

Double-layer structure, sorption and magnetism properties of metal–organic frameworks with trigonal planar ligand



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ARTICLE INFO

Article history:

Received 5 November 2014

Received in revised form 7 January 2015

Accepted 9 March 2015

Available online 12 March 2015

Keywords:

Trigonal planar ligand

Metal–organic framework

Gas adsorption

Magnetic studies

ABSTRACT

A new double-layer metal–organic framework [Co₃(tcpt)₂(H₂O)₂] (**1**) has been synthesized using trigonal planar ligand 2,4,6-tris(4-carboxyphenoxy)-1,3,5-triazine (H₃tcpt) as a bridging ligand and characterized by single-crystal X-ray diffraction, elemental analyses, IR, PXRD and TGA. Structure analysis reveals that compound **1** has a double-layer structure. Gas sorption measurements indicate that compound **1** exhibits selective adsorption capabilities for CO₂ over CH₄ and N₂. Furthermore, the magnetic studies of compound **1** show antiferromagnetic interactions between Co(II) ions.

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Over the past decades, considerable attention has been given to control the structures of metal–organic frameworks (MOFs) because of their enormous diverse structures and great potential applications in gas storage, magnetism, luminescence and so on [1–8]. The variety of coordination interactions between metal ions/clusters and organic ligands leads to MOF infinite structures and interesting properties. In order to get predictable structures and properties, a large quantity of studies have been attracted on preparing novel MOFs by using extension organic ligands and functional metal ions. Among numerous ligands to construct diverse MOF structures, trigonal planar ligands played an important role due to their topological features. Trigonal planar ligands such as H₃BTB (4,4',4''-benzene-1,3,5-triyltribenzoic acid), H₃BBC (4,4',4''-(benzene-1,3,5-triyltris(benzene-4,1-diyl)) tribenzoic acid), H₃TATAB (4,4',4''-s-triazine-1,3,5-triyltrip-aminobenzoate acid), and H₃BTATB (4,4',4''-(benzene-1,3,5-triyl-tris(azanediyl)acid)tribenzoate) have been used to prepare many famous MOFs [1,9,10]. Compared to benzene derivatives, the increased quadrupole moment of the triazine ring makes them more likely to give π–π stacking [11], which would strengthen the thermal stability of the MOFs obtained.

In this paper, 2,4,6-tris(4-carboxyphenoxy)-1,3,5-triazine (H₃tcpt) was selected as a ligand and one new MOF was obtained under solvothermal conditions. H₃tcpt (0.1 mmol, 0.0489 g), p-phthalic acid

(0.1 mmol, 0.0166 g) and Co(NO₃)₂·6H₂O (0.3 mmol, 0.0582 g) were added to a N,N'-dimethylacetamide (DMA)/acetonitrile (ACN)/H₂O mixture (v/v/v = 4:4:1, 4.5 ml) with two drops of pyridine, ultrasonicated to dissolved in a vial and heated at 90 °C for 24 h. After cooling to room temperature, needle red crystals were collected by filtration. Before the yield calculation and elemental analysis, the as-synthesized bulk products were activated under high vacuum at an optimized temperature of 110 °C for 2 h. (Yield: 48.5% based on H₃tcpt). Anal. Calcd for

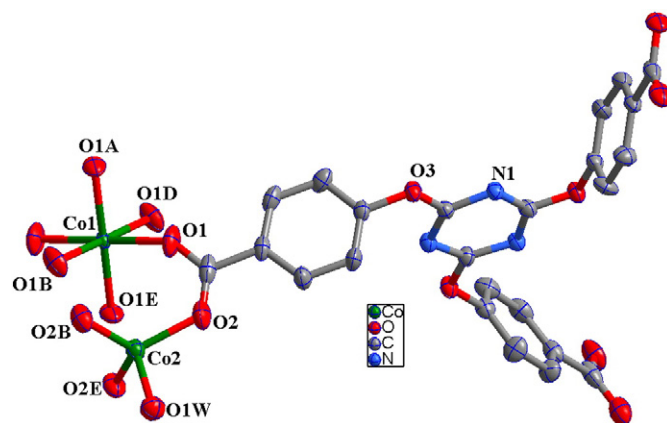


Fig. 1. Coordination environment of the Co(II) in compound **1** (H atoms omitted for clarity). Symmetric codes: A $-x + y + 1, y, -z + 1/2$; B $-y + 1, x - y, z$; C $-y + 1, x + 1, -z + 1/2$; D $x, x - y, -z + 1/2$; and E $-x + y + 1, -x + 1, z$.

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$C_{48}H_{24}N_6O_{20}Co_3$ (%): C, 48.78; H, 2.05; N, 7.11. Found: C, 48.83; H, 2.07; N, 7.03. The IR (KBr pellets) spectrum of compound **1** is shown in Fig. S1. Detailed crystallographic data for **1** are summarized in Table S1 and relevant bond lengths and angles are listed in Table S2.

X-ray single-crystal structure analysis reveals that compound **1** crystallizes in the trigonal system, space group $P\bar{3}1c$. In the structural unit of compound **1**, there exist two crystallographically distinct cobalt ions. Co1(II) adopts a six-coordinated octahedron geometry by coordinating to six O atoms of carboxylate from five $tcpt^{3-}$ ligands. The Co2(II) atom is coordinated by three O atoms of carboxylate from three $tcpt^{3-}$ ligands and one water molecule, showing a tetrahedral geometry (Fig. 1).

