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An unprecedented ten-connected 3D metal–organic framework based on hexanuclear cobalt(II) cluster building blocks

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ABSTRACT

A 3D metal–organic framework (MOF), $[Co_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)(BPT)(HBPT)(DMF)_2]$ (DMF)(H_2O) (**1**) (DMF = N, N′-dimethylformamide) has been synthesized by self-assembly of cobalt(II) oxide and biphenyl-3, 4′, 5-tricarboxylate (H_3BPT) under solvothermal reaction. Compound **1** displays unique (2,3,10)-connected trinodal connected topology. Besides, **1** represents a rare example of MOF possessing free carboxylic acids. In addition, the magnetic property of the compound is investigated.

The synthesis and characterization of porous metal–organic frameworks (MOFs) have attracted much attention, owing to their enormous variety of interesting structural topologies and potential applications as functional materials [1]. Of the structural types commonly found in MOFs, the majority are based on three-, four-, and six-connected topologies in which d- and f-block ions act as nodes [2]. Compared to these commonly encountered 3–6-connected topologies, the development of higher connectivity nets (>6), neither with high-symmetry nor low-symmetry structures, is still uncommon, which can be attributed, at least partially, to the limited coordination numbers of single metal centers and steric hindrance of the most commonly used organic ligands [3]. Recently, polynuclear metal cluster entities as secondary building units (SBUs) have been proved as an effective and powerful synthetic strategy in constructing highly connected frameworks, in which zinc and cadmium carboxylate clusters are most commonly used [4,5]. Some novel MOFs with penta-, hepta-, and nona-nuclear (and even higher) SBUs have been constructed in recent years [6–9]. On the other hand, porous magnets are currently in the forefront of molecular materials research because the synergism of magnetic and porous properties opens a new route to the development of low-density magnetic materials, magnetic sensors, and multifunctional materials [10,11]. Paramagnetic Co^{II} is a good candidate for dynamic porous magnets because it can adopt diverse coordination geometries responsive to various magnetic properties [12]. However, the Co^{II} generally exhibits large molecular anisotropy, resulting in a limited number of high-nuclearity clusters [13–20].

In an attempt to obtain a metal–organic framework with high nuclear Co^{II} SBUs, we employed biphenyl-3, 4′, 5-tricarboxylate (H_3BPT) as the bridge ligand, which contains chemically inequivalent carboxylates with distinct coordination environments [21,22]. Herein, we report a new polynuclear compound $[Co_3(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)(BPT)(HBPT)(DMF)_2]$ (DMF)(H_2O), which contains a $Co_6(\mu_3\text{-}OH)_2(\mu_2\text{-}H_2O)_2(CO_2)_{10}$ building block that contains a ten-connected network. To the best of our knowledge, this building block topology is unique and unprecedented.

1 was synthesized as purple-red crystals by a solvothermal method from CoO (7.5 mg, 0.10 mmol) and H_3BPT (15 mg, 0.05 mmol) in a mixture solution of N, N′-dimethylformamide (DMF, 1.0 mL) and water (0.5 mL) in a 20 ml Parr Teflon-lined stainless steel vessel at 100 °C for 48 h. Crystals of **1** were collected in 48% yield (based on H_3BPT ligand). Calcd for $Co_3C_{39}H_{41}O_{18}N_3$: C, 46.08%; H, 4.07%; N, 4.13%. Found: C, 46.03%; H, 4.09%; N, 4.04%. Its structure and composition were further confirmed by powder X-ray diffraction (PXRD) (Fig. S1), elemental analysis, infrared (IR) spectroscopy, and thermogravimetry analysis (TGA). Furthermore, the magnetic property of compound **1** was investigated.

