



The effect of reaction conditions on the nature of cadmium 1,3,5-benzenetricarboxylate metal–organic frameworks

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ABSTRACT

The product from the reaction between $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 1,3,5-benzenetricarboxylic acid (H_3btc) in DMF at 95 °C depends on the reaction time, with $[\text{Cd}(\text{Hbtc})(\text{H}_2\text{O})_2]$ **1** and $[\text{Cd}(\text{Hbtc})(\text{DMF})_2]$ **2** isolated after heating for 10 min, the latter after standing the solution for 1–2 weeks at room temperature. $[\text{Cd}_3(\text{btc})_2(\text{H}_2\text{O})_9] \cdot 4\text{H}_2\text{O}$ **3** was isolated after heating for 1 h, whereas $[\text{Cd}_{12}(\text{btc})_8(\text{DMF})_{14}(\text{OH}_2)_2] \cdot 1.5\text{DMF}$ **4** was isolated after heating for 2 days. Compounds **1** and **3** have been previously reported, whereas **2** and **4** are both new. Compound **2** adopts a two-dimensional sheet structure, with the coordinated DMF ligands projecting from both sides of the sheets, whereas **4** has a complex three-dimensional structure related to the **fsc** net. When the reaction was repeated in the presence of pyrazine (pyz), the product $[\text{Cd}(\text{Hbtc})(\text{pyz})(\text{DMF})] \cdot \text{DMF}$ **5** was isolated as a minor compound. Compound **5** has a two-dimensional structure, with Cd–Hbtc zig-zag chains linked into sheets through the pyrazine ligands.

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1. Introduction

Coordination polymers, often referred to as metal–organic frameworks (MOFs), are currently attracting a high level of attention in inorganic and materials chemistry [1–4]. These compounds have extended structures and typically contain either metal centres or polynuclear metal aggregates interconnected by bridging ligands into one-, two- or three-dimensional networks. The interest in these materials arises in part from their structural variety, and the ability to control the structure through use of secondary building units (SBUs) [5] and linkers in which the number and orientation of the donor groups is pre-determined. The open framework structure of many MOFs gives them the potential for porosity. Although elegant structural chemistry has been undertaken on coordination polymers for many years [6,7], the recent upsurge of interest in these materials has resulted largely because some are sufficiently robust for the structure to be maintained on loss of included solvent molecules from the pores. The resultant ‘activated’ materials have been investigated for a range of applications including hydrogen storage [8,9], catalysis [10,11] and drug delivery [12,13].

Zinc MOFs, in which polycarboxylate ligands link di-, tri- and tetranuclear SBUs, are amongst the most well-studied of this class

of material [14–16]. MOFs containing the heavier congener cadmium have received less attention, with the majority of reported work focussing on systems containing polypyridine co-ligands [17,18]. We have recently reported the syntheses, structures and properties of cadmium MOFs containing 1,4- and 1,3-benzenedicarboxylate linkers [19]. In the current paper, we extend these studies to the ligand 1,3,5-benzenetricarboxylate (btc).

Previous work on the reaction between Cd(II) and H_3btc has yielded a number of MOF structures, with the majority of these formed under hydrothermal conditions. Thus, the network compounds $\text{Na}_3[\text{Cd}_3(\text{btc})_3(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ [20], $[\text{Cd}_3(\text{btc})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ [21], $\text{Na}[\text{Cd}(\text{btc})(\text{H}_2\text{O})_2]$ [22], $[\text{Cd}_3(\text{btc})_2(\text{H}_2\text{O})_9] \cdot 4\text{H}_2\text{O}$ [23] and $[\text{Cd}_3(\text{btc})_2] \cdot 8\text{H}_2\text{O}$ [23] were formed from the reaction of a Cd(II) salt with H_3btc in water between 150 °C and 200 °C, in some cases in the presence of an added base. Two MOFs were formed on milder heating in mixed solvents – $[\text{Cd}(\text{Hbtc})(\text{H}_2\text{O})_2]$ [24–26] and $[\text{Cd}_4(\text{btc})_3(\text{H}_2\text{O})_2(\text{DMF})_2] \cdot 1.5\text{H}_2\text{O}$ [27] – whereas another – $[\text{Cd}_3(\text{btc})_2(\text{H}_2\text{O})_9] \cdot 2\text{H}_2\text{O}$ [28] – was crystallised at room temperature using a silica gel method.

