A novel metal–organic framework based upon cobalt cluster: Synthesis, structure and gases uptakes

Ruirui Yun *, Yaqin Jiang, Gang Xu

The Key Laboratory of Functional Molecular Solids, Ministry of Education, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, China
College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, China

ABSTRACT

A novel three-dimensional *ant*-type metal–organic framework, $[Na_{0.5}CoL(OH)_{0.5}(H_2O)]\cdot G$ (**1**) (L = 5-(pyridin-4-yl)isophthalic acid, G = guest molecules), has been designed and synthesized. Singe crystal of **1** was characterized by X-ray single crystal analysis and power X-ray diffraction methods. Network analysis reveals that **1** is a two-nodal (3, 6)-connected $(4^2.6)_2(4^4.6^2.8^8.10)$. Additionally, the permanent porosity of **1** was confirmed by N_2 gas adsorption investigation with the BET specific surface area of $477 \ m^2 \ g^{-1}$. At 1 bar, **1** exhibits hydrogen adsorption amount of 1.08 wt% at 77 K and CO_2 uptakes of 13.7 wt% at 273 K, respectively.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Metal–organic frameworks (MOFs) are hybrid crystalline solids composed of organic structure and inorganic nodes and have emerged as a novel type of highly porous materials [1–4]. Recent years, owing to these materials' tunable but uniform pore size and functionalizable pore walls, the number of reports of MOFs has increased dramatically relevant to their wide range of applications in gas storage and others [5–7]. From the structural point of view, the successful construction of MOFs usually depends on the rational selection of polytopic ligand, metal ions or second building units as well as reaction conditions. Additionally, it is well known that the choice of metal ion and organic ligand can dictate the framework topology (affecting pore size and shape) and influence the overall chemical functionality of the framework [8–10]. MOFs prepared from ligands of high symmetry have been well studied because of synthetic and crystallographic considerations. However, organic linkers with less symmetry containing mixed carboxylate and pyridine coordinating groups are rarely in MOFs studies [11,12].

We are interested in construction of novel coordination nanostructures and metal–organic frameworks from high symmetric multidentate ligands with attractive properties [13–17]. In this article, we report a novel three-dimensional MOF with interconnected channel structure which assembled from the C_2-symmetric ligand of 5-(pyridin-4-yl)isophthalic acid (H_2L) and

six-connected cobalt (II) clusters under solvothermal conditions. **1** was characterized by X-ray crystallography, powder X-ray diffraction and gases adsorption uptakes. Interestingly, this MOF material exhibits moderate BET specific surface area ($477 \ m^2 \ g^{-1}$) and large hydrogen uptake capacity (1.08 wt%) if compared to that of MOFs with similar specific surface area at 77 K and 1 bar [18,19].

2. Experimental section

2.1. Materials and methods

Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000–$400 \ cm^{-1}$ region. ^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 ml/min) with a heating rate of 5 °C/min using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 5–50° on a Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation ($\lambda = 1.54184 \ \text{Å}$) at room temperature with a step size of 0.02 in 2θ.

2.2. Synthesis of H_2L

4-iodopyridine (0.205 g, 1.0 mmol), benzene-1,3-dicarboxy-thylester-5-boronic acid (0.64 g, 1.2 mmol), and K_2CO_3 (2.10 g, 10.0 mmol) were added to 1,4-dioxane (30 mL). After stirring, $Pd(PPh_3)_4$ (0.05 g, 0.043 mmol) was added, then the mixture was

* Corresponding author. Tel.: +86 015395396117.
E-mail address: yunruirui@gmail.com (R. Yun).

heated to 80 °C for 3 days under N$_2$. The resultant was evaporated to dryness and taken up in CH$_2$Cl$_2$ which later had been dried over MgSO$_4$. This CH$_2$Cl$_2$ solution was evaporated to dryness and the residue was washed briefly with ethanol (20 mL). The crude product was hydrolyzed by refluxing in 2 M aqueous NaOH followed by acidification with 37% HCl to afford H$_2$L. Yield: 0.53 g, 71.8%. ^{1}H NMR (DMSO-d_6, 500 MHz), PIP: 8.7 (d, 2H), 8.54 (s, 1H) 8.48 (s, 2H), 8.24 (d, 1H, J) 6.1 Hz), 7.81 (d, 2H). Anal. Calc. for H$_2$L, C$_{13}$H$_9$O$_4$N: C, 64.20; N, 5.76; H, 3.73. Found: C, 64.03; N, 5.68; H, 3.79%.

2.3. Synthesis of complex 1

1 was synthesized by reaction of H$_2$L (12.7 mg, 0.05 mmol), NaOH (2 mg, 0.05 mmol), Co(NO$_3$)$_2$·6H$_2$O (14.5 mg, 0.05 mmol) and 8 drops of concentrated nitric acid in N,N′-dimethylformamide (DMF) at 65 °C for 3 days. The purple polyhedral crystals were collected and washed with DMF. Yield 17 mg, (~67% based on ligand). Anal. Calc. for activated **1**, C$_{13}$H$_9$CoNNa$_{0.5}$O$_{5.5}$: C, 46.24; N, 4.15; H, 2.69. Found: C, 46.53; N, 4.02; H, 2.71%.

