A 2D metal-organic framework with two different rhombus-shaped cavities: a rare example of a (4,4)-net with alternating metal and organic nodes

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Abstract

The synthesis and crystal structure of the metal-organic framework \([\text{Co(acetate)}_2(rctt-tetrakis(4-pyridyl)cyclobutane)}\cdot 2(\text{methanol})]_\infty\) (I) are described. The structure of I is based on a (4,4)-grid topology with Co(II) ions and 4,4′-tpcb cyclobutane molecules as 4-connected nodes and two different rhombus-shaped cavities in the framework. Solvent methanol molecules are clathrated between the grids. A model involving pseudo-merohedral twinning was required to arrive at a satisfactory single-crystal structure solution. Crystal data for I: triclinic, space group P1, \(a = 9.006(2), b = 9.127(2), c = 9.129(2), \alpha = 78.57(3), \beta = 88.99(3), \gamma = 88.98(3), V = 735.4(3), \) and \(Z = 1\) for \(R = 0.0362\) (2539 reflections with \(I > 2\sigma(I)\), 184 parameters).

Keywords: Metal-organic framework; Linear template; [2+2] photodimerization; Rhombus cavity; Grid

1. Introduction

Strategies for the construction microporous and mesoporous solids based on metal-organic frameworks (MOFs) [1] are of importance to several areas of materials science such as recognition [1], clathration [2], and catalysis [3]. In addition to holding an aesthetic appeal, MOFs have made significant contributions to structural chemistry, producing frameworks and topologies less realized by more traditional approaches to porous solids [4,5].

We are developing an approach to construct porous MOFs using organic linkers derived from the solid state [6]. Using a method to control reactivity in molecular solids based on molecules that function as linear templates [7], we enforce topochemical alignment of stilbenes in the solid state such that the olefins undergo [2+2] photoreaction [8]. In particular, co-crystallization of 1,3-dihydroxybenzene (resorcinol) with trans-1,2-bis(4-pyridyl)ethylene (4,4′-bpe) has produced the four-component molecular assembly, 2(resorcinol)·2(4,4′-bpe), wherein two molecules of 4,4′-bpe are positioned, by four O–H···N hydrogen bonds, for [2+2] photodimerization (Scheme 1) [7a]. UV-irradiation of the solid produced rctt-tetrakis(4-pyridyl) cyclobutane (4,4′-tpcb) in 100% yield. Owing to the presence of four divergent pyridyl groups attached along the periphery of the cyclobutane, we have shown that 4,4′-tpcb can serve as a 4-connected node of a porous MOF. Thus, reaction of 4,4′-tpcb with \([\text{Cu}_4(\text{acetate})_8(\text{H}_2\text{O})_2]\) produced the two-dimensional (2D) MOF \([\text{Cu}_4(\text{acetate})_8(4,4′-\text{tpcb})]_\infty\) with a network structure based on a (4,4)-topology [6]. The framework consisted of rhombus-shaped cavities that accommodated aromatic solvent molecules as guests (e.g. benzene) and were stable to guest removal. Indeed, the ability to construct a MOF using a linker derived from the solid state provided access to a porous solid less available using a more traditional covalent approach to synthesis [4,5].

With this in mind, we wish to report here application of 4,4′-tpcb to construct the 2D MOF \([\text{Co(acetate)}_2(4,4′-\text{tpcb})\cdot 2(\text{methanol})]_\infty\) (I). In a similar way to \([\text{Cu}_4(\text{acetate})_8(4,4′-\text{tpcb})]_\infty\), the components of I assemble in the solid state to form 2D grids with rhombus-shaped cavities that host molecules as guests. In contrast to \([\text{Cu}_4(\text{acetate})_8(4,4′-\text{tpcb})]_\infty\), however, the metal and cyclobutane units of I define alternating...
nodes within the grid to produce a 2D net based on a (4,4)-topology [9] that, owing to the geometry of the cyclobutane linker, possesses two different rhombus-shaped cavities within the framework structure. In addition to providing access to hosts difficult to achieve using a more traditional approach to synthesis, the design and construction of I provides insight into design criteria for the construction MOFs with two or more different cavities, which is of current interest [10].