Compound **1** was well characterized by single crystal X-ray diffraction analysis. **1** crystallized in the triclinic space group P-1 [23]. In the asymmetric unit of **1**, there are three independent octahedral Co^{II} atoms, one $HBPT^{2-}$ and one fully-deprotonated BPT ligands, one μ_2-H_2O, one μ_3-OH group and two coordinated DMF molecules (Fig. S2). Co1 is coordinated by four oxygen atoms from four BPT ligands, one μ_3-OH group and one DMF molecule; Co2 is surrounded by four carboxylate oxygen atoms and one μ_2-H_2O group and one DMF molecule; and Co3 is coordinated by three carboxylate oxygen atoms, two μ_3-OH groups and one μ_2-H_2O group (Fig. 1). To the best of our knowledge, the simultaneous presence

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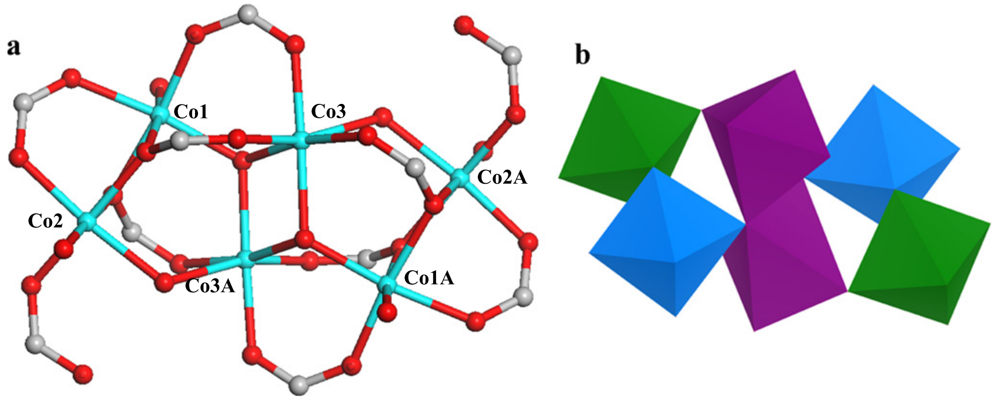

Fig. 1. (a) View of one of the $[Co_6(\mu_3\text{-}OH)_2(\mu_2\text{-}H_2O)_2(CO_2)_{10}]$ SBUs in **1** and (b) polyhedral view of the hexanuclear cluster. Color code: Co1, green; Co2, light blue; Co3, violet.

of three different cobalt(II) coordination environments in **1** is still rare [15,20]. The Co – O bond lengths in **1** are in the range of 2.005 to 2.286 Å, a range that is comparable with that observed in other cobalt(II)-containing compounds [19,24].

There are two μ_3-OH groups and two μ_2-H_2O groups, which connect six Co^{II} atoms to form a Co_6 cluster. The BPT ligands further enlace the Co_6 unit in the bi- and tridentate bridging modes. Thus the Co_6 unit is enveloped by the organic groups. As is illustrated in Fig. 2a and c, each Co_6-based building block is linked to eight adjacent Co_6 blocks through six BPT and four HBPT bridging ligands. The six BPT bridging ligands, which all of them had been fully deprotonated, adopt two coordination modes: a bidentate bridging mode (isophthalate ring of the linker, mode A in Fig. S3) and a monodentate mode (carboxyphenyl ring of the linker, mode B in Fig. S3). As illustrated in the figure, six BPT bridging ligands connect six Co_6-based building blocks to form a 2D layered sheet which is almost planar (Fig. 2b). The two carboxylate groups of HBPT are deprotonated and adopt a μ_3-η^2:η^1 bridging mode (isophthalate ring of the linker, mode C in Fig. S3) to connect three Co atoms. The remaining carboxylate group is protonated (carboxyphenyl ring of the linker, mode D in Fig. S3) and does not take part in coordination, which provides hydrogen bonding donors. The 2D layered sheet was further connected by HBPT bridging ligands to give rise to a three dimensional porous framework with rhombus channels along b axis (Fig. 2c). The dimensions of the channels are 9.9 × 17.5 Å along b axis direction. However, the channels were mostly occupied by the HBPT ligands. The free water molecules reside in the rhombus channels by forming relatively strong hydrogen bonds with the protonated uncoordinated carboxylate groups ($O_6 \ldots O_{1W}$ distance: 2.589 Å). As far as we know, **1** is a rather rare example of MOFs that contains free carboxylic acids [25–27]. The overall structure of **1** adopts a novel trinodal (2,3,10)-coordinated net (Fig. 2d).

