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A novel 2D (4,4) cobalt(II)-organic framework based on tetranuclear cluster nodes and double stranded organic linkers

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ABSTRACT

A novel 2D cobalt(II)-organic framework, $[Co_2(\mu_2-H_2O)(hfipbb)_2(py)_3] \cdot 2(py)]_n(1)(H_2hfipbb = 4,4'-(hexa-fluoroisopropylidene)bis(benzoic acid), py = pyridine), has been synthesized under hydrothermal reaction. Single-crystal X-ray diffraction revealed that$ **1**is a noninterpenetration (4,4) network based on unique tetranuclear clusters and double stranded organic linkers. The powder X-ray diffraction and thermogravimetric analysis of**1**have also been investigated.

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Crystal engineering of metal-organic frameworks is currently attracting significant attention not only for their potential applications as functional crystalline materials, but also for their fascinating topologies and structural diversity [1–2]. The most important goal in the field is always to obtain tailor-made solids with the required structures and properties starting from well-characterized inorganic and organic species. Particular attention has been attracted to the isolation and characterization of 2D topologies that contain three-, four-, five- or six-sided polygons with the features as 4⁴ square-grid, 6³ honeycomb, 6³ brick-wall, 6³ herringbone, 3²6² Kagomé lattice, 3⁶ net, 3³4² net, 4¹8² net, basket-weave, helical-layer, and so on [3–10]. Moreover, the controlled syntheses of 2D functional coordination polymers have also been well investigated [11–15].

Along with our research of assembly of novel 2D metal-organic coordination polymers [9,10], our current synthetic strategy is extending to identify new multinuclear building blocks for the construction of novel frameworks with unusual architectures. Recently, polynuclear metal centres with substituted single metal atoms have been used as potential nodes for high-connected metal-organic frameworks [16]. Herein we employed a bent ligand, 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H₂hfipbb) as excellent candidate for the construction of targeted frameworks based on the following considerations: (i) the synthesis of metal clusters is usually by the controlled hydrolysis of metal salts with the aid of carboxylate ligands, because the carboxylate group may

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induce core aggregation and it should be feasible to link discrete clusters into an extended network via its bridging ability; (ii) the assemblies of extended solids from the long and bent arenedicarboxylate linker are considerably less studied despite that they would likely offer new topologies with channels and, consequently, a great potential for the design and synthesis of functional materials [17–22]. As expected, we successfully isolated a novel 2D Co(II)-organic framework with H₂hfipbb and pyridine as co-ligands, $[Co_2(\mu_2-H_2O)(hfipbb)_2(py)_3] \cdot 2(py)]_n$ (1). Interestingly, compound 1 is a novel noninterpenetration (4,4) network based on tetranuclear clusters and double stranded organic linkers. The powder X-ray diffraction and thermogravimetric analysis of 1 have also been investigated.

The hydrothermal reaction of CoCl₂ · 6H₂O, H₂hfipbb and pyridine (ratio of 2:1:50) in agua afforded pink crystals of **1** [23], which are characterized by elemental analysis, IR spectra, and XPRD. Single-crystal X-ray analyses [24] revealed that the compound **1** is composed of a 2D polymeric structure with guest solvent molecules. Its asymmetric unit consists of two cobalt atoms, two hfipbb ligands, three coordinated pyridine co-ligands, one μ_2 -bridged water molecule, and two free pyridine molecules. As shown in Fig. 1, all Co atoms locate in distorted octahedron, Co-O and Co-N bond distances are in the range of 2.041(3)-2.212(2) and 2.154(3)–2.160(3) Å, respectively. Two Co atoms are bridged by two carboxylate groups and one μ_2 -bridged water molecule to form a dinuclear unit. The Co…Co separation is 3.617 Å, and the angle of Co-O_{water}-Co is 110.53(10)°. Two dinuclear Co units is further bridged by two carboxylate groups to form a tetranuclear moiety with a centre of inversion, which can be considered as