We have shown that heating $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and H_2btc (btc = 1,4-benzenedicarboxylate) in DMF below the boiling point of the solvent can afford access to new MOF materials, and that the structures of these can often be controlled by careful variation of the reaction conditions [19,29]. Systematic variation of the reaction conditions can allow a more complete exploration of a particular metal–ligand system, in an attempt to ensure that as many as possible of the attainable MOFs are isolated and, if possible,

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structurally characterised. In this way, those with the most interesting structures can be studied further. We sought to continue this approach by investigating the reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with H_3btc in DMF. Despite some structures from this system having been described previously, we show that systematic variation of the reaction time leads to two new phases at 95 °C. In addition, we show that attempts to generate three-dimensional MOFs by pillaring between two-dimensional sheets can lead to unexpected results.

2. Experimental

2.1. Materials and methods

Chemicals were purchased from Fisher Scientific and Aldrich Chemical Co. and used without further purification. Microanalysis (C, H and N) were carried out by Mr. Alan Carver (University of Bath Microanalytical Service). Thermogravimetric analyses were recorded on a Perkin–Elmer TGA 7 analyser. Powder diffraction data were recorded on a Bruker D8 diffractometer fitted with Goebel mirrors and a 0.2 mm beam slit, and in each case, unless noted below, the experimental pattern showed a good match with that simulated from the single crystal analysis.

2.2. Synthesis of $[\text{Cd}(\text{Hbtc})(\text{H}_2\text{O})_2] \mathbf{1}$ and $[\text{Cd}(\text{Hbtc})(\text{DMF})_2] \mathbf{2}$

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.500 g, 1.62 mmol) and H_3btc (0.340 g, 1.62 mmol) were dissolved in DMF (60 cm³) and the solution heated for 10 min at 95 °C then allowed to cool to room temperature over 1 h. During the reaction a colourless solid formed, which was identified by X-ray powder diffraction as **1**. Crystals of **2** deposited on top of the powder after 1–2 weeks as a minor product. Combined yield 0.22 g (38% based on **1** as product).

2.3. Synthesis of $[\text{Cd}_3(\text{btc})_2(\text{H}_2\text{O})_9] \cdot 4\text{H}_2\text{O} \mathbf{3}$

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.500 g, 1.62 mmol) and H_3btc (0.340 g, 1.62 mmol) were dissolved in DMF (60 cm³) and the solution heated at 95 °C for 1 h. A crystalline powder of **3** was present at the end of the reaction. This was separated by filtration, washed with fresh DMF and allowed to air dry. Yield 0.208 g (39%). The compound was identified as **3** by comparison of its powder X-ray diffraction pattern with that simulated from the crystal structure [23].

2.4. Synthesis of $[\text{Cd}_{12}(\text{btc})_8(\text{DMF})_{14}(\text{OH}_2)_2] \cdot 1.5\text{DMF} \mathbf{4}$

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.500 g, 1.62 mmol) and H_3btc (0.340 g, 1.62 mmol) were dissolved in DMF (30 cm³) and the solution heated at 95 °C for 2 days. Crystals of **4** were present at the end of the reaction and these were separated by filtration, washed with fresh DMF and allowed to air dry. Yield 0.231 g (41%). *Anal. Calc.* for $\text{C}_{118.5}\text{H}_{136.5}\text{Cd}_{12}\text{N}_{15.5}\text{O}_{65.5}$: C, 34.1; H, 3.30; N, 5.20. *Found*: C, 34.1; H, 3.28; N, 5.38%. $\nu_{\text{max}}/\text{cm}^{-1}$: 1655s, 1606s, 1552s, 1430s, 1358s, 1251s.

