A High-connected Cobalt(II) Pyromellitate MOF Displaying An Uncommon Decadentate Coordination Mode

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Received June 16, 2014, Accepted July 18, 2014

Key Words: Cobalt-organic framework, Pyromellitic acid, Trinodal network

Introduction

Metal–organic frameworks (MOFs) from organic ligands and transition metals have become a field of quick growth in supramolecular and material chemistry due to their intriguing structural diversity and potential applications in several aspects such as gas adsorption/separation, catalysis, optics, magnetism, and molecular recognition. In particular, topology focuses on the coordination network connectivity generated via the reduction of periodic nets into node-and-linker/vertex-and-edge representations, which helps greatly the understanding of the significance of MOFs for theoretical crystal chemistry consists in close relations between their composition, physical properties and topology of the corresponding atomic net. To date, thousands of new MOFs have been synthesized. In these reported coordination networks, the majority are commonly uninodal- and low connected (< 7) nodes, trinodal networks containing highly connected nodes such as (3,4,6)-, (3,4,7)-, (3,6,10)-, (3,8,10)-, (4,4,7)- and (4,8,16)-connected MOFs are relatively rare. The formation of the highly connected MOFs is greatly affected by the organic ligands, the nature of the metal ions, the counterions, and other factors. Among the reported research, organic ligands with carboxylate groups are especially interesting in the field of crystal engineering and coordination chemistry. Pyromellitic acid (H₄pm) as an outstanding organic ligand containing four exo-carboxyl groups around the benzene ring, shows diverse coordination modes and bridges central metal atoms to assemble multidimensional architectures. Therefore, a number of highly connected MOFs based on H₄pm have been synthesized and presented by our group and others during the past several years. Based on H₄pm, and mixed with bis(pyridyl)-1,2,4-triazolate ligands, two novel 3D zinc(II) coordination polymers were synthesized and characterized by Yu and his co-workers, the topological analysis results reveal the two MOFs can be simplified to a trinodal (3,4,10) and (3,4,5)-connected topology, respectively. Very recently, we found that introduction of rod-like neutral N,N'-donor btx (1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene) ligands into the Co-pm system can generate novel compound [{Co₂(pm)(btx)(H₂O)}₂(H₂O)]₈n, which is an unusual 3D binodal (4,10)-connected MOF. In continuation of our exploratory research toward developing new coordination polymers constructed from H₄pm with secondary bridging flexible two-connector N-containing coligands, herein, we report the synthesis, crystal structure and characterization of an unique trinodal (4,4,7)-connected 3D MOF, formulated as [Co₂(pm)(bib)₅(H₂O)₉]₈ (1) (bib = 1,4-bis(2-methyl-imidazol-1-yl)butane) with a Schläfli symbol of (4².5.6.7)(4².6³)(4².5.6⁴), in which pyromellitate anions show an unprecedented decadentate coordination mode. In addition, TGA, XRPD and fluorescence spectra determinations were performed for 1.

Experimental

Materials and Characterization Methods. All reagents were purchased commercially and used without further purification. The N-containing ligand bib was synthesized in accordance with previously reported literature. The elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Thermal analysis was performed on a Netzsch TG 209 thermal analyzer from room temperature to 800 °C under N₂ at a heating rate of 10 °C/min. FT-IR spectrum was recorded from KBr pellets in the range of 4000–400 cm⁻¹ on an Avatar 360 (Nicolet) spectrophotometer. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. The X-ray powder diffraction (XRPD) pattern was recorded on a Rigaku D/MAX-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator.

