Two novel metal-organic frameworks based on linear dicarboxylic acid and 5-(4-pyridyl)tetrazole

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ABSTRACT

Two isomorphic metal-organic frameworks, $[Co_2(4-Ptz)_2(BDC)(DMA)]_n$ (**1**) and $[Co_2(4-Ptz)_2(2-NH_2-BDC)(DMA)]_n$ (**2**) (4-Ptz=5-(4-Pyridyl)tetrazole, H_2BDC=Terephthalic Acid, $2-NH_2-H_2BDC$=2-Aminoterephthalic Acid, DMA=N,N-dimethylacetamide), have been successfully constructed through solvothermal reactions. Crystallographic data analysis reveals a binuclear Co(II) cluster-based structure for **1** and **2**, which were constructed by bridging two neighboring Co(II) ions with teterazole rings of 4-Ptz ligand together with one DMA oxygen atom. Simplifying Co_2 cluster as a 6-connecting node, complexes **1** and **2** reveal **bcu-6** net. The CO_2 adsorption isotherms measurement at 273 K manifests higher adsorption quantities for **2** (33.8 cm^3/g) than **1** (26.2 cm^3/g), which was attributed to the introduction of NH_2-group in **2**.

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1. Introduction

Porous metal-organic frameworks (MOFs), constructed from the coordination assembly of organic ligands with metal ions or metal clusters, are an exciting class of materials with unprecedented properties and exhibit great application potential in catalysis, gas storage, and separations [1–7]. The utilization of multitopic ligands has been provided to be one efficient method to construct MOFs with unique structures and properties [8–15]. However, the design and synthesis of well-designed ligands is a time-consuming and laborious procedure, which becomes the key factor to limit the development of MOFs. As an alternative method, mixed-ligands strategy has been developed and widely used to construct novel MOFs, taking advantage of the combined effect of different ligands with various structures and properties [16–18].

Recently, a series of highly porous MOFs have been built successfully by using bifunctional linkers [19–23]. Pyridylcarboxylate ligands, containing both pyridine unit and carboxylate group, are one of the typical bifunctional ligands and much attention has been paid in their utilization in constructing desirable MOFs [24–29], where metal clusters are normally bundled by carboxylate group and pyridine unit usually serves as a challenging group against the coordinating solvent molecule [30,31]. In comparison with pyridyl-carboxylate ligands, 5-(4-pyridyl)tetrazole (4-Ptz) is

less explored in mixed-ligand systems [32–34]. The 4-Ptz ligand has similar backbone length to that of terephthalic (BDC), meanwhile the tetrazole group possesses similar coordination modes to that of carboxylic acid. Therefore, using 4-Ptz together with BDC may produce interesting MOFs geometry.

In addition, the functionalization of ligand is an effective approach to decorate the properties of target MOFs [35]. For example, the introduction of NH_2 group to MOFs may be an effective method to adjust the adsorption behaviors toward CO_2 or H_2 [36,37]. Besides primary BDC, the NH_2-functionalized BDC is also easily available and can be used as an ideal model to evaluate the influence of NH_2 group on the adsorption properties of MOFs by comparing with BDC ligand. Based on above analyses, the coordination of 4-Ptz together with H_2BDC or with $2-NH_2-H_2BDC$ (see Scheme 1) toward Co(II) ion has been studied and two isomorphic MOFs, $[Co_2(4-Ptz)_2(BDC)(DMA)]_n$ (**1**) and $[Co_2(4-Ptz)_2(2-NH_2-BDC)(DMA)]_n$ (**2**) were obtained. Adsorption measurement shows a ca. 30% enhancement of CO_2 adsorption for **2** in comparison with **1**, which was attributed to the additional attracting interaction occurring between NH_2 group and CO_2 molecule.

2. Experimental

2.1. Materials and general methods

All the chemicals used for synthesis are of analytical grade and commercially available. IR spectra were measured on a Tensor 27

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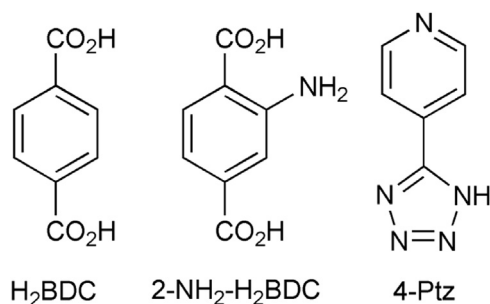
Scheme 1. The applied ligands in two complexes.

OPUS (Bruker) FT-IR spectrometer in KBr pellets. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 diffractometer equipped with a Cu-target tube and a graphite monochromator at 40 kV, 100 mA. Simulations of the PXRD patterns were carried out by using the single-crystal data with the Mercury 3.0 (Hg) program available free of charge via the Internet at http://www.iucr.org. Thermogravimetric analyses (TGA) were carried out on a Rigaku standard TG-DTA analyzer under N_2 with a heating rate of 10 °C min^{-1}, using an empty Al_2O_3 crucible as reference.

The samples for measurement were pretreated with supercritical CO_2 in a Tousimis™ Samdri® PVT-30 critical point dryer. Prior to drying, the DMA solvated MOF samples were soaked in absolute ethanol to exchange the occluded solvent with C_2H_5OH for 48 h. Then the ethanol-containing samples were placed inside the dryer and the ethanol was exchanged with CO_2 (liquid) over a period of 6 h according to the literatures. The processed samples were loaded in sample tubes and activated under high vacuum (less than 10^{-5} Torr) at 100 °C. Degassed samples were used for gas sorption measurements using an ASAP 2020 M gas adsorption analyzer.