2. Experimental

All reactions were performed in air under ambient pressure and temperature using sealed 10 g sample vials as reaction vessels. Thermal analyses were conducted under nitrogen using a heating range of 25–600 °C with a heating rate of 5.0 °C/min using a TA Instruments TGA 2950 Thermogravimetric Analyzer. Powder X-ray diffraction data were obtained using a Siemens D-5000 diffractometer. All reagents were purchased from Aldrich Chemical Company and were used as-received unless otherwise stated. 4,4'-tpcb was prepared according to a literature procedure [7a]

2.1. Preparation of I

Reaction of 4,4'-tpcb (0.14 g, 0.4 mmol) with Co(acetate)$_2$·4H$_2$O (0.10 g, 0.4 mmol) in methanol (20 ml) produced a pink solution. Pink single-crystals of I precipitated from the solution after a period of approximately five days (yield: 80%). Thermal analysis of I reveals that the material decomposes in three steps. The first step occurs between 25 and 115 °C and can be ascribed to the decomposition of methanol (9.8%, calculated 10.6%). The remaining steps occur between 185–365 and 505–531 °C and can be ascribed to the decomposition of [Co(acetate)$_2$(4,4'-tpcb)]$_\infty$ to give Co$_2$O$_3$ (remaining mass: 13.9%, calculated 14.5%) and CoO (remaining mass: 12.4%, calculated 12.6%), respectively.

2.2. X-ray crystallography

Crystal data for I: triclinic, space group P$_1$, $a = 9.006(2)$, $b = 9.127(2)$, $c = 9.129(2)$, $\alpha = 78.57(3)$, $\beta = 88.99(3)$, $\gamma = 88.98(3)$, $V = 735.4(3)$, $D_{calc} = 1.37$ g cm$^{-3}$, MoK$\alpha$ radiation ($\lambda = 0.71073$ Å) for $Z = 1$. Least-squares refinement based on 2539 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 2581 unique reflections) led to a final value of $R = 0.0362$. A single crystal of I was mounted on the end of a glass fiber and optically centered in the X-ray beam of an Nonius Kappa system for data collection. Cell constants were calculated from reflections obtained from the data collection. The structure was solved using direct methods. The original cell and structure data for I suggested a monoclinic C-centered crystal system. Refinement of the structure in the C-centered monoclinic space group C 2/m was unsatisfactory and the possibility of twinning was considered. There were no unusual absences, but $E^2 - 1$ was very low (0.6) and there were many more $F_o > F_c$ than the reverse. The equality of the two axes and angles in the primitive cell suggested a possibility of pseudo-merohedral twinning, while no evidence of non-merohedral twinning was noted in precession syntheses. Simple pseudo-merohedral twinning (twin law = 100 001 010) as a 50/50 twin in the primitive space group P1 gave immediate and substantial improvement in the refinement. The twinning emulates a mirror about the 0 1 1 plane and is simple to treat in the primitive cell. The included methanol molecule was disordered and modeled with 50% occupancy over two sites. After anisotropic refinement of non-hydrogen atoms, aromatic, methine, and hydroxyl hydrogen atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. Structure calculations were conducted using SHELXL-93 [11] locally implemented on a Pentium-based IBM compatible computer. A summary of crystal data for I is given in Table 1. Crystallography data for I have been deposited with the Cambridge Crystallography Data Centre (CCDC reference number: 217194).

3. Results and discussion

An ORTEP perspective of I is shown in Fig. 1. The asymmetric unit of I consists of one half Co(II) atom, one half 4,4'-tpcb molecule, one acetate ion, and one methanol molecule. The overall coordination geometry
of the Co(II) ion can be described as a distorted octahedron and consists of two oxygen atoms of two acetate ions and four nitrogen atoms of four different 4,4'-tpcb ligands located in the axial positions and equatorial plane, respectively. In a similar way to [Cu4(acetate)]6(4,4'-tpcb)2, each 4,4'-tpcb unit serves as an exo-tetradentate ligand such that a neutral 2D grid with rhombus-shaped cavities has formed (Fig. 1a). In contrast to [Cu4(acetate)]6(4,4'-tpcb)2, however, both the metal and cyclobutane units serve as 4-connected nodes within the framework. Specifically, the components have assembled such that the metal and organic nodes alternate within the grid to produce a 2D framework with a (4,4)-topology [9]. Owing to the geometry of the cyclobutane, the positioning of the nodes produces two different cavities, Cavity A and Cavity B, within the grid that exhibit identical edge lengths (7.3 Å) and corner angles based on the acute (75.9°) and obtuse (104.2°) corner angles of the cyclobutane, respectively. In this arrangement, the cavities form continuous rows, along