Synthesis of [Co₂(pm)(bib)₅(H₂O)₉]₈. A mixture of CoCl₂·6H₂O (0.1 mmol, 23.8 mg), H₄pm (0.1 mmol, 25.0 mg), bib (0.1 mmol, 22.0 mg), methanol (5 mL) and H₂O (10 mL) was placed in a Teflon-lined stainless steel vessel and then, the pH value was adjusted to 6.5 by NaOH (0.1 M). The mixture was sealed and heated at 140 °C for 3 days under autogenous pressure. After the mixture cooled to room temperature at a rate of 5 °C/h, purple block single crystals of the complex, suitable for X-ray diffraction, were collected by filtration. Yield: 58% (based on Co). Anal. Calc. for C₂₃H₂₃Co₇N₉O₁₇ (%): C, 39.53; H, 2.49; N, 5.76%. Found: C, 39.68; H, 2.31; N, 5.52%. IR (KBr, cm⁻¹): 3435s, 2923w,
Crystallography. Single crystal X-ray diffraction analysis of the titled compound was carried out on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) and $\omega-2\theta$ scan mode at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multiscan techniques; the structure of the complex was solved by direct methods and refined by full-matrix least-squares fitting on $F^2$ by SHELXL-97. Multi-scan absorption corrections were applied to the data using the SADABS program. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. The H-atoms of organic ligands were generated theoretically onto the specific atoms and refined isotropically. The complex showed disorder in N1, N2, C11-C16 of the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restraining the bib ligands; these atoms were refined with a split model with site occupation factor 0.63, SADI for restrain...
bouring Co2 via a bridging bib ligand, and three pm4− ligands, and can be regarded as a 4-connected node. The bib ligand is a linker (Figure S1 showing three types of nodes). Thus, the 3D high-connected MOF can be simplified as unique mixed nodes, a trinodal (4,4,7)-connected network with a Schläfli symbol of (4.5.6.7)(4.6.2)(4.5.6) analyzed by the TOPOS 4.0 program15 (Figure 4). To the best of our knowledge, the topology of this net has not appeared in MOF chemistry, according to the reticular Chemistry Structure Resource Database.16

IR Spectrum and XRPD Pattern. The IR spectrum displays characteristic absorption band for water molecule, carboxyl groups of pm4−, and bib ligand. There is no absorption peak between 1730 and 1690 cm−1, indicating that all carboxyl groups of the organic moieties are deprotonated.17 The infrared spectra of the title complex represents a broad band centered at ca. 3435 cm−1 which is due to the O-H stretching vibration of water molecules involved in extensive hydrogen bonding interactions or the coordinated water molecule. The bands at 2923 cm−1 and 1272 cm−1 are related to ν(−CH3) and ν(C-N) of the bib ligand, respectively. The splitting of COO− bands suggests the different coordination mode of carboxylate groups from the pm4− ligands.18 This is also in agreement with the crystal structure of the complex.

The simulated and experimental XRPD patterns of compound, obtained at room temperature, are shown in Figure S2. Their peak positions are in good consistency with each other, indicating the phase purity of the as-synthesized samples.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed on a sample of 1 under N2 atmosphere with a heating rate of 10.0 °C/min. As shown in Figure S3, the complex possessed a two-step weight-loss process. The first step occurred from 110.0 °C to 147.0 °C, with a weight-loss of 2.0%, which can be attributed to the loss of coordinated water molecules (calcd: 1.9%). Furthermore, there is almost no weight loss from 148.0 °C to 358.0 °C. The second step with a weight-loss of 24.9% occurred in a temperature range from 359.0 °C to 579.0 °C, corresponding to the decomposition of the organic ligands. And finally, the remnants are 29.8%, which should be CoO (calcd. 30.9%).

Luminescence Properties. The solid-state photoluminescence spectrum of compound 1 was measured at room temperature, and the result is depicted in Figure S4. The complex exhibits a fluorescent emission band with maximum at 384 nm upon excitation at 235 nm. The main emission peak of H4pm is at 342 nm (λex = 308 nm),19 while the free bib ligand displays very weak fluorescent emission centered at 465 nm (λex = 280 nm).20 When comparing the title complex with the H4pm ligand, the emission band of the complex is 42 nm red-shifted, which can be assigned according to intraligand n→π* transitions.21

Conclusion

In summary, we present an unusual trinodal (4,4,7)-connected MOF with an uncommon coordination model of pm4− ligand. The results clearly reveal that the H4pm ligand acts as a rich library of tectons in designing and construction of highly-connected MOFs. Furthermore, the bib ligand may influence the functional properties of these coordination polymers.

Acknowledgments. Publication cost of this paper was supported by the Korean Chemical Society.

Supplementary Material. CCDC number: 993735 for the complex. The data can be obtained free of charge via https://services.ccdc.cam.ac.uk/structure_deposit (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033(44); or deposit@ccdc.cam.ac.uk).

References