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Fig. 1. Ortep drawing of complex **1** shows the coordination atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

the secondary building unit (SBUs) for construction of the metalorganic architecture of compound 1 (Fig. 2). Within the tetranuclear structure, the intramolecular O-H--O hydrogen-bonding interactions play a key role in forming the novel SBUs. The μ_2 bridged H₂O molecules donate H atoms to the adjacent carboxylate O atoms to generate strong O-H…O hydrogen-bonding interactions (2.546(5) and 2.734(3) Å). Consequently, each tetranuclear cluster unit links to another four neighboring tetranuclear clusters by eight hfipbb organic ligands to result in a 2D layer network, as shown in Fig. S1 and Fig. 3. The dihedral angles between benzene rings of bent hfipbb ligands are 101.0 and 78.3°, respectively. In 1, the hfipbb ligands adopt two kinds of different coordinated modes as μ_3 -bridged and μ_4 -bridged linkers. Interestingly, this 2D sheet can be described as a (4,4) network based on 4-connected tetranuclear nodes and double stranded organic linkers. It is noteworthy that this topology type is rarely reported to date, to our best knowledge, the complex 1 is the first (4,4) network based on tetranuclear cluster nodes and double stranded organic linkers



Fig. 2. The tetranuclear cobalt cluster units and interlinked modes of adjacent clusters in complexes 1.



Fig. 3. Schematic representation of the (4,4) network of **1** based on double stranded organic linkers.

[25]. In addition, the guest pyridine molecules fill in the window of layer and the void of interlayer.

XRD data of complex **1** was collected on a Rigaku D_max/3b diffractometer with CuK α radiation (λ = 1.5418 Å). The experimental XRD patterns agreed well with the simulated ones generated on the basis of the single-crystal analyses for **1** (Fig. S2), suggesting the phase purity of the products. Thermogravimetric analysis (TGA) experimental results indicate that **1** lost its isolated and coordinated pyridine molecules from 50 to 360 °C. Then, the remaining sample suffers incessant weight loss from 400 °C corresponding to the removal of the organic hfipbb species (Fig. S3).

In conclusion, a novel 2D cobalt coordination polymer has been synthesized under hydrothermal reaction. Compound **1** displays the first noninterpenetration (4,4) network based on tetranuclear cluster nodes and double stranded organic linkers. The successful isolation of the 2D (4,4) network may spark a broad spectrum of interest in the field of crystal engineering chemistry. We are currently extending this work into additional metal ions.

Acknowledgments

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Appendix A. Supplementary data

X-ray crystallographic file in CIF format, additional Figures, PXRD patterns, and TGA diagram for complex **1**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.06.008.

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- [23] Preparation of 1: The mixture of $CoCl_2 \cdot 6H_2O$ (48 mg, 0.2 mmol), $H_2hfipbb$ (40 mg, 0.1 mmol), pyridine (400 mg, 5 mmol) and water (8 mL) was homogenized at room temperature for 30 min, then the final solution was sealed in a 20 mL stainless-steel autoclave at 170 °C for 72 h. A quantity of pink single crystals of 1 was obtained after the solution was cooled to room temperature. The yield of 1 is ca. 70% based on CoCl₂ · 6H₂O. Anal. Calcd. for $C_{59}H_{43}Co_2F_{12}N_5O_9(\%); C, 54.02; H, 3.30; N 5.34. Found (\%); C, 53.73; H, 3.64; N, 5.19. IR (KBr, <math display="inline">\nu/cm^{-1});$ 3421(m), 2364(w), 1603(vs), 1545(s), 1404(vs), 1253(vs), 1167(vs), 959(w), 727(m).
- [24] Crystal data for 1: $C_{59}H_{43}Co_2F_{12}N_5O_9$, M = 1311.84, triclinic, space group P-1(No. 2), a = 13.631(3), b = 14.668(3), c = 16.375(3)Å, $\alpha = 111.12(3)$, $\beta = 99.23(3)$, $\gamma = 105.46(3)^\circ$, V = 2821.4(10)Å³, Z = 2, $D_c = 1.544$ g/cm³, $F_{000} =$ 1332, Mo K α radiation, $\lambda = 0.71073$ Å, T = 298(2) K, $\mu = 0.690$ mm⁻¹. Final S = 1.023, $R_1 = 0.0486$, $wR_2 = 0.1385$. The hydrogen atoms of the crystalline pyridine molecules are not generated because of the disorder of C atoms.
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