Table 1
Crystal data for I

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<thead>
<tr>
<th>Property</th>
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<td>b (Å)</td>
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<tr>
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<tr>
<td>Data collection temperature (K)</td>
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</tr>
<tr>
<td>Radiation</td>
<td>λ (MoKα) = 0.71073 Å</td>
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<tr>
<td>μ (MoKα) (mm⁻¹)</td>
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<tr>
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<tr>
<td>R1 (I &gt; 2σ(I))</td>
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</tr>
<tr>
<td>wR2 (I &gt; 2σ(I))</td>
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</tr>
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</table>

Fig. 1. ORTEP perspective of the grid I. Selected interatomic distances (Å) and angles (°): Co(1)–N(1) 2.195(3), Co(1)–N(2) 2.181(3), Co(1)–O(1) 2.069(2), N(1)–Co(1)–N(2) 83.7(6), N(1)–Co(1)–N(2) 96.24(9), O(1)–Co(1)–O(1) 180.0. Symmetry operators: (i) -x+2, -y+1, -z+1; (ii) x, y+1, z-1; (iii) -x+2, -y+2, -z. Hydrogen atoms omitted for clarity.
The crystallographic $a$-axis, that alternate ABAB within the grid (Scheme 2). The methyl groups of the carboxylate anions project approximately orthogonal from the plane of the grid to give a 2D structure with a hydrophobic surface.

A view of the packing of the grids is shown in Fig. 2. The grids of 1 exhibit an ABAB stacking pattern wherein the metal nodes lie above and below Cavity A and the organic nodes lie above and below Cavity B. In this arrangement, the methyl groups of the acetate ions exhibit a tongue-in-groove fit with the pyridyl groups of Cavity A while interstices have formed between the cyclobutane linkers and Cavity B (Fig. 2a). Each interstice is clathrated by a single methanol molecule, which sits disordered across two equally occupied positions, that interacts with the carboxylate groups via O–H···O hydrogen bonds (Fig. 2b) and represents approximately 20% of the volume of the unit cell [12].

Results of a thermal study of 1 are shown in Fig. 3. Thermogravimetric analysis of 1 reveals that the included methanol molecules are liberated from 1 between 25 and 115 °C (9.8%, calculated 10.6%) (Fig. 3). To investigate the stability of the framework, IR and powder X-ray diffraction studies were performed on a freshly evacuated sample of 1 prepared by heating 1 to 140 °C in an oven. The resulting solid was found to rapidly absorb 2.5 equivalents of water from the air, as revealed by IR and thermogravimetric analysis (7.3%, calculated 7.6%), reaching saturation after $\approx$2 h. A powder X-ray diffraction study, despite line broadening, reveals that the structure of the solid that remains upon removal of the methanol and absorption of water is similar to the structure of 1 (Fig. 3b). Experiments are underway to determine the range of guests that may be included within the framework solid.

![Scheme 2.](image)

![Fig. 2.](image)

4. Conclusion

In this report, we have described the structure and stability of a 2D MOF that possesses two different rhombus-shaped cavities [9]. The organic linker of the MOF has been obtained by way of a template-controlled [2+2] photodimerization conducted in the solid state. Organic groups, in the form of carboxylates, project from the surface of the grid. With these observations realized, we plan to extend our strategy to construct 2D frameworks with two or more cavities and/or different organic anions by design. Such solids could open a possibility for unique shape selective effects involving more than one guest [13], where the stereocontrol afforded by the linear templates provides access to MOFs difficult to achieve using more conventional covalent methods. Such studies should also reveal whether grids based on rhombus-shaped cavities exhibit structure behaviors akin to square grid predecessors [1].
Acknowledgements

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References