2.4. X-ray structure determination

Suitable single crystal was sealed in a capillary to prevent desolvation during data collection, and the X-ray diffraction data were measured on a Bruker smart Apex CCD diffractometer at 296 K using graphite monochromated Mo Kα radiation (λ = 0.7173 Å). Data reduction was made with the BRUKER SAINT program. Absorption corrections based on multiscan were obtained by the SADABS program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package [20]. Displacement parameters were refined anisotropically, and the positions of the H-atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The lager volume fractions of disordered solvent in the lattice pores of **1** could not be modeled in terms of atomic sites and so they were treated using the SQUEEZE routine in the PLATON software package and the structure was refined again using the data generated [21,22]. Unfortunately, the wR_2 of the structure was higher and many warnings were not solved due to the lower data quality and bad quality of the crystal. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.

Table 1
Crystallographic data for MOF material **1**.

Complex	1
Empirical formula	C$_{13}$H$_7$CoNNa$_{0.5}$O$_{5.5}$
Formula weight (g mol^{-1})	335.62
λ (Å)	0.71073
Space group	C2/c
a (Å)	15.947(5)
b (Å)	15.391(4)
c (Å)	19.064(5)
α (°)	90
β (°)	101.182(4)
γ (°)	90
V (Å^3)	4590(2)
Z	8
ρ (g cm^{-3})	0.971
F(000)	1364
μ (mm^{-1})	0.771
Data/restraints/parameters	4205/3/230
Goodness-of-fit (GOF)	1.085
R [I > 2σ(I)], wR [I > 2σ(I)]	0.0815, 0.2287
Maximum/minimum peaks (e Å^{-3})	1.47, −1.18
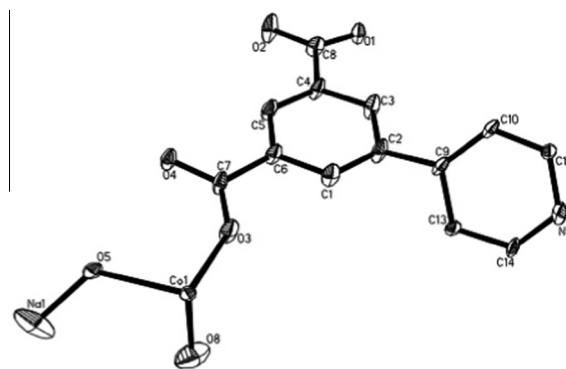
Fig. 1. the asymmetric unit of **1** with atom labeling scheme at 30% probability thermal ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity. Selected distances/Å for **1**: N(1)–Co(1) 2.15(3), O(1)–Co(1) 2.022(5), O(3)–Co(1) 2.013(5), O(4)–Co(1) 2.110(5), O(5)–Co (1) 2.168(4), O(8)–Co(1) 2.125(5).
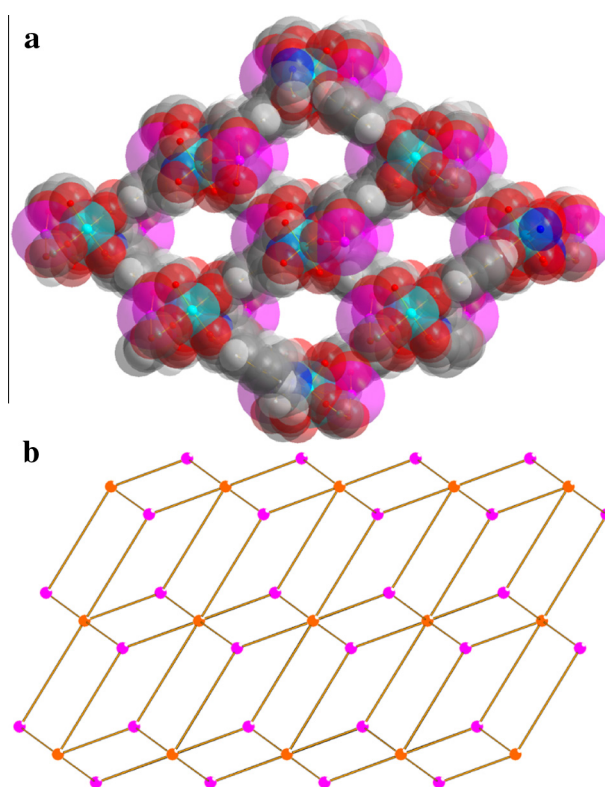
Fig. 2. Structure packing of complex **1**. (a) 1-D channel of **1** with the space fill; (b) 3,6-connected ant topology (pink: ligand, orange: metal cluster). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.5. Gas sorption measurements

As-synthesized **1** crystals were washed with DMF three times and then removed DMF by decanting, the sample was further activated by drying under a dynamic high vacuum at 100 °C overnight to obtain the activated sample. The gases adsorption measurements up to 1 atm were performed on an ASAP 2020 surface area and pore size analyzer. Adsorption measurements were performed using high purity nitrogen (99.999%) and hydrogen (99.9995%) on a sample of ca. 100 mg with the temperature maintained at 77 K by liquid nitrogen. For the CO$_2$ (99.999%) adsorption measurement, the temperature maintained at 273 and 298 K, respectively.