



Porous pcu-type Zn(II) framework material with high adsorption selectivity for CO₂ over N₂



Yiping Lu ^a, Yanli Dong ^{b,*}, Jing Qin ^c

^a Hebei North University, Zhangjiakou 075000, PR China

^b College of Sciences, Agricultural University of Hebei, Baoding 071001, PR China

^c Hebei University of Architecture, Zhangjiakou 075000, PR China

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ABSTRACT

Reported here is a new Zn(II) compound, namely [Zn₂(tdc)₂(MA)]_n (H₂tdc = 2,5-thiophenedicarboxylic acid, MA = melamine), which has been constructed by the self-assembly reaction of Zn(NO₃)₂, H₂tdc and MA under solvothermal conditions. Single crystal X-ray diffraction analysis reveals that this compound features a 3D porous framework with 6-connected pcu topology. Notably, this compound exhibits high CO₂ sorption capacity and high sorption selectivity for CO₂ over N₂ at 298 K.

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1. Introduction

The design and construction of porous metal-organic frameworks as adsorbents for CO₂ capture is a vital technology to address the green house effect caused by the large emissions of CO₂ from modern industry [1–4]. In order to enhance the CO₂ sorption capacity in MOFs, many successfully strategies for tuning the MOFs' surface properties, such as polar functional groups, uncoordinated metal sites and extraframework cations and so on, have been well established [5–7]. Through these methods, the CO₂ adsorption capacity in MOFs can be significantly improved owing to the strong interactions between the MOFs' active sites and CO₂ molecules [8,9]. Thus, selection of appropriate organic ligands and metal ions is crucial to synthesize porous MOFs.

As we all know that the amino groups of MOFs have great affinity for CO₂ molecules. Melamine (MA), which has three amino groups, is a good multidentate organic ligand and can bridge metal ions in various coordination modes. Using MA as the organic ligand provides huge potential for building porous MOFs with high CO₂ sorption capacity. 2, 5-thiophenedicarboxylic acid (H₂tdc) has two carboxylate groups and can bridge metal ions in linear mode, which

may help us to construct porous MOFs with high thermal stabilities [10]. In previously reported literature, numerous porous MOFs are constructed from linear organic ligands [11–13]. Considering that, in this work, we select linear H₂tdc and amino-containing MA as the organic ligands to assemble with Zn(II) ions, successfully obtaining a new porous pcu-type Zn(II) compound, namely [Zn₂(tdc)₂(MA)]_n (H₂tdc = 2,5-thiophenedicarboxylic acid, MA = melamine). This compound exhibits high CO₂ sorption capacity and high sorption selectivity for CO₂ over N₂ at 298 K.

2. Experimental

2.1. Materials and methods

All the starting materials and reagents used in this work were obtained commercially and used without further purification. Element analyses (C, H and N) were determined with an elemental Vairo 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. TGA analyses were carried out on a NETSCH STA-449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. Powder X-ray diffraction (PXRD) analyses were recorded on a PANalytical X'Pert Pro powder diffractometer with Cu/Kα radiation (λ = 1.54056 Å) with a step size of 0.05°. Gas adsorption measurement was performed in the ASAP (Accelerated

* Corresponding author.

E-mail address: yanli_dong3157@163.com (Y. Dong).

Surface Area and Porosimetry) 2020 System. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System. Single crystal X-ray diffraction was carried out by an Oxford Xcalibur E diffractometer.

2.2. Synthesis of $[Zn_2(tdc)_2(MA)]_n$

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 0.0297 g), H_2tdc (0.1 mmol, 0.0172 g) and MA (0.1 mmol, 0.0126 g) and DMA (2 mL) was sealed in a small vial, which was kept at 100 °C for 60 h and then cooled to the room temperature slowly. Colorless prism crystals yield in 43% based on $Zn(NO_3)_2 \cdot 6H_2O$. Anal. Calcd. (%) for $C_{15}H_{10}N_6O_8S_2Zn_2$ (597.19): C, 30.14; N, 14.07; H, 1.67. Found (%): C, 30.22; N, 14.02; H, 1.68. IR(cm^{-1} , KBr pellet): 3076 (w), 1702 (s), 1618(s), 1589(w), 1566(w), 1506(m), 1430(s), 1372(s), 1263(s), 1224(s), 1031(m), 963(m), 833(m).

2.3. X-ray crystallography

Single crystal X-ray structure analysis of this compound was performed on Oxford Xcalibur E diffractometer (Mo/ $K\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 293(2) K. Empirical absorption corrections were applied to the data using the SADABS program [14]. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 program [15]. All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon atoms were located at their ideal positions. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and angles for this compound are listed in Table 2.

3. Result and discussion

3.1. Structural description

Single crystal structural analysis reveals that this compound crystallizes in the orthorhombic $Pnma$ space group. The asymmetric unit consists of two Zn(II) ions, one and two halves tdc^{2-} ligands and one MA ligand. As shown in Fig. 1, both Zn1 and Zn2 ions are five-coordinated by four carboxylate oxygen atoms and

Table 1
Crystallographic data for this Zn(II) compound.

