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# 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*

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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.

## 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 $2\theta$ range 5–50° on a Bruker D8 ADVANCE X-ray diffractometer using Cu K$\alpha$ radiation ($\lambda$ = 1.54184 Å) at room temperature with a step size of 0.02 in $2\theta$.

### 2.2. Synthesis of $H_2L$

4-iodopyridine (0.205 g, 1.0 mmol), benzene-1,3-dicarboxyethylester-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

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

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heated to 80 °C for 3 days under $N_2$. The resultant was evaporated to dryness and taken up in $CH_2Cl_2$ which later had been dried over $MgSO_4$. This $CH_2Cl_2$ 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 $H_2L$. 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 $H_2L$, $C_{13}H_9O_4N$: 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 $H_2L$ (12.7 mg, 0.05 mmol), NaOH (2 mg, 0.05 mmol), $Co(NO_3)_2{\cdot}6H_2O$ (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**, $C_{13}H_9CoNNa_{0.5}O_{5.5}$: 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 ($\lambda$ = 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 | $C_{13}H_7CoNNa_{0.5}O_{5.5}$ |
| Formula weight (g mol$^{-1}$) | 335.62 |
| $\lambda$ (Å) | 0.71073 |
| Space group | *C*2/*c* |
| *a* (Å) | 15.947(5) |
| *b* (Å) | 15.391(4) |
| *c* (Å) | 19.064(5) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 101.182(4) |
| $\gamma$ (°) | 90 |
| *V* (Å$^3$) | 4590(2) |
| *Z* | 8 |
| $\rho$ (g cm$^{-3}$) | 0.971 |
| *F*(000) | 1364 |
| $\mu$ (mm$^{-1}$) | 0.771 |
| Data/restraints/parameters | 4205/3/230 |
| Goodness-of-fit (GOF) | 1.085 |
| $R\ [I > 2\sigma(I)]$, $wR\ [I > 2\sigma(I)]$ | 0.0815, 0.2287 |
| Maximum/minimum peaks (e Å$^{-3}$) | 1.47, −1.18 |

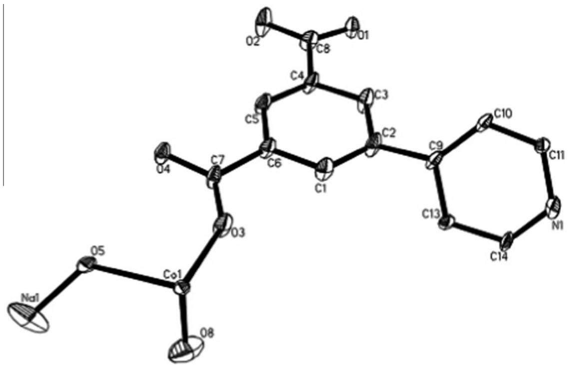

**Fig. 1.** the asymmetric unit of **1** with atom labeling scheme at 30% probability thermal ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity. Selected distances/Å for **1**: N(1)–Co(1) 2.15(3), O(1)–Co(1) 2.022(5), O(3)–Co(1) 2.013(5), O(4)–Co(1) 2.110(5), O(5)–Co (1) 2.168(4), O(8)–Co(1) 2.125(5).

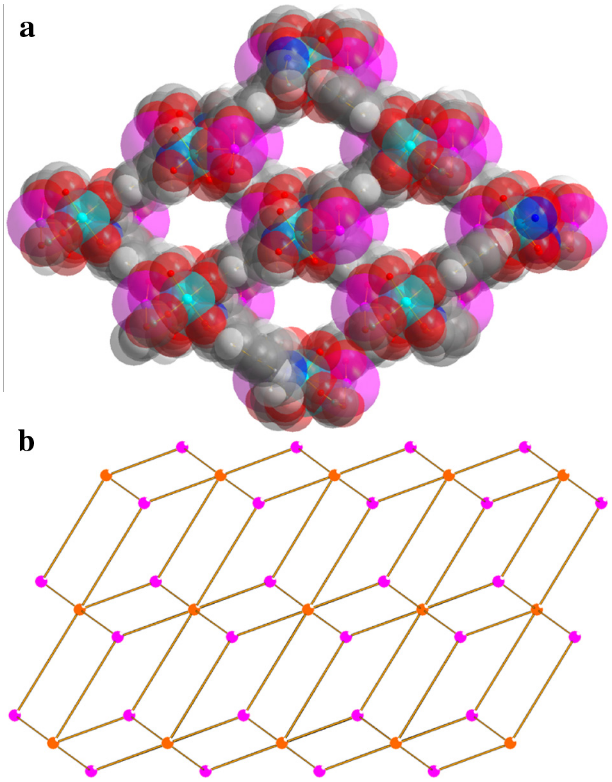

**Fig. 2.** Structure packing of complex **1**. (a) 1-D channel of **1** with the space fill; (b) 3,6-connected *ant* topology (pink: ligand, orange: metal cluster). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 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.

## 3. Results and discussion

### 3.1. Crystal structure of **1**

Solvothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ with $H_2L$ and NaOH in DMF (N,N-dimethylformamide) afforded purple polyhedral crystals of $[Na_{0.5}CoL(OH)_{0.5}(H_2O)] \cdot G$ (**1**), (G = guest molecules) which crystallizes in centro-symmetric monoclinic space group *C*2/*c*. In this structure, free solvent molecules were removed using the SQUEEZE routine of PLATON and the structure was refined again using the data generated.