2.5. Synthesis of $[\text{Cd}(\text{Hbtc})(\text{pyz})(\text{DMF})] \cdot \text{DMF} \mathbf{5}$

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.500 g, 1.62 mmol), H_3btc (0.340 g, 1.62 mmol) and pyrazine (0.130 g, 1.62 mmol) were dissolved in DMF (30 cm³) and the solution heated for 2 days at 95 °C. Crystals of **5** formed together with a powder on cooling the sample slowly to room temperature. The major product was identified by powder X-ray diffraction as **4**. Combined yield 0.42 g.

2.6. X-ray crystallography

X-ray data for compounds **2** and **5** were collected on a Nonius Kappa CCD diffractometer using Mo K α radiation, whereas X-ray data for compound **4** were collected at Daresbury Station 16.2 SMX using synchrotron radiation. Details of the data collections, solutions and refinements are given in Table 1. Unless noted below, all non-hydrogen atoms were refined anisotropically in the final least squares run, and hydrogen atoms were included at calculated positions. The structures were solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97 [30].

The absolute structure parameter refinement for **2** (0.51(5)) indicates racemic twinning of the crystal. This, coupled with pseudosymmetry in the asymmetric unit, suggested that perhaps the incorrect space group had been assigned. Analysis with PLATON ADSYMM indicated that space group *Pbcm* might be a feasible alternative, however with 1160 systematic absence violations and poor convergence, this was not viable.

The large asymmetric unit of **4**, coupled with difficulties resolving the solvent and disorder led to slow convergence of the structure. Partial occupancy atoms arising from disorder were treated isotropically throughout. The DMF molecule coordinated to Cd(1) is disordered over two sites. One half of this – based on partial occupancy oxygen atom O(11) – was resolved but the remainder – based on O(11C) – could not be. It is clear that there is residual electron density in this area (difference Fourier map maximum located in this region), but no plausible model that could be refined was obtained. All bond distances in the refined DMF fractions were restrained to ideal values, and the partial occupancy atoms therein were restrained to being co-planar. The water hydrogen atoms on O(11A) and O(23) could not be located and consequently were omitted from the refinement. The DMF molecules containing O(19) and O(110) were, with the exception of the oxygen atoms, located evenly over two sites. Four C–N distances in the two fragments of DMF containing O(19) were restrained to ideal values, as were all bond distances in the refined fractions of DMF based on O(110). The partial occupancy atoms in each of these fragments

Table 1
Crystallographic details for compounds **2**, **4** and **5**.

	2	4	5
Formula	$\text{C}_{15}\text{H}_{16}\text{CdN}_2\text{O}_8$	$\text{C}_{118.5}\text{H}_{136.5}\text{Cd}_{12}\text{N}_{15.5}\text{O}_{65.5}$	$\text{C}_{19}\text{H}_{22}\text{CdN}_4\text{O}_8$
<i>M</i>	464.69	4174.73	546.81
<i>T</i> (K)	173(2)	150(2)	150(2)
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.2040(1)	10.2409(7)	7.5670(2)
<i>b</i> (Å)	14.1920(2)	19.6102(14)	16.1280(5)
<i>c</i> (Å)	18.1270(2)	37.787(3)	17.9040(5)
α (°)	90	89.025(1)	90
β (°)	90	89.263(1)	95.516(2)
γ (°)	90	76.471(1)	90
<i>U</i> (Å ³)	2367.81(5)	7376.7(9)	2174.90(11)
<i>Z</i>	4	2	4
μ (Mo K α) (mm ⁻¹)	0.957	1.790	1.058
Reflections collected	45854	57031	9593
Independent reflections	5402	25905	4969
<i>R</i> _{int}	0.0520	0.1009	0.0885
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0456, 0.1383	0.0855, 0.1900	0.0492, 0.0822
<i>R</i> indices (all data)	0.0485, 0.1411	0.1340, 0.2120	0.1233, 0.0975
Largest difference in peak and hole (e Å ⁻³)	1.233, -0.588	2.258, -1.886	0.950, -0.589

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