Empirical formula	$C_{15}H_{10}N_6O_8S_2Zn_2$
Temperature(K)	293
Crystal color	colorless
Formula weight	597.19
Crystal system	orthorhombic
Space group	$Pnma$
a (Å)	20.1368(10)
b (Å)	20.2976(8)
c (Å)	17.4633(12)
α (°)	90
β (°)	90
γ (°)	90
Volume(Å ³)	7137.8(7)
Z	8
Density (calculated)	1.112
Abs. coeff. (mm^{-1})	1.495
$F(000)$	2408
θ for data collection (°)	2.53 to 25.00
Reflections collected	17376
Unique reflections	6441
R_{int}	0.0273
Goodness-of-fit on F^2	1.152
$R1, wR_2$ [$I > 2\sigma(I)$]	0.0392, 0.0953
$R1, wR_2$ (all data)	0.0686, 0.1093

Table 2
Selected bond lengths (Å) and angles (°) for this Zn(II) compound.

Zn(1)–O(2)	2.011(5)	Zn(1)–O(8) ^a	2.020(6)
Zn(1)–O(6)	2.046(5)	Zn(1)–N(3) ^b	2.053(6)
Zn(1)–O(4)	2.058(5)	Zn(2)–O(3)	2.022(5)
Zn(2)–O(5)	2.022(6)	Zn(2)–O(7) ^a	2.051(6)
Zn(2)–O(1)	2.052(5)	Zn(2)–N(1)	2.063(7)
O(2)–Zn(1)–O(8) ^a	86.9(2)	O(2)–Zn(1)–O(6)	87.8(2)
O(8) ^a –Zn(1)–O(6)	157.9(2)	O(2)–Zn(1)–N(3) ^b	104.6(2)
O(8) ^a –Zn(1)–N(3) ^b	102.1(3)	O(6)–Zn(1)–N(3) ^b	100.0(3)
O(2)–Zn(1)–O(4)	153.1(2)	O(8) ^a –Zn(1)–O(4)	87.8(2)
O(6)–Zn(1)–O(4)	87.3(2)	N(3) ^b –Zn(1)–O(4)	102.4(2)
O(3)–Zn(2)–O(5)	86.6(3)	O(3)–Zn(2)–O(7) ^a	86.5(2)
O(5)–Zn(2)–O(7) ^a	153.8(2)	O(3)–Zn(2)–O(1)	157.9(2)
O(5)–Zn(2)–O(1)	90.7(3)	O(7) ^a –Zn(2)–O(1)	86.3(2)
O(3)–Zn(2)–N(1)	101.4(2)	O(5)–Zn(2)–N(1)	102.7(3)
O(7) ^a –Zn(2)–N(1)	103.4(3)	O(1)–Zn(2)–N(1)	100.6(3)

^a Symmetry codes: $x + 1/2, y, -z + 1/2$.

^b $-x + 1/2, -y + 1, z + 1/2$.

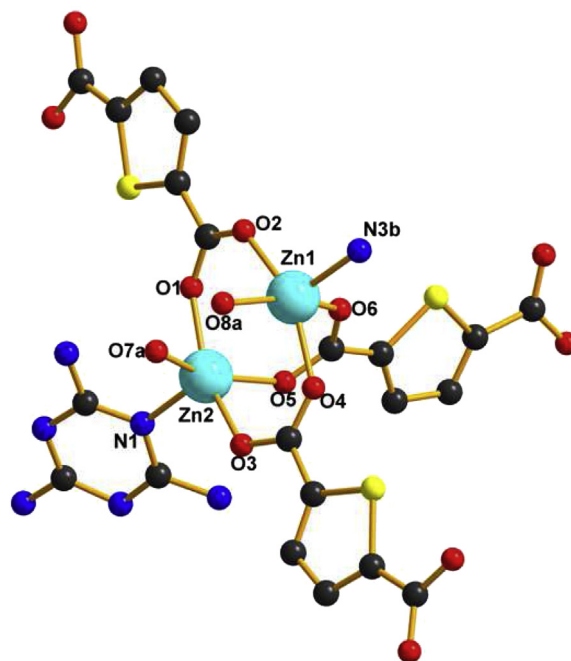


Fig. 1. View of the coordination environments of Zn(II) ions in Zn(II) compound. All hydrogen atoms were omitted for clarity. Symmetry codes: (a) $x + 1/2, y, -z + 1/2$; (b) $-x + 1/2, -y + 1, z + 1/2$.

one nitrogen atom, showing distorted square pyramidal geometries. The Zn–O and Zn–N distances are in the range of 2.011(5)–2.058(5) Å, 2.053(6)–2.063(7) Å, respectively. Each tdc^{2-} ligand links four Zn(II) ions with its two carboxylate groups in uniform bis-monodentate mode. Zn1 and Zn2 ions are bridged by four bis-monodentate carboxylate groups into a paddle wheel shaped dinuclear $[Zn_2(COO)_4]$ subunits with the Zn ... Zn separation of 3.069 Å (Fig. 2a). These dinuclear $[Zn_2(COO)_4]$ subunits are further bridged together by the tdc^{2-} ligands, generating a 2D layer extending along ab plane (Fig. 2b). These adjacent 2D layers are further linked into a 3D porous framework via the connection of MA ligands, which adopt μ_2 -N1, N2 mode (Fig. 2c).

The solvent accessible volume of this compound is estimated to be about 52.3% of the total crystal volume calculated by the PLATON program. In this 3D pillar-layer framework, there exist abundant hydrogen bonds between the carboxylate oxygen atoms and nitrogen atoms from MA ligands, which further consolidate the

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