

Short communication

## A novel cobalt(II) metal–organic framework based on an unprecedented ribbon-shaped secondary building unit

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## ABSTRACT

A novel 3D metal–organic framework (MOF)  $\{[\text{Co}_{2.5}(\text{dcp}) (\mu_3\text{-OH}) (\mu\text{-H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  ( $\text{H}_4\text{dcp}$  = 4,5-bis(4'-carboxylphenyl)-phthalic acid) with unprecedented ribbon-shaped secondary building units (SBUs), has been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, and IR. In addition, the thermal stability and magnetic behavior of the complex were also investigated.

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Studies of metal–organic frameworks (MOFs) are of considerable interest due to their fascinating network topologies and potential applications including gas storage and separation, luminescence, catalysis and magnetism [1]. In particular, structures constructed from metal-containing secondary building units (SBUs) have been shown to be amenable to systematic variation [2]. Commonly, metal-containing SBUs refer to finite polyatomic cluster with two or more metal atoms or an infinite unit [3]. Under the guidance of crystal engineering, different geometries of SBUs are constructed such as paddle wheel [4] triangle [5], and rare rod-shaped SBUs [6]. Infinite rod SBUs are of interest as they usually have parallel channels and often exhibit pronounced “breathing” [7]. However, the studies of infinite SBUs are still in their infancy and MOFs constructed from high nuclear infinite SBUs are rare.

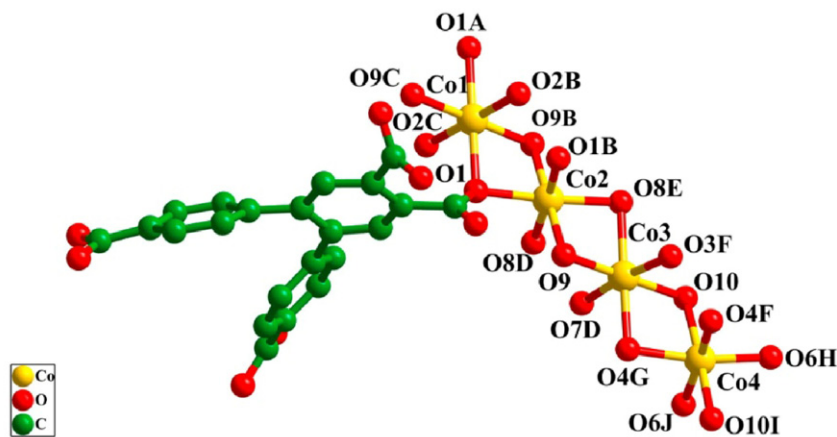
For constructing diverse SBU, the selection of organic ligands is very important and the ligand plays critical effects on the resulting structures [8]. In comparison to common organic ligands, multidentate carboxylic ligands have been widely selected due to their quantity of coordination sites and a wide variety of coordination modes, deriving by partially or completely deprotonated carboxylic groups [9]. Moreover, the multidentate carboxylic ligand could connect more than one metal to increase the multinuclearity and dimensionality [10].

With the background above and a continuation of our previous work [11], we employed a tetradentate carboxylic ligand 4,5-bis(4'-carboxylphenyl)-phthalic acid ( $\text{H}_4\text{dcp}$ ) as the organic linker, and synthesized an unprecedented infinite ribbon-shaped SBU based metal–organic framework, namely,  $\{[\text{Co}_{2.5}(\text{dcp}) (\mu_3\text{-OH}) (\mu\text{-OH}_2)] \cdot \text{H}_2\text{O}\}_n$  (**1**). The crystal structure was characterized by single-crystal X-ray diffraction [12], elemental analysis, XRD and IR. Moreover, the thermal stability and magnetic behavior were also investigated.

