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A new Co-based metal–organic framework constructed from infinite sinusoidal-like rod-shaped secondary building units

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ABSTRACT

A novel Co-based metal–organic framework $\{[Co_4(1,3\text{-bdc})_3(bta)_2(CH_3CH_2OH)_2]\cdot CH_3OH\cdot H_2O\}_n$ (**1**) (H_2bdc = 1,3-benzenedicarboxylate, Hbta = benzotriazolate), has been synthesized and characterized by elemental analysis, IR and single-crystal X-ray diffraction analysis. Compound **1** represents a new structural topology constructed by infinite sinusoidal-like rod-shaped Co–$\{Co_3\}$-chains as secondary building units. Moreover, the magnetic properties of **1** have been well investigated.

Metal–organic frameworks (MOFs) with adjustable functionalities combining with accessible structure modification have been increasingly accelerated and sustained expansion, which point directly toward their potential applications in nanoscale magnetism [1], catalysis [2], gas storage and separation [3], drug delivery [4], and sensor devices [5]. From a synthetic point of view, an effective strategy has been developed to synthesize new MOF species, namely, the *reticular chemistry*, which concept is defined by using a controlled approach based on secondary building units (SBUs), and devised by Yaghi and co-workers [6]. This strategy in situ generates rod-shaped or cluster precursors as SBUs by the rational establishment of the appropriate chemical conditions, which undoubtedly helps to shed light on the prediction, design, and synthesis of the target compounds. Among multifarious structures of MOFs, using infinite rod-shaped SBUs to prepare novel MOFs has been far less explored. Remarkably, most of the rod-shaped SBUs are constructed by monotonous carboxylates as chelating ligands to polymerize metal ions in the previous reports [7]. The research on combination of both O-donor and N-donor groups as mixed ligands to prepare rod-shaped SBUs has never been investigated. In this system, we should better introduce the chelating and the bridging ligands at the same time to guarantee the formation of rod-shaped SBUs and the extension of 3D non-interpenetrating frameworks. The multidentate chelating ligands often display stronger coordination ability to metal ions to easily isolate rod-shaped chains as SBUs, and the bridging ligands usually replenish the other coordination of the metal ions to obtain high-dimensional space. On the basis of these considerations, we deliberately chose benzotriazolate (Hbta) as the N-donor chelating ligand because the tri-N-donor property of the triazolate group can provide more coordination sites for "capturing" metal centers to form rod-shaped chains or polynuclear clusters as SBUs, which have been proved by some heuristic works [8]. At the same time, we also introduced 1,3-benzenedicarboxylate (1,3-H_2bdc) as the bridging ligand to increase the dimension between the rod-shaped SBUs [7]. With these points in mind, we successfully isolated a novel Co^{II}-based MOF, $\{[Co_4(1,3\text{-bdc})_3(bta)_2(CH_3CH_2OH)_2]\cdot CH_3OH\cdot H_2O\}_n$ (**1**). Compound **1** is constructed from the infinite sinusoidal-like rod-shaped Co–$\{Co_3\}$-chains, which represents a new structural topology in Co-based MOFs. Furthermore, the crystal structure, topological analyses, and magnetic properties of **1** have also been investigated.

Block-like purple crystals of **1** were obtained via solvothermal reaction of $Co(NO_3)_2\cdot 6H_2O$ with 1,3-H_2bdc, and Hbta in CH_3CH_2OH/CH_3OH mixed solution at 120 °C for 3 days [9]. Phase purity of the bulky crystals was confirmed by the similarity between the experimental and simulated powder X-ray diffraction (PXRD) patterns (Fig. S1, SI).

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group *C*2/*c* [10]. As shown in Fig. 1a, there are three crystallographically independent Co^{2+} centers ($Co1^{2+}$, $Co2^{2+}$ and $Co3^{2+}$), one 1,3-bdc^{2-} ligand, two thirds

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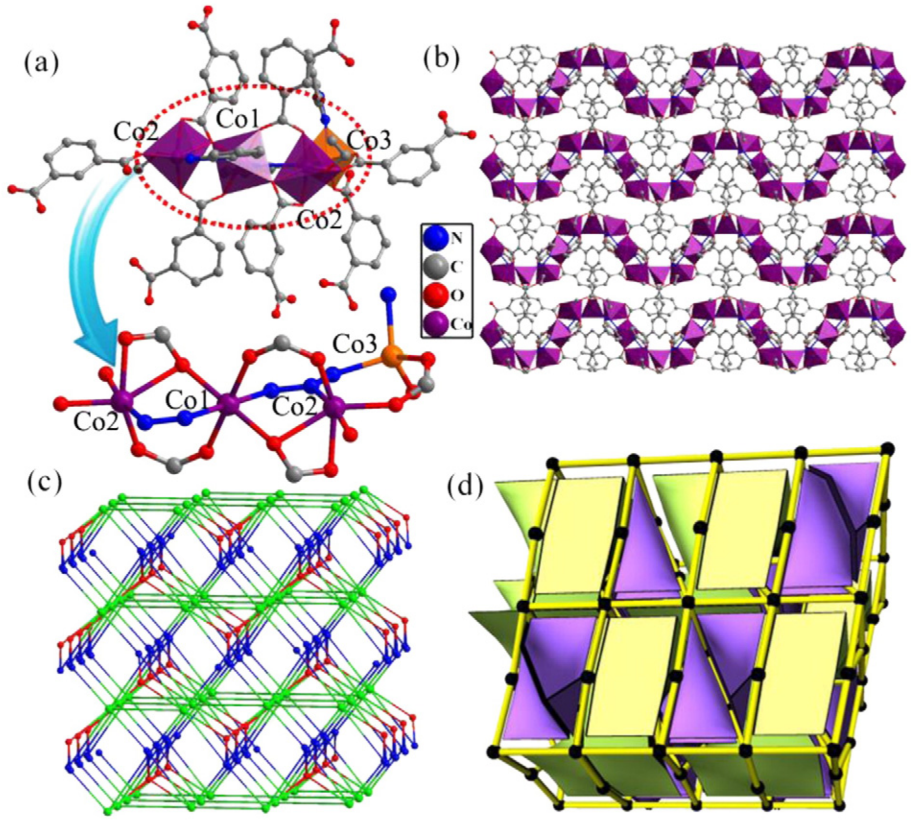

