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Short communication

Synthesis and thermal stability study of a cobalt-organic framework with tetrahedral cages

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ABSTRACT

A new stable cobalt-organic framework, namely $[Co_2(oba)_2(H_2Me_4bpz)]_n$ (**1**) (H_2oba = 4.4′-oxydibenzoic acid, H_2Me_4bpz = 3.3′,5,5′-tetramethyl-4,4′-bipyrazole), has been synthesized by combining the mixed H_2oba and H_2Me_4bpz with $Co(CH_3COO)_2 \cdot 4H_2O$ under solvothermal conditions, which was characterized by infrared spectroscopy, single-crystal X-ray diffraction, powder X-ray diffraction, and thermogravimetric analyses. Single-crystal X-ray diffraction analysis reveals that **1** features a three-dimensional framework, which is built from interesting tetrahedral cages. The thermal stability of the complex has also been investigated.

Metal-organic frameworks (MOFs) are porous species featuring extended architectures, in which inorganic subunits and organic ligands are periodically linked *via* coordination bonds [1–4]. These promising crystalline materials as an exceptional class of gas capture and separation materials have been intensively explored because of their great advantages over other adsorbents with diverse structures, high surface areas, and modifiable pores [5–10]. However, rational design of MOFs with predicted structures and properties is still a challenge for chemists and material scientists, the current studies show that the employment of various polynuclear metallic units as secondary building units (SBUs) to link numerous organic linkers is a promising synthetic strategy for MOFs [11–14]. Among those reported MOFs, aromatic polycarboxylates ligands are always dominant research objects because they have rigid organic skeletons, excellent coordination capability, simple synthesis and easy functionalization with specific groups [15–17]. Although the structural stability toward moisture in flue gas is one of crucial criteria for MOFs as adsorbents, most carboxylate-based MOFs have to suffer hydrolysis in water or even humidity, yet due to weak metal-O bonds [18–22].

In contrast to undefined coordination fashions of carboxylate, azolates reveal simple and predictable coordination modes, and its MOF is more designable. Moreover, recent studies show that the employment of an azolate linker can be built chemically stable MOFs because of great robustness of M-N bonds arising from stronger basicity of azolates relative to carboxylates [23–25]. Based on this finding, there is every reason to believe that the employment of aromatic carboxylates and azolate mixed ligands was a very effective approach to improve the stability of carboxylate-based MOFs. Herein, we have reported that this design concept is indeed viable. For the realization of this concept, we chose 4, 4′-oxydibenzoic acid (H_2oba) and methyl-functionalized 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (H_2Me_4bpz) as ligands. H_2oba has a 'V′ shape structure and nanosize length (11.3 Å), as well as flexibility due to the free rotation between the two phenyl rings, which are crucial factors for the assembly of polyhedral pore. In contrast to undefined coordination fashions of carboxylate, H_2Me_4bpz reveals simple and predictable coordination modes, and its MOF is more designable. Furthermore, the presence of methyl groups on the H_2Me_4bpz ligand may be beneficial to tune the size and facilitating the interactions with gas molecules. Therefore, using these two unique ligands can be expected to build unusual MOFs. Herein, a stable MOF, $[Co_2(oba)_2(H_2Me_4bpz)]_n$ (**1**), was constructed using these two ligands. Remarkably, it shows high thermal stability and water stability.

Solvothermal reaction of $Co(CH_3COO)_2$ with H_2oba and H_2Me_4bpz in DMF and MeCN mixed solvent at 160 °C for 3 days afforded purple block crystals of **1** [26]. The structure of **1** is characterized by single-crystal X-ray diffraction, elemental analysis, thermogravimetric analysis (Fig. 2b), and IR spectrum. The purity of the crystalline materials generated has been investigated by X-ray diffraction on powder samples. The latter study reveals that almost only one phase has been observed for **1** because of a rather good fit between its simulated and observed patterns.

Single-crystal X-ray diffraction study revealed that **1** crystallized in the tetragonal $I\bar{4}2d$space group [27]. There are one independent cobalt

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(II) ions, one oba^{2-} ligands, and half of H_2Me_4bpz ligands in the asymmetric unit. In the structure of **1**, each deprotonated oba^{2-} ligand acts as a μ_4-linker and connects two paddle wheel $[Co_2(COO)_4]$ units, while each paddle wheel $[Co_2(COO)_4]$ unit is surrounded by four carboxylate groups from four oba^{2-} ligands with the Co···Co distance of 2.786 Å (Fig. 1a). Meanwhile, two apical sites of this $[Co_2(COO)_4]$ unit are located by two non-deprotonated pyrazole group from two H_2Me_4bpz ligands. All Co–O and Co–N bond distances fall in the normal range of 2.000–2.092 Å [28,29]. The prominent structural feature of **1** is the presence of tetrahedral cages in the framework (Fig. 1b). Each tetrahedral cage with an inner diameter of 6 Å consists of four $[Co_2(COO)_4]$ units, four oba^{2-} ligands and two H_2Me_4bpz ligands. Each tetrahedral cage further links the same four cages by sharing $[Co_2(COO)_4]$ units (Fig. 1c). Finally, this cage-by-cage mode generates the 3D framework of **1**. To the best of our knowledge, such framework based on tetrahedral cage is extremely scarce. In the 3D framework, the $[Co_2(COO)_4]$ units and oba^{2-}/H_2Me_4bpz ligands act as nodes and linkers, respectively. Thus, the whole framework of **1** can be topologically represented as a 6-connected net with a point (Schläfli) symbol of $3^6 \cdot 6^6 \cdot 7^3$ (Fig. 1d).