Thermogravimetric analysis of **1** (Fig. S4) indicates the loss of the free DMF and water molecules between room temperature and around 210 °C; the calculated loss is 9.1%, and the observed loss is 9.3%. Between 210 and 390 °C **1** decomposes as the result of the loss of coordinated DMF molecules; the calculated loss is 14.4%, and the observed loss is 14.2%. The loss of these DMF molecules results in the chemical decomposition of **1**. Fourier transform IR spectroscopy for the powder sample of **1** further confirmed the presence of free carboxylic acid (Fig. S5). The peak at 1725 cm^{-1} and a broad absorbance in the range

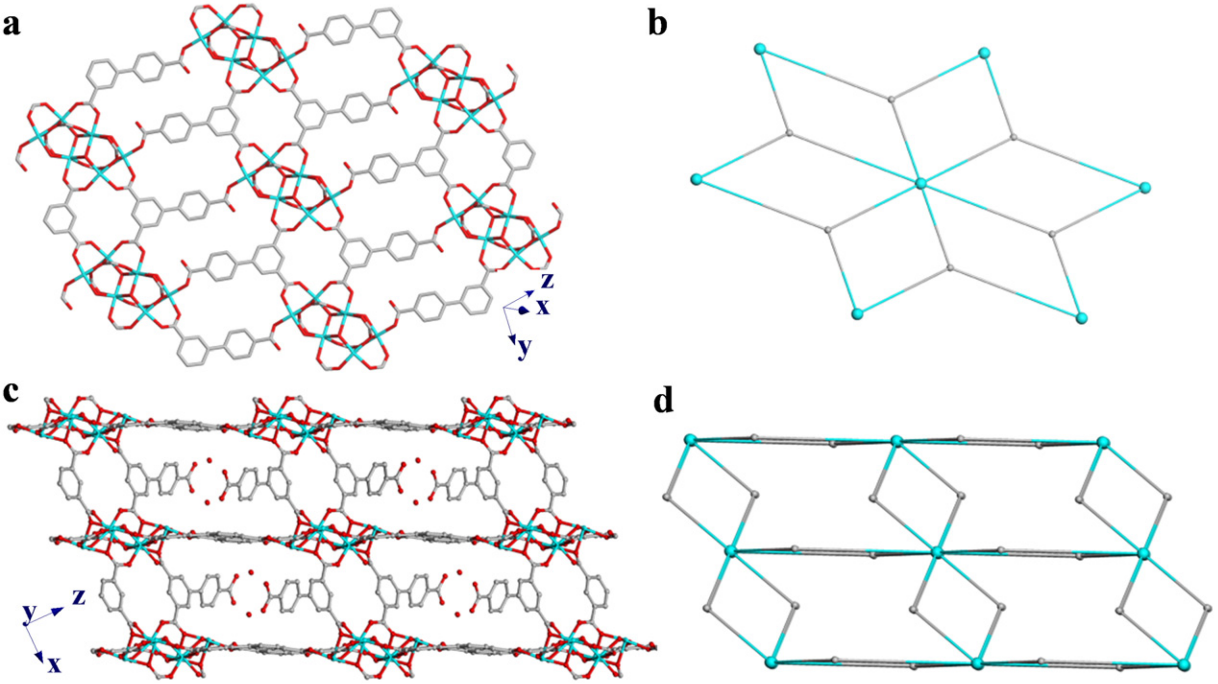

Fig. 2. (a) The 2D $\{[Co_3(L)(OH)(H_2O)]^{2-}\}_n$ layer based on Co(II) ions, OH^-, L^{3-} and H_2O. (b) Connection illustrated for the 2D layer. (c) 3D complicated framework of **1**. (d) Overall topological network for compound **1**.