The structure of **1** is a 3D coordination polymer that based on six-connected trinuclear cluster as nodes and 5-(pyridin-4-yl)isophthalic acid ligands. The asymmetric unit of **1** confirms the assignment of 1:1 stoichiometry for the Co(II): 5-(pyridin-4-yl)isophthalic acid ligand (Fig. 1). Single crystal X-ray determination of complex **1** reveals that each Co(II) center is six-coordinated with the $\mu_3$-OH ion, one nitrogen atom of the ligand, one water, and three oxygen atoms from three separate ligands, respectively. We can be seen from the overall structure, the metal clusters are linked by the ligands to form a framework which contains a 3.3 × 3.4 Å channel.

For easy comprehension, we simplified the ligand as a 3-connected nodes and trinuclear clusters as a six-connected nodes, the topology of the structure can be described as a (3, 6)-connected net with stoichiometry (3-c)2(6-c). The point (Schälfli) symbol for **1** is $(4^2.6)_2(4^4.6^2.8^8.10)$ as calculated using TOPOS [23]. Consequently, the topology of **1** is assigned with RCSR symbol *ant* [24], as shown in Fig. 2b. In addition, we can see from Fig. 2a, it exhibits one-dimensional channel in the structure of **1**. The calculated free volume in fully desolvated **1** is 39% by PLATON program.

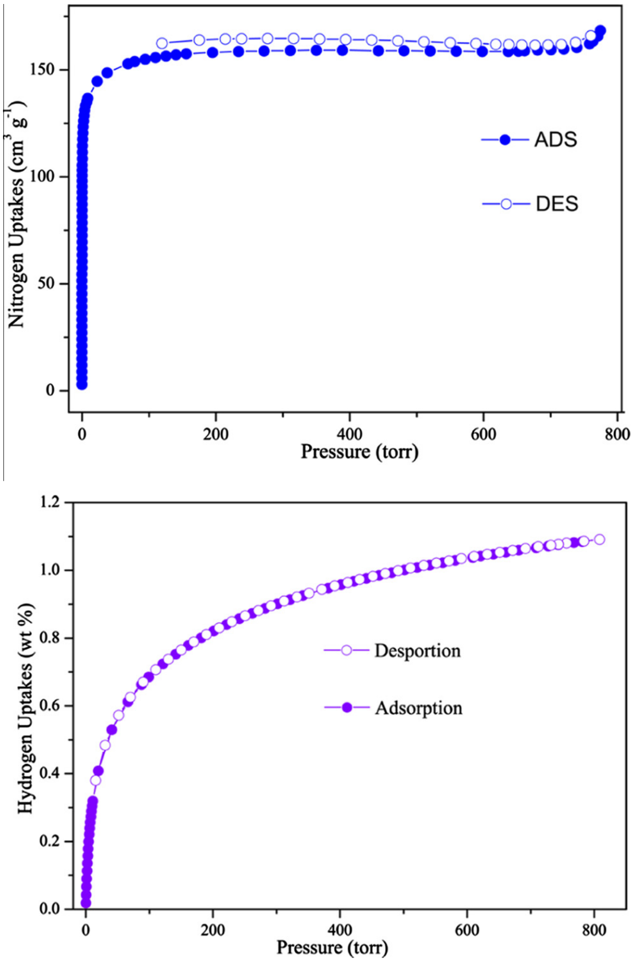

**Fig. 3.** Experimental $N_2$ (blue) and $H_2$ (purple) adsorption isotherms for **1** at 77 K; ● adsorption, ○ desorption. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To confirm the permanent porosity of **1**, a large amount of pure **1** can be readily prepared (Fig. S1). As shown in Fig. 3, the sorption measurement of 1 for $N_2$ gave typical type-I isotherm, which is the characteristic of a microporous material. The BET and langmuir specific surface area were estimated from the $N_2$ isotherm at 77 K to be 477 and 700 $m^2\,g^{-1}$, respectively. The total pore volume of **1** calculated from the maximum amount of $N_2$ adsorbed at 77 K reaches up to 0.21 $cm^3\,g^{-1}$. Owing to the porous nature of the framework, **1** can uptake considerable amounts of $CO_2$ at 273 and 298 K (70 and 51 $cm^3\,g^{-1}$, respectively Fig. S2).

Moreover, we measured the $H_2$ adsorption of **1** due to its smaller pore size. Hydrogen sorption isotherm was measured at 77 K under 1 atm. As shown in Figs. 3 and 1 can reversibly adsorb 1.08 wt% (excess) hydrogen at 1 bar and 77 K. This uptake capacity is higher than the values reported for some other MOF materials with comparable specific surface area under the same conditions, such as PCN-19 (723 $m^2\,g^{-1}$, 0.95 wt%) [25] and $Zn(bpe)(tfbdc)_3$ (512 $m^2\,g^{-1}$, 1.04 wt%) [26]. The higher $H_2$ adsorption of **1** can be ascribed to its much smaller pore size.

## 4. Conclusions

In summary, we have designed and synthesized a novel porous MOF with an *ant* topology, which was constructed by pyridyl-aromatic multi-carboxylate acid ligand. The complex was characterized by X-ray crystallography and gases adsorption. The complex displays a three-dimensional framework with the topology of *ant* and two-connected channels of different size. Our study demonstrates the mixed donor ligand, in this case pyridine-carboxylates, in forming porous structure which exhibits interesting adsorption properties with a specific surface area of 477 $m^2\,g^{-1}$ as well as affords its high hydrogen uptake capacity of 1.08 wt% at 77 K and 1 atm.

## Appendix A. Supplementary data

CCDC 943878 contains the supplementary crystallographic data **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.02.001.

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