The empty spaces of such 3D framework are filled by the other two identical frameworks, leading to a 3-fold interpenetrated network with 1D channels about 4.8 × 8.5 Å along the *a* axis (Fig. 2). Significantly, some solvent molecules can be detected, but most of them are highly disordered and could not be well-located during the refining of the crystal structure, which is, indeed, supported by thermogravimetric analysis (Fig. 3a). Accordingly, the contribution of all of the solvent molecules is subtracted from the data using SQUEEZE during the refinement [30].

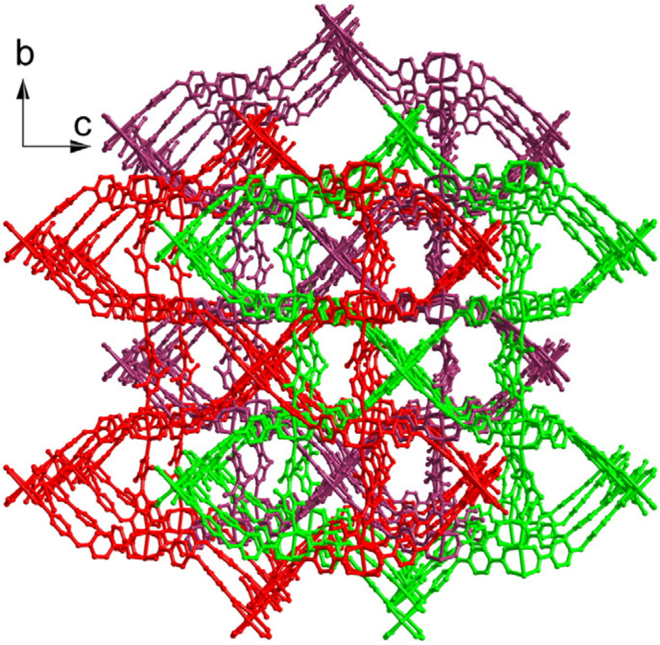

Fig. 2. Packing diagram of **1** shows 3-fold interpenetrated frameworks.

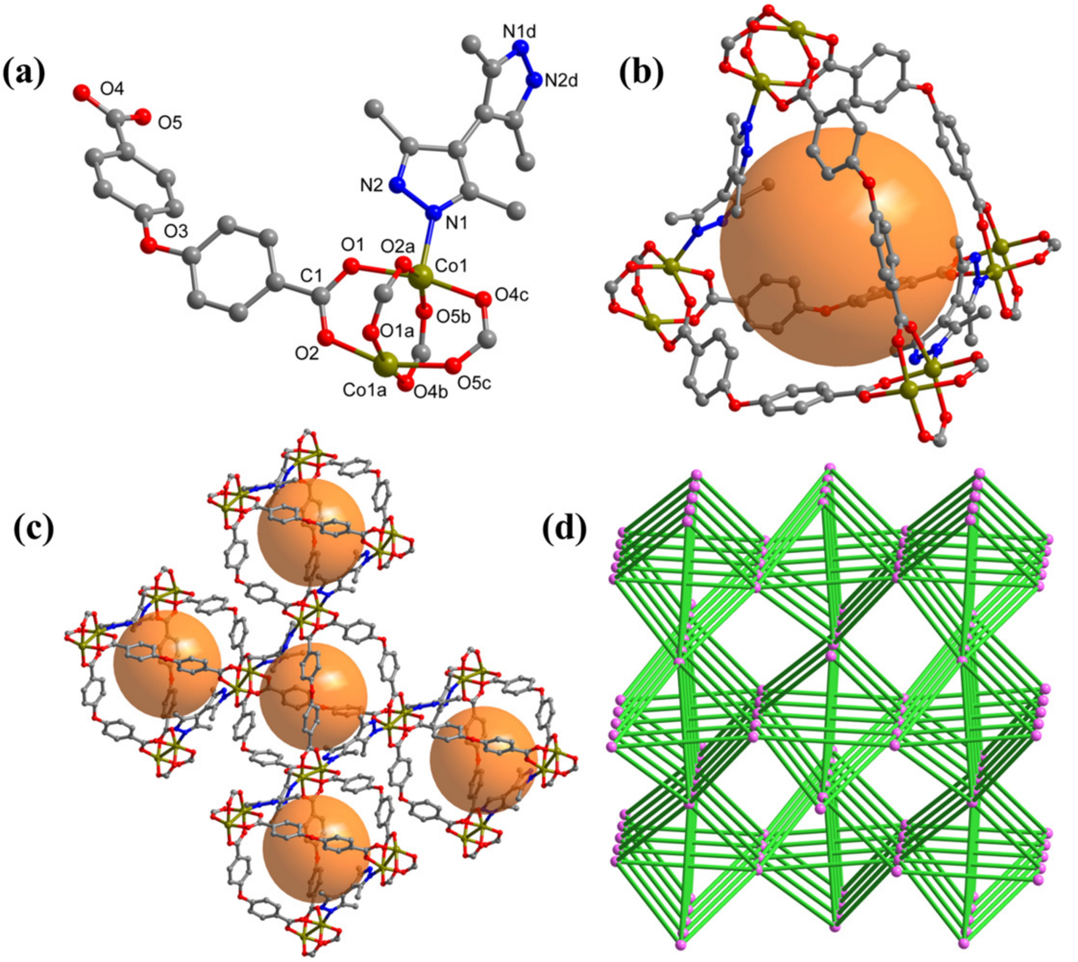

Fig. 1. (a) View of the coordination environment of the Co(II) ions in **1**; symmetry codes: (a) x, 0.5-y, 0.25-z; (b) y, 1-x, 1-z; (c) y, −0.5 + x, −0.75 + z. (b) The tetrahedral cage substructure in 1. (c) View of the 3D framework of **1**. (d) Schematic representation of six-connected topology, with the paddlewheel binuclear units as the six-connected node.