The red block crystals of the complex were produced via hydrothermal reaction of  $\text{Co}(\text{AC})_2 \cdot 4\text{H}_2\text{O}$  and 4,5-bis(4'-carboxylphenyl)-phthalic acid ( $\text{H}_4\text{dcp}$ ) in  $\text{H}_2\text{O}$  at 160 °C for 4 days [14]. Single-crystal X-ray diffraction analysis reveals that the complex displays a 3D architecture with the monoclinic space group  $C2/c$  symmetry. The asymmetric unit contains two and a half cobalt(II) ions, one deprotonated  $\text{dcp}^{4-}$  ligand, one  $\mu_3\text{-OH}$  ion (O9), one  $\mu_2\text{-OH}_2$  molecule (O10) and one guest water molecule. As shown in Fig. 1, Co1 and Co2 exhibit the same octahedral coordination environment, furnished by four  $\text{dcp}^{4-}$  oxygen atoms and two  $\mu_3\text{-OH}$  oxygen atoms. Notably, the connection of  $\text{O}-\text{Co}1-\text{O}$  is completely linear with  $\text{O}-\text{Co}1-\text{O}$  angle of 180°. Co3 adopts an octahedral geometry and coordinated by four carboxylic oxygen atoms, one  $\mu_3\text{-OH}$  oxygen and one  $\mu_2\text{-OH}_2$  oxygen. As for Co4, it is octahedrally coordinated by four ligand oxygen atoms and two  $\mu_2\text{-OH}_2$  oxygen atoms. The  $\text{Co}-\text{O}$  bond lengths are in the range of 2.019 Å to 2.211 Å, a range that is comparable with that observed in other cobalt (II)-containing complexes [15]. Moreover, the four carboxylate groups of the  $\text{dcp}^{4-}$  ligand adopt the  $(\kappa^1)-(\kappa^1-\mu_2)-(\kappa^1-\mu_2)-(\kappa^1-\mu_2)-\mu_1$

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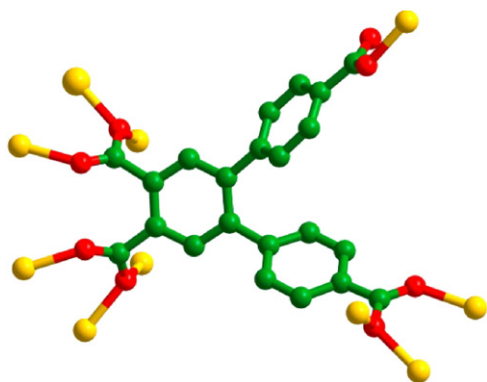
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**Fig. 1.** Coordination environment of the Co(II) ions. Hydrogen atoms have been omitted for clarity. Symmetry codes: A =  $2 - x, 2 - y, 2 - z$ ; B =  $2 - x, y, 1.5 - z$ ; C =  $2 - y, 0.5 + z$ ; D =  $1.5 - x, 0.5 + y, 1.5 - z$ ; E =  $0.5 + x, 0.5 + y, z$ ; F =  $2 - x, 2 - y, 1 - z$ ; G =  $x, 2 - y, -0.5 + z$ ; H =  $0.5 + x, 2.5 - y, -0.5 + z$ ; I =  $2 - x, y, 0.5 - z$ ; J =  $1.5 - x, 2.5 - y, 1 - z$ .

coordination mode (Fig. 2). With this kind of connection mode, ten Co(II) ions are connected in one  $dcp^{4-}$  ligand. To our knowledge, it is rare that one organic ligand links ten Co(II) ions.

The main original feature of the structure is the infinite inorganic ribbon-shaped SBU (Fig. 3). The ribbon is built of infinite quadrangles of  $Co_8O_{14}$  units. Each unit is composed of two Co1, three Co2, two Co3, one Co4, eight carboxylic oxygen atoms, four  $\mu_3$ -OH oxygen atoms and two  $\mu_2$ -OH<sub>2</sub> oxygen atoms. The eight Co(II) ions locate in a quadrangle. On the one side, Co1 is connected by two Co2 with two carboxylate oxygen atoms and two  $\mu_3$ -OH. Two Co2 occupy two endpoints of one line, and Co1 stays at the center with Co1...Co2 separation of 3.113 Å. Co2, Co3 and Co4 locate at another side of the quadrangle. Co2 and Co3 are connected by one carboxylate oxygen and one  $\mu_3$ -OH while Co3 and Co4 are linked by one carboxylate oxygen and one  $\mu_2$ -OH<sub>2</sub>. The separations of Co2–Co3 and Co3–Co4 are 3.061 Å and 3.2000 Å, respectively. Each quadrangle of  $Co_8O_{14}$  units is connected by sharing one edge to form the infinite ribbon. Then the ribbon is further linked to neighboring ribbons, forming a complicated 3D framework (Fig. 4) with 1D microchannels running along the *c* axis. The solvent-accessible volume and porosity are 470.2 Å<sup>3</sup> and 11.0%, respectively, calculated by PLATON [16]. From the topological point of view, if each Co(II) ion, the  $\mu_3$ -OH and the ligand are viewed as 6-connected, 3-connected and 10-connected nodes, respectively, the 3D framework could be described as a (3,6,6,6,6,10)-connected net with a point symbol of  $(3^2 \cdot 4^{23} \cdot 5^8 \cdot 6^{12})_2(3^2 \cdot 4^8 \cdot 5^3 \cdot 6^2)_2(3^4 \cdot 4^5 \cdot 5^4 \cdot 6^2)(4^{10} \cdot 5^2 \cdot 6^3)(4^{12} \cdot 6^3)(4^3)_2 5^3 \cdot 6^2)_2(3^4 \cdot 4^5 \cdot 5^4 \cdot 6^2)(4^{10} \cdot 5^2 \cdot 6^3)(4^{12} \cdot 6^3)(4^3)_2$  (Fig. S1).



