

Short communication

An unprecedented twelve-connected 3D metal-organic framework based on heptanuclear cobalt cluster building blocks

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ABSTRACT

Solvothermal reaction of flexible tetrapodal linker tetrakis[4-(carboxyphenyl) oxamethyl]methane acid (H_4L) with cobalt salt yields a new metal-organic framework $[Co_7(L)_3(\mu_3-O)_3(DMF)_3](DMF)_{13}(H_2O)_{25}$. X-ray crystallography reveals that the structure exhibits a unique 2-nodal (4,12)-connected topology with the Schläfli symbol of $(4^{33}.6^{30}.8^3)(4^6)_3$, constructed from heptanuclear cobalt clusters as 12-connected nodes and tetrahedral ligands as 4-connected nodes. Temperature-dependent magnetic susceptibility measurements reveal that the heptanuclear cobalt clusters exhibit antiferromagnetic property.

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The construction and synthesis of porous metal-organic frameworks (MOFs) have attracted tremendous attention in the field of chemistry and materials science due to their potential applications in gases separation [1–3], catalysis [4,5], chemical sensing [6,7] and controlled release of drugs [8,9] as well as their variety of intriguing architectures and topologies [10]. A large number of ligands of certain geometry with different lengths and flexibilities have been employed in exploring MOFs of certain functions [11,12]. Many of them possess expected, while sometimes exceptional structures and properties. The understanding of their assembly process is still in its infancy, and much effort is required to achieve rationally targeted functional MOF materials in the near future. The preparation of MOFs with highly-connected secondary building units (SBUs) remains elusive because the SBUs with corresponding high-connectivity SBUs are usually hard to be attained [13]. The usage of polynuclear metal clusters is a good method to construct MOFs, as it will result in the formation of MOFs not only with an unusual highly-connected MOF structure, but also with interesting properties. Herein, we report a 3-dimensional (3D) MOF based on heptanuclear cobalt cluster building blocks, which possess an unusual twelve-connected structure with antiferromagnetic interactions between the metal clusters.

Compound **1** was synthesized by a solvothermal reaction of H_4L (H_4L = tetrakis[4-(carboxyphenyl)oxamethyl]methane acid) and $Co(NO_3)_2 \cdot 6H_2O$ in the N,N' -dimethylformamide (DMF) solvent [14]. Single-crystal X-ray diffraction analysis shows that **1** crystallizes in the

trigonal space group $R\bar{3}c$ (No. 167) [15], and contains a heptanuclear cobalt with C_3 symmetry. The asymmetric unit consists of three independent Co atoms, two halves of L^{4-} ions, one disordered DMF molecule and one μ_3-O bridge atom. The occupancies of Co1, Co2 and Co3 are 1, 1 and 1/3, respectively. All the cobalt atoms are six-coordinated to six O atoms with distorted octahedral geometries. Oxidation states that the cobalt atoms have been assigned on the basis of bond valence sum (BVS) analysis, and by consideration of bond lengths [16]. The three cobalt atoms are all in the 2+ oxidation state according to the BVS calculations (BVS values of 1.94, 1.99 and 2.31 for Co1, Co2 and Co3, respectively). The structure is shown in Fig. 1a. The center Co3 atom, sitting on a 3-fold symmetric axis, is coordinated by three μ_3-O atoms (bond length of 2.093(3) Å) and three μ_1-O atoms (bond length of 1.993(6) Å) from three carboxylate groups (μ_1-O is used in this instance to describe an oxygen atom bound to only one Co atom). The outer Co1 atom is coordinated by three μ_1-O atoms from three carboxylates, two μ_2-O atoms and one μ_3-O bridge atom. The outer Co2 atom is coordinated by two μ_1-O atoms, two μ_2-O atoms, one μ_3-O bridge atom and one μ_1-O atom from DMF molecule. Of the surrounding six Co atoms, three Co1–Co2 atoms are bridged by two μ_2-O bridges from two carboxylates, the other three Co1–Co2 atoms are bridged by one μ_3-O bridge and two carboxylate groups. The Co1...Co2, Co2...Co3 and Co1...Co3 distances within the cluster are 3.332(1), 3.4646(7) and 3.4886(8) Å, respectively, forming an approximately regular hexagon. The heptanuclear cobalt cluster is in a disk-like shape with the surrounding six cobalt atoms approximately co-planar, and the center C_3 -symmetric Co3 atom deviates the plane a little (Fig. 1b). There have been some reported disk-like heptanuclear cobalt clusters, but most of

