6665
Unique reflections	3240 (Rint = 0.0237)
Goodness of fit on F^2	0.979
Final R indices [$I > 2$sigma(I^2)]	$R = 0.0436$, $wR_2 = 0.1117$
R (all data)	$R = 0.0553$, $wR_2 = 0.1216$

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**.

Compound 1			
Zn(1)−O(1)	1.909(3)	Zn(1)−N(5)	1.990(4)
Zn(1)−N(8)^a	2.010(4)	Zn(1)−N(1)	2.014(4)
Zn(2)−O(1)	1.902(3)	Zn(2)−N(4)^b	1.990(4)
Zn(2)−N(12)^c	1.998(4)	Zn(2)−N(9)	2.037(4)
O(1)−Zn(1)−N(5)	109.67(14)	O(1)−Zn(1)−N(8)^a	109.01(15)
N(5)−Zn(1)−N(8)^a	111.86(15)	O(1)−Zn(1)−N(1)	106.90(14)
N(5)−Zn(1)−N(1)	107.70(15)	N(8)^a−Zn(1)−N(1)	111.57(16)
O(1)−Zn(2)−N(4)^b	113.02(14)	O(1)−Zn(2)−N(12)^c	110.35(14)
N(4)^b−Zn(2)−N(12)^c	116.73(15)	O(1)−Zn(2)−N(9)	101.25(14)
N(4)^b−Zn(2)−N(9)	104.62(15)	N(12)^c−Zn(2)−N(9)	109.49(16)

Symmetry codes: compound **1** (a) $1 - x$, $-0.5 + y$, $0.5 - z$; (b) x, $1.5 - y$, $0.5 + z$; (c) $-x$, $0.5 + y$, $0.5 - z$.

coordinated by three N atoms from three different μ_2-mtz$^-$ ligands and one O atom (O1) from one μ_2-OH$^-$ ligand. The Zn-N distances are in the range of 1.990(4)-2.037(4) Å, and the Zn-O distance is 1.909(3) Å. As shown in Fig. 2b, fourteen Zn(II) are bridged by twelve μ_2-mtz$^-$ ligands and six μ_2-OH$^-$ ligands, generating a dia-type cage. Finally, these dia-type cages are further connected together by the connections of μ_2-mtz$^-$ and μ_2-OH ligands, affording a 3D framework (Fig. 1c). Viewing along crystallographical c axis, there exist large 1D channels which were occupied by the lattice DMF molecules. The solvent−accessible volume in this framework is approximate 624.9 Å^3 per unit cell volume, and the pore volume ratio is to be 34% calculated by the PLATON program. If the Zn(II) ions were reduced into 4-connected nodes, and the μ_2-mtz$^-$ and μ_2-OH$^-$ ligands were reduced into linear connectors, the whole framework of **1** can be simplified into a 4-connected dia-type topological network with the point symbol of {6^6} (Fig. 1d).

3.2. Powder X-ray diffraction patterns (PXRD) and thermal analysis of compound **1**

The phase purity of compound **1** has been identified by the powder X-ray diffraction analysis. As shown in Fig. 2a, the experimental pattern of compound **1** matches well with the simulated one based on the single crystal diffraction data, demonstrating the bulk samples of compound **1** are in pure phase. In addition, the thermal stability of compound **1** was also investigated by thermogravimetric analysis (TGA) under N_2 atmosphere in the temperature range of 30−800 °C (Fig. 2b). From the TGA curve of compound **1**, we found that the first weight loss of 15.78% occurs from 30 to 235 °C, corresponding to the departure of one lattice DMF molecule per unit cell (calcd: 15.56%). Then the desolvated samples can be stable up to 340 °C, and after 340 °C, the framework started to collapse owing to the decomposition of the organic ligands. Finally, the residues may be powder ZnO (obsd: 34.23%, calcd: 34.53%).

3.3. Gas adsorption properties

The permanent porosity of the desolvated **1** was established by reversible gas adsorption experiments using N_2 at 77 K. Before gas adsorption, compound **1** was activated under vacuum at 320 °C for 24 h to obtain the desolvated **1**. As shown in Fig. 3a, the N_2 sorption isotherm of the desolvated samples at 77 K shows a type-I behavior with the maximum N_2 uptake of 174.8 cm^3/g at 1 bar, giving the BET and Langmuir surface areas of 596.2 and 734.6 m^2/g, respectively. A single data point at a relative pressure of 0.99 bar gives a pore volume of 0.283 cm^3/g by the Horvath-Kawazoe equation. To demonstrate the potential of this rigid framework material in CO_2/ N_2 gas separation, we performed the sorption behaviors for CO_2