Fig. 1. (a) The polyhedral view of Co–{Co_3}-cluster showing different Co^{II} coordination environments and the ball-and-stick view of corresponding Co–{Co_3} core in **1**; (b) the polyhedral view of 3D structure constructed by 1D sinusoidal-like rod-shaped Co-chains; (c) schematic view of new trinodal (3,4,8)-connected topology for 1; (d) the tiling of the framework 1. (The hydrogen atoms have been omitted for clarity.)

bta^- ligands, two thirds coordinated CH_3CH_2OH molecules, one third solvent CH_3OH molecule and one third solvent H_2O molecule. The three Co^{2+} ions have two kinds of coordination modes, which are, the hexa-coordinated distorted octahedron geometry ($Co1^{2+}$ and $Co2^{2+}$) and the tetra-coordinated distorted tetrahedron geometry ($Co3^{2+}$). The $Co1^{2+}$ is coordinated with two monodentate oxygen atoms deriving from two different 1,3-bdc^{2-} ligands, two bidentate oxygen atoms originating from two other different 1,3-bdc^{2-} ligands, and two monodentate nitrogen atoms originating from two different bta^- ligands. The $Co2^{2+}$ is coordinated with two monodentate oxygen atoms deriving from two different 1,3-bdc^{2-} ligands, two bidentate chelating oxygen atoms originating from the third 1,3-bdc^{2-} ligand, one monodentate nitrogen atom originating from one bta^- ligand, and one monodentate oxygen atom deriving from one coordinated CH_3CH_2OH molecule. The $Co3^{2+}$ is coordinated with two monodentate oxygen atoms deriving from two different 1,3-bdc^{2-} ligands and two monodentate nitrogen atoms originating from two different bta^- ligands. The selected bond lengths and angles are listed in Table S1 (SI). The 1,3-bdc^{2-} ligands have two different coordination modes: one is a bridging mode with four monodentate oxygen atoms connecting four different Co^{2+} ions. The other adopts a pentadentate coordination mode with one carboxylate group chelating one Co^{2+} ion and at the same time one of the chelating oxygen atom bridging another Co^{2+} ion; while the second carboxylate group bridging the other two different Co^{2+} ions. All bta^- ligands possess the same typical tridentate coordination mode, that is, the three N-donors from the triazolate group “capture” three different Co^{2+} ions to generate a trinuclear cluster {Co_3} ($Co2^{2+}$ … $Co1^{2+}$ … $Co2^{2+}$, purple color as shown in Fig. 1a). These trinuclear clusters {Co_3} and the $Co3^{2+}$ ions are further bridged by one carboxylate of 1,3-bdc^{2-} ligands and two adjacent N-donors of bta^- ligands to form an interesting infinite sinusoidal-like rod-shaped 1D Co–{Co_3}-chain. This sinusoidal-like Co–{Co_3}-chain presents a different component feature as the reported classic rod-shaped metal-chains. The reported rod-shaped SBUs are usually constructed only by monotonous carboxylates as chelating ligands to assemble metal ions, while the sinusoidal-like Co–{Co_3}-chain in this communication combines both O-donor carboxylate groups and N-donor triazolate groups as mixed ligands to produce the new type of rod-shaped SBUs. Moreover, these sinusoidal-like rod-shaped 1D Co–{Co_3}-chains are further linked by other 1,3-bdc^{2-} ligands to give a 3D framework (see Fig. 1b). Comparing to the previously reported Co(II) and 1,3-bdc^{2-} compounds which are constructed from mononuclear or multinuclear Co(II)-clusters as SBUs, while compound **1** is constructed from infinite sinusoidal-like rod-shaped SBUs [11].

From the above description we can see that the connectivity pattern of the $Co1^{2+}$ and $Co2^{2+}$ ions in the Co–{Co_3}-chain are repeated infinitely as {Co2–Co1–Co2} to create parallel trinuclear $\{Co_3\}_n$ clusters, so the trimeric {Co_3} clusters can be abstracted as eight-connected nodes which link with two neighboring $Co3^{2+}$ ions in the same 1D Co–{Co_3}-chain and six other trinuclear $\{Co_3\}_n$ clusters in the different 1D Co–{Co_3}-chains [12]. The $Co3^{2+}$ ions can be rationalized as four-connected nodes which connect with two neighboring trimeric {Co_3} clusters in the same 1D Co–{Co_3}-chain and two other trinuclear $\{Co_3\}_n$ clusters in the different 1D Co–{Co_3}-chains. The 1,3-bdc^{2-} ligands can be simplified as three-connected nodes which link with two different trimeric {Co_3} cluster SBUs and another $Co3^{2+}$ ion. From the topological point of view [12], the bta^- ligands only act as linear connection and the coordination CH_3CH_2OH molecules only act as decorating ligands, so they are all not necessary to consider in the topological analysis. Based on this simplification, the overall 3D network of **1** can be rationalized as a trinodal (3,4,8)-connected topology with the Schläfli symbol of $\{3 \cdot 5 \cdot 6\}_2\{3^2 \cdot 5 \cdot 6^3\}\{3^2 \cdot 5^2 \cdot 6^{14} \cdot 7^2 \cdot 8^5 \cdot 9^3\}$