As shown in Fig. 2b, the three adjacent Co(II) are bonded together to generate a six-connected paddlewheel secondary building unit [SBU, $Co_3(COO)_6$] with Co1–O and Co2–O bond length being 2.056 (5) Å and 1.915 (6) Å, respectively. The axial sites of such paddlewheel unit are occupied by the O atoms of water molecules with the Co2–O1W

distance of 1.920 (10) Å. Each SBU is linked by six $tcpt^{3-}$ ligands to form a double-(6,3)-layer (Fig. 2a, c).

For a layered framework, two different arrangements of the layers are included: one is interpenetrating, and the other is stacking. For the stacking arrangement of the layers, which may generate chirality from stacking around one fixed axis, there are infinite arrangements, such as AAAA and ABAB, which are supramolecular isomers mutually [12].

As shown in Fig. S2, the stacking arrangement of the layers in the structure of **1** is ABAB via π – π stacking interactions (3.7610 Å) of triazine rings between the adjacent layers, which gives rise to a three-dimensional (3D) supramolecular achiral architecture with 1D channels running through the c axis. The effective free void volume of **1** estimated by PLATON [S5] is 38.5% of the total volume when the guest molecules are removed (1285.5 Å³ out of the 3341.7 Å³ per unit cell volume).

The framework stability of compound **1** was analyzed by thermogravimetric analysis (TGA) measurements. The TGA curve of compound **1** displayed two steps weight loss, and the first weight loss before

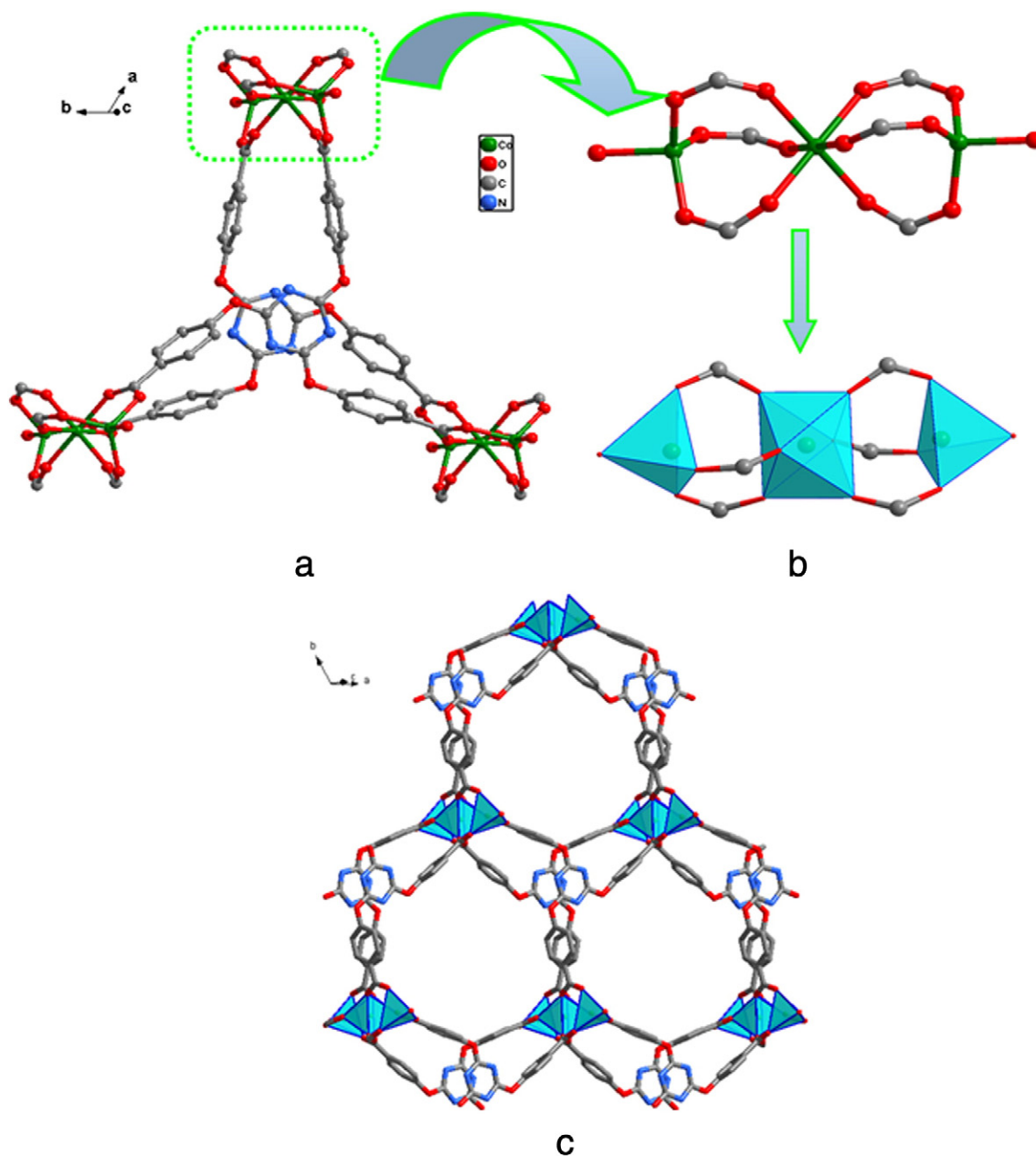


Fig. 2. (a) The coordination mode of $tcpt^{3-}$ and trinuclear Co^{2+} . (b) View of the secondary building unit [SBU, $Co_3(COO)_6$] and the localized geometry of the SBU in compound **1**. (c) One double-(6,3)-layer in compound **1** (H atoms omitted for clarity).

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