



Two new metal–organic framework structures derived from terephthalate and linear trimetallic zinc building units



Nathalie Saffon-Merceron^a, Marie-Claire Barthélémy^c, Christophe Laurent^c, Isabelle Fabing^b, Pascal Hoffmann^{b,*}, Alain Vigroux^{b,*}

^a Université de Toulouse, UPS, Institut de Chimie de Toulouse, ICT FR 2599, 118 route de Narbonne, F-31062 Toulouse, France

^b Université de Toulouse, UPS, LSPCMIB, UMR CNRS 5068, 118 route de Narbonne, F-31062 Toulouse, France

^c Université de Toulouse, Institut Carnot CIRIMAT, UMR CNRS UPS INP 5085, 118 route de Narbonne, F-31062 Toulouse, France

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ABSTRACT

Two new zinc-terephthalate MOFs, (H₂NEt₂)[Zn₃(BDC)₃(HCO₂)₂]-1.5DEF (**1**) and Zn₄(BDC)₃(HCO₂)₂(DEF)₄ (**2**), based on trinuclear zinc secondary building units have been solvothermally synthesized from the well-studied MOF-5 system Zn–H₂BDC–DEF (H₂BDC = 1,4-benzenedicarboxylic acid or terephthalic acid; DEF = *N,N*-diethylformamide). It is shown that adding small amounts of formic acid to this system has a great influence on the formation of 3D networks based upon trimetallic zinc building units Zn₃(O₂CR)₆. The structures of **1** and **2** comprise stacked 3⁰ tessellated 2D zinc-terephthalate layers which are linked into 3D frameworks either by bridging formate monoanions (**1**) or by *in situ* generated neutral bridging units Zn(HCO₂)₂(DEF)₄ (**2**). Flowing supercritical-CO₂ activation of **1** led to a partially (~80%) desolvated and probably collapsed structure (**1-SC**) with a measured BET (Brunauer–Emmett–Teller) surface area of 38 m² g⁻¹.

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1. Introduction

Metal–organic frameworks (MOFs) represent a new class of crystalline materials that have attracted considerable interest during the last decade [1–3]. This is largely a result of their potential for porosity, and their high degree of tunability and structural diversity due to the hybrid nature of their building units (metal ions and organic linkers). In principle, the proper selection of inorganic building blocks as nodes and organic ligands as linkers should offer the possibility for designing tailor-made materials for a wide range of applications including gas storage [4], separation processes [5], catalysis [6,7], chemical sensing [8], and drug delivery [9,10]. However, in practice, successfully obtaining tailor-made solids with the desired structures and properties remains a challenging issue for chemists as spectacular changes in structure often arise from subtle differences in experimental conditions.

The synthesis of MOFs is frequently performed by solvothermal methods, i.e., by heating a mixture of organic linker and metal salt in a system solvent that usually contains *N,N*-diethylformamide (DEF) or *N,N*-dimethylformamide (DMF). These conceptually

simple methods often yield crystals suitable for single crystal X-ray analysis, but are in general very sensitive to small changes in the reaction parameters leading to reproducibility problems and discrepancies in the resulting structures. This is particularly true for the well-studied Zn–H₂BDC–DEF reaction system (H₂BDC = 1,4-benzenedicarboxylic acid also referred to as terephthalic acid) which is very sensitive to the water content of the solvent. Indeed, the now-iconic MOF-5 structure, Zn₄O(BDC)₃, can be prepared from Zn(NO₃)₂·6H₂O and H₂BDC under solvothermal conditions in DEF [11], but other compounds such as Zn₃(OH)₂(BDC)₂·2DEF [12] (referred to as MOF-69c) [13] and (H₂NEt₂)₂[Zn₃(BDC)₄]-2.5DEF [14] emerge predominantly from this system depending on the water content and/or the degree of hydrolysis that has occurred in the DEF sample used.