**Fig. 2.** Coordination mode of the  $dcp^{4-}$  ligand.

In addition, there exists thriving O–H...O hydrogen bonds between the  $\mu_2$ -OH<sub>2</sub> molecules,  $\mu_3$ -OH ions, carboxylate oxygen atoms and guest water molecules in the complex. Related distances and angles are listed in Table S3. The  $\mu_2$ -OH<sub>2</sub> molecule forms two intermolecular hydrogen bonds with the carboxylate oxygen O(5<sup>l</sup>) and guest water oxygen O(11<sup>l</sup>), respectively [symmetry operators: (I)  $x + 1/2, -y + 5/2, z - 1/2$ ; (II)  $-x + 1, y + 1, -z + 3/2$ ]. The corresponding O(10)...O(5) distance is 2.555(6) Å and the O(10)...O(11) distance is 2.709(10) Å, which indicates the strong hydrogen bond interactions. Besides the intermolecular hydrogen bonds, there are two intramolecular hydrogen bonds between the  $\mu_3$ -OH (O9) and the carboxylate oxygen atoms (O1, O2). The distances of O(9)...O(1) and O(9)...O(2) are 3.199(5) Å and 2.870(5) Å, respectively. The inter- and intramolecular hydrogen bonds further stabilize the 3D framework.

In order to confirm the phase purity of the complex, the PXRD pattern was recorded. It was clear that the peak positions in the experimental pattern was comparable to the corresponding simulated one calculated from the single-crystal X-ray diffraction data (Fig. S2), indicating a pure phase of the bulky sample. The thermal stability of the complex was investigated by the thermogravimetric analysis (Fig. S4). The first step weight loss, attributed to the release of one guest water molecules, was observed at about 80 °C (obsd 2.82%, calcd 2.99%). The second step weight loss from 350 °C to 490 °C corresponded to the decomposition of organic ligand, leading to the formation of  $Co_2O_3$  as the residue (obsd 33.80%, calcd 34.41%). The thermal analysis indicated that the cobalt-MOF possessed high thermal stability.

The variable-temperature magnetic susceptibility of the complex was measured in the temperature range of 2.0–300.0 K under an outer field of 1000 Oe. As shown in Fig. 5, the  $\chi_M T$  value is 15.96 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K, which is larger than the spin-only value of five isolated high-spin Co(II) ions ( $s = 3/2, g = 2$ ) due to the unquenched orbital-moment as a result of spin-orbit coupling from the single octahedral Co(II) ions [17]. The  $\chi_M T$  value continuously decreases with lowering temperature and reaches a minimum value of 7.66 cm<sup>3</sup> K mol<sup>-1</sup> at 10 K. With further decreasing temperature, the  $\chi_M T$  value sharply increases to a value of 29.70 cm<sup>3</sup> K mol<sup>-1</sup> at 2.0 K. The temperature dependence of magnetic susceptibilities above 100 K follows the Curie–Weiss law with a Weiss constant  $\theta = -37.56$  K and Curie constant  $C = 17.98$  cm<sup>3</sup> mol<sup>-1</sup> K (Fig. S5). The Curie constant is much larger than the expected spin-only value due to the orbital contribution of Co(II) ions which exists in the complex. Thereby the negative value of  $\theta$  is incapable of indicating the antiferromagnetic coupling between Co(II) because of the strong spin-orbital coupling through the <sup>4</sup>T<sub>1g</sub> state of the octahedral Co(II) centers [18]. The existence of tightly interconnected Co<sup>2+</sup> ions within the ribbon-shaped SBU (the Co...Co

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