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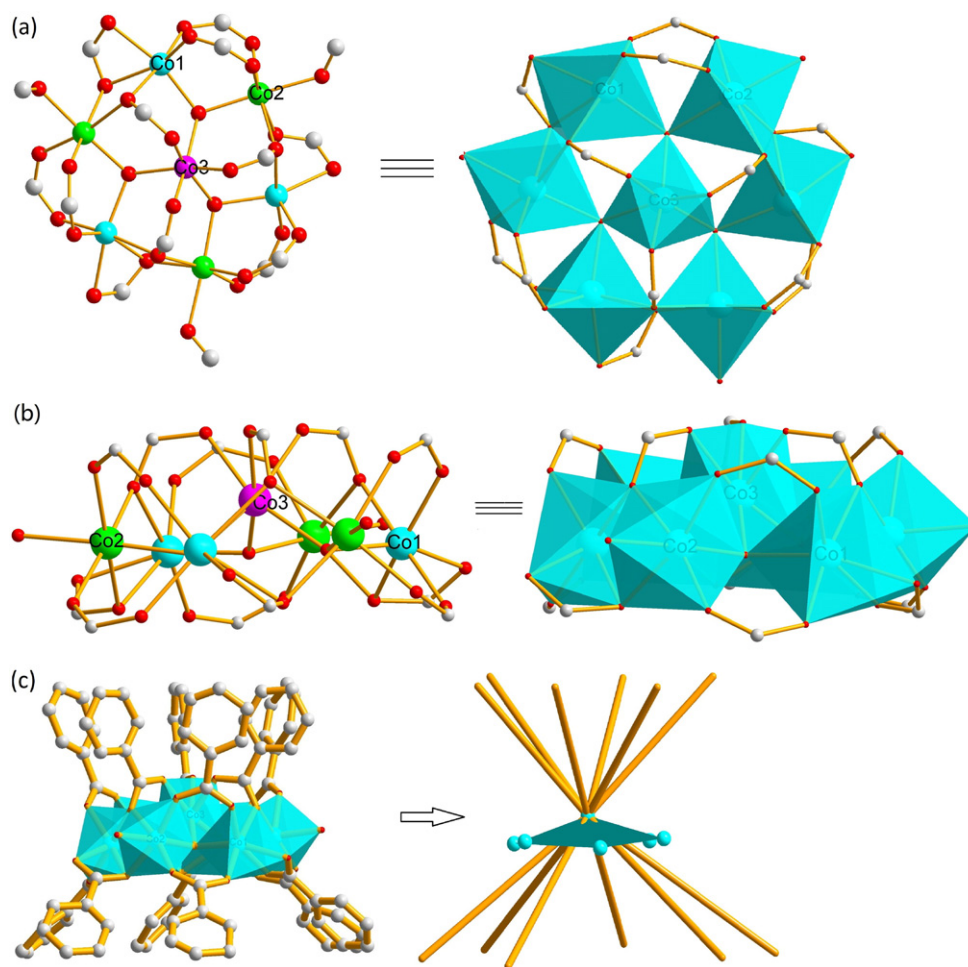


Fig. 1. (a) Schematic and polyhedral representation of **1** showing the heptanuclear cluster. (b) The heptanuclear disk with six cobalt atoms nearly co-planar and the Co3 atom lying in the center. (c) Schematic presentation of the 12-connected heptanuclear disk.

them with the structure of 0 dimensional clusters [17–20]. This disk-like heptacobalt structure with only three μ_3 -bridge atoms in **1** is quite different from those reported. The heptanuclear cobalt cluster is connected by six benzoates on the top and six benzoates on the bottom of the disk. So the heptanuclear cobalt cluster is connected to twelve benzoates to form a twelve-connected SBU (Fig. 1c).

The tetrahedral L^{4-} ligands are all deprotonated and four-connected to four heptanuclear cobalt clusters. The two halves of tetrahedral L^{4-} ligands are both in a similar distorted tetrahedral coordination geometry of the angles ($C_{\text{carboxyl}} \cdots C_{\text{center}} \cdots C_{\text{carboxyl}}$) between four arms ranging from $74.74(8)$ to $140.51(8)^\circ$ and $68.63(5)$ to $154.88(6)$, respectively.

The four carboxylate groups of one L^{4-} ligand exhibit two different kinds of coordination modes: two carboxylates link neighboring Co1 and Co2 atoms through a chelating mode; two bridge Co1 and Co2 atoms through a chelating and a μ_3 -O atom. For the other L^{4-} ligand, there carboxylates link Co1 and Co2 atoms through a chelating mode, and the fourth carboxylate connects Co1, Co2 and Co3 atoms through a chelating mode. So the tetrahedral L^{4-} ligands can be both considered as 4-connected nodes (Fig. 2). Each 4-connected node connects four 12-connected nodes, and each 12-connected node connects twelve 4-connected nodes. From a topological analysis perspective, **1** can be simplified to a (4,12)-connected network with a Schläfli symbol of

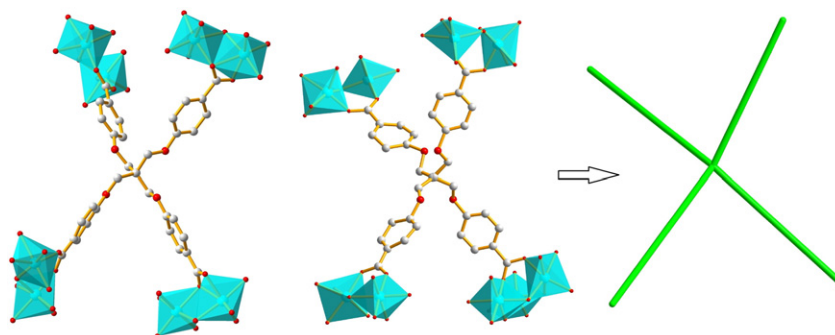


Fig. 2. The coordination modes of the two kinds of L^{4-} ligands (the disordered C atoms have been simplified for clarity).

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