Specifically, Rosi et al. [13] established that MOF-69c can reliably be prepared by adding additional water to the MOF-5 starting mixture, while Burrows et al. [14] demonstrated that (H₂NEt₂)₂[Zn₃(BDC)₄] arises either in partially hydrolyzed DEF or in fresh DEF to which diethylammonium chloride had been added, suggesting that the diethylammonium counter-cation plays a templating role in the crystallisation of this anionic network. In the absence of added H₂NEt₂⁺Cl⁻, the incorporated diethylammonium ion clearly results from the hydrolysis reaction of DEF (Eq. (1)). It is indeed well known that solvent systems containing formamide

* Corresponding authors. Tel.: +33 561 556 297; fax: +33 561 556 011.

E-mail addresses: pascal.hoffmann@univ-tlse3.fr (P. Hoffmann), vigroux@chimie.ups-tlse.fr (A. Vigroux).

functionality like DMF or DEF may undergo a significant degree of hydrolysis under solvothermal conditions depending on the initial water content.



We are interested to explore further the large structural versatility of the extensively studied Zn–H₂BDC–DEF system for the purpose of discovering new zinc-terephthalate MOF structures. As frequently as DEF or DMF hydrolysis may be concerned, we are aware of no report describing Zn–BDC MOFs in which the formate anion is incorporated in the resulting zinc-terephthalate framework structure [15]. This is somewhat surprising as formate often serves as an anionic bridging ligand in the construction of MOFs [16]. In this study, we report how the presence of a small amount of added formic acid in the solvent DEF is crucial in influencing the production of two new Zn–BDC MOF structures containing the formate anion.

2. Experimental

2.1. General

All chemicals and DEF used in the syntheses were of analytical grade and used as received without further purification. Unless otherwise stated, DEF was obtained from Sigma–Aldrich. Single-crystal X-ray diffraction were performed on a Bruker-AXS kappa APEX II Quazar (2) diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 193(2) K. Powder X-ray diffraction patterns were collected on a XPert Pro (Theta–Theta mode) Panalytical diffractometer with λ (Cu K α 1, K α 2) = 1.54059, 1.54439 \AA .

2.2. Synthesis of (H₂NEt₂)[Zn₃(BDC)₃(HCO₂)]·1.5DEF (1)

H₂BDC (99.7 mg, 0.6 mmol) and Zn(NO₃)₂·6H₂O (446 mg, 1.5 mmol) were dissolved in 15 mL of DEF containing 277 μL of HCO₂H and sealed in a glass vial. The vial was heated to 110 °C for 18 h. Colorless crystals of the product were formed. After cooling to room temperature, the crystals were collected by filtration and washed with DEF several times. Yield: 96 mg (50% based on H₂BDC). Elemental analysis. C_{36.5}H_{41.5}N_{2.5}O_{15.5}Zn₃: found (calc.) C 45.78% (45.69%), H 4.53% (4.36%), N 3.85% (3.65%).

2.3. Crystal data for 1

Space group *P*21/*c*, monoclinic, $a = 12.4391(3) \text{ \AA}$, $b = 20.6318(5) \text{ \AA}$, $c = 17.7916(4) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 91.0980(10)^\circ$, $V = 4565.22(19) \text{ \AA}^3$, $Z = 4$, 61943 reflections measured, 11261 independent reflections ($R_{\text{int}} = 0.0427$). The final R_1 value was 0.0732 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.1769 (all data). The goodness-of-fit on F^2 was 1.276. Largest difference in peak and hole 1.253 and $-1.084 \text{ e \AA}^{-3}$. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program.

2.4. Synthesis of Zn₄(BDC)₃(HCO₂)₂(DEF)₄ (2)

H₂BDC (13.3 mg, 0.08 mmol), Zn(OAc)₂·2H₂O (30.7 mg, 0.14 mmol) and Zn(NO₃)₂·6H₂O (17.8 mg, 0.06 mmol) were dissolved in 2 mL of DEF containing 18.5 μL of HCO₂H and sealed in a glass vial. The vial was heated to 110 °C for 18 h. Small colorless diamond-shaped crystals of the product were formed. After cooling to room temperature, the crystals were collected by filtration and washed with DEF several times. The crystals remain stable over time in the mother liquor or after drying at room temperature. Crystallization experiments were conducted with molar ratios Zn(OAc)₂·2H₂O/Zn(NO₃)₂·6H₂O of 1/1 and 7/3. In both cases, the

new phase **2** could be obtained, from nominally identical reactions, either in seemingly pure form, as determined from X-ray diffraction analyses of several representative single crystals picked from the bulk, or contaminated with compound **1** in a range of ratios.