2.2. Synthesis of complexes 1 and 2

Synthesis of 1: A mixture of $Co(NO_3)_2$ (0.1 mmol), H_2BDC (0.1 mmol), 4-Ptz (0.1 mmol) and DABCO (triethylenediamine, 0.05 mmol) in DMA (6 mL) solution was sealed in a 10 mL glass vial, and heated to 95 °C for 3 days. The mixture was cooled slowly to room temperature and block red crystals were obtained with a yield of ca. 45% based on Co^{II} salt. FT-IR (KBr pellets, cm^{-1}): 3399w, 1596s, 1384s, 1015s, 843m, 716m, 534m. The IR spectrum is shown in Fig. S1 (SI).

Synthesis of 2: The synthesis of 2 was carried out likewise to that of 1 except that 2-NH$_2$-H$_2$BDC was used instead of H$_2$BDC. Yield: ca. 30% based on Co^{II} salt. FT-IR (KBr pellets, cm^{-1}): 3393w, 2360s, 2341w, 1594s, 1497m, 1384s, 1235s, 1015s, 834m, 752s, 716s, 834m. The IR spectrum is shown in Fig. S1 (SI).

2.3. X-ray crystallography

Single crystal X-ray diffraction measurements were carried out on Rigaku Saturn70 diffractometer at 133(2) K with Mo-Kα radiation ($\lambda=0.71075$ Å). The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [38]. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factor. It should be noted that the guest molecules in the complexes are too disordered to model properly, therefore the resulted diffusing electron densities were removed by the SQUEEZE routine in PLATON [39], which was appended in the CIF files. The elemental analysis (EA) of two complexes was not performed because highly disordered guest molecules cannot be

Table 1
Crystal data and structure refinement parameters for complexes **1** and **2**.

	1	2
Formula	$C_{24}H_{12}Co_2N_{11}O_5$	$C_{24}H_8Co_2N_{12}O_5$
FW	652.31	696.25
Space group	$P4_2/ncm$	$P4_2/ncm$
a (Å)	14.126(3)	14.2323(9)
b (Å)	14.126(3)	14.2323(9)
c (Å)	28.683(6)	28.235(3)
β (deg)	90	90
V (Å^3)	5724(2)	5719.2(8)
Z	4	4
D (g/cm^{-3})	0.757	0.769
μ (mm^{-1})	0.606	0.612
T (K)	133	133
$R^a/wR2^b$	0.0816/0.2320	0.0589/0.1520

^{a} $R=\Sigma(\|F_0\|-\|F_c\|)/\Sigma\|F_0\|$.
^{b} $Rw=[\Sigma w(\|F_0\|^2-\|F_c\|^2)^2/(\Sigma w\|F_0\|^2)^2]^{1/2}$.

located through refinement and removed by the SQUEEZE routine. The crystal structures for complexes **1** and **2** have been deposited on the Cambridge Crystallographic Data Centre with assigned CCDC number of 1018850 and 1018851, respectively. (E-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk). Crystal data and structure refinement parameters for complexes **1** and **2** are summarized in Table 1, and some selected bond lengths and bond angles for complexes **1** and **2** are listed in Table S1 (SI).

3. Results and discussion

3.1. Description of the crystal structures

Due to the isomorphism of complexes **1** and **2**, only **1** with a formula of $[Co_2(4-Ptz)_2(BDC)(DMA)]_n$ is discussed in detail. Single crystal X-ray diffraction analysis reveals that **1** crystallizes in the $P4_2/ncm$ space group and the asymmetric unit contains one cobalt ion, one 4-Ptz, one-half of BDC and one-half of DMA molecule. The Co ion locates in the center of an octahedron completed by three N atoms from one pyridine and two tetrazole group and three O atoms from one DMA and one carboxylate group. Two neighboring Co ions are bridged by two tetrazole rings and one DMA-O atom to form a binuclear Co_2 cluster (Fig. 1). The Co_2 clusters are further connected with six neighboring binuclear clusters through four 4-Ptz ligands and two BDC to produce a three-dimensional (3-D) network. On the other hand, each of two carboxylate group of BDC
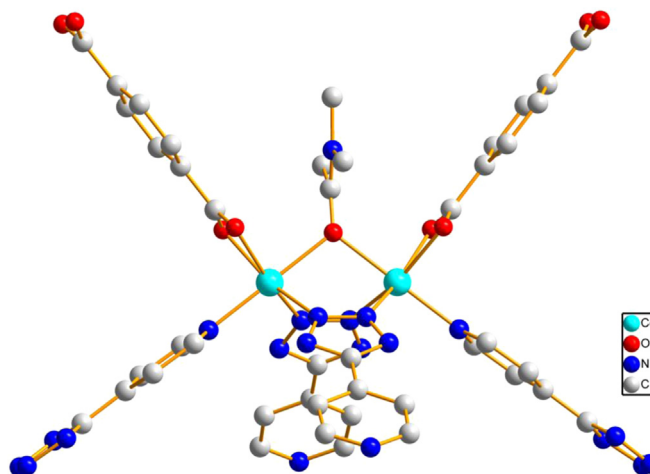

Fig. 1. The 6-connected node in **1**.