2.5. Crystal data for 2

Space group *P*21/*c*, monoclinic, $a = 15.2170(10) \text{ \AA}$, $b = 9.8509(5) \text{ \AA}$, $c = 18.2741(13) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 102.036(4)^\circ$, $V = 2679.1(3) \text{ \AA}^3$, $Z = 4$, 20978 reflections measured, 5424 independent reflections ($R_{\text{int}} = 0.0971$). The final R_1 value was 0.0456 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.0932 (all data). The goodness-of-fit on F^2 was 0.968. Largest difference in peak and hole 0.432 and $-0.526 \text{ e \AA}^{-3}$. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program.

2.6. Flowing SC-CO₂ activation

As synthesized DEF-solvated crystals of **1** (84.5 mg) were transferred into a 3.2 mm i.d \times 30 mm stainless steel column. The column was then connected to a supercritical CO₂ system (SFC-PICLAB Analytic apparatus equipped with HPLC K-501 Knauer pumps) with a back pressure regulator set at 150 bar. The CO₂ was pumped at a flow rate of 4 mL/min and the column was heated at 40 °C through a column heater. Detection of DEF was achieved with a UV–Vis monitor (Smartline UV 2600 Knauer detector) set at 210 nm. Under such conditions, a flowing time of 6.5 h was required to get zero detection. Thus, after flowing of CO₂ for 6.5 h, the flow was stopped and supercritical CO₂ in the column was gradually released to atmosphere. The activated sample (**1-SC**) in the column was transferred to a sorption cell in a N₂ glove box and the surface area was measured. Elemental analysis for **1-SC**: found C 41.53%, H 3.25%, N 2.18% in agreement with the chemical formula (H₂NEt₂)[Zn₃(BDC)₃(HCO₂)]·0.3DEF·2H₂O (C_{30.5}H_{32.3}·N_{1.3}O_{16.3}Zn₃, calc. C 41.91%, H 3.72%, N 2.08%).

3. Results and discussion

When Zn(NO₃)₂·6H₂O and H₂BDC were heated in DEF at 110 °C for 18 h, colorless block-shaped crystals appeared from the solution. These were identified from single-crystal X-ray diffraction analyses as being the well-known zinc oxide terephthalate MOF-5. When Zn(NO₃)₂·6H₂O and H₂BDC were heated under the same conditions, but in DEF containing ca. 5.4% added formic acid (molar ratio Zn:H₂BDC:HCO₂H:DEF = 2.5:1:12:224), colorless block-shaped crystals were again isolated. However, in this case, single-crystal and powder X-ray diffraction (PXRD) analyses indicated that a new framework **1** of formula (H₂NEt₂)[Zn₃(BDC)₃(HCO₂)]·1.5DEF was obtained in pure phase. It is worth noting that **1** could also be produced in pure phase without the addition of formic acid when the reaction was performed in fresh DEF recently purchased from certain suppliers.¹

The structure of **1** is based on formate anions bridging between nearly-linear trinuclear zinc carboxylate clusters Zn₃(O₂CR)₆ (the Zn–Zn–Zn angle is 160.5°). Each of these clusters is joined to six adjacent clusters through the linear terephthalate linkers which radiate at approximately 60° angles, leading to an overall 2D triangular-grid structure (Fig. 1) containing cavities large enough to include H₂NEt₂⁺ ions and DEF molecules.

The Zn₃(O₂CR)₆ secondary building units (Fig. 2) and the resulting 3⁶ tessellated layers are similar to those observed in previously reported zinc-terephthalate 2D frameworks. The Zn₃(O₂CR)₆ SBUs

¹ The use, as received, of fresh DEF recently purchased from Alfa Aesar led exclusively to compound **1** in ca. 50% yield.

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