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

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Two new zinc-terephthalate MOFs, (H₂NEt₂)[Zn₃(BDC)₃(HCO₂)]·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.

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

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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.

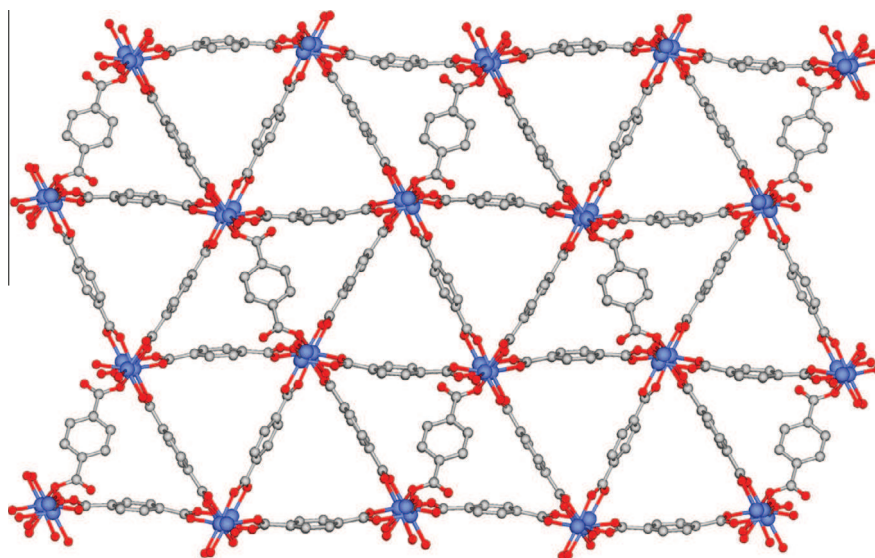


Fig. 1. The 3^d tessellated Zn₃(BDC)₃ layers present in the structure of (H₂NEt₂)[Zn₃(BDC)₃(HCO₂)]·1.5DEF (**1**). The diethylammonium cations, hydrogen atoms and DEF molecules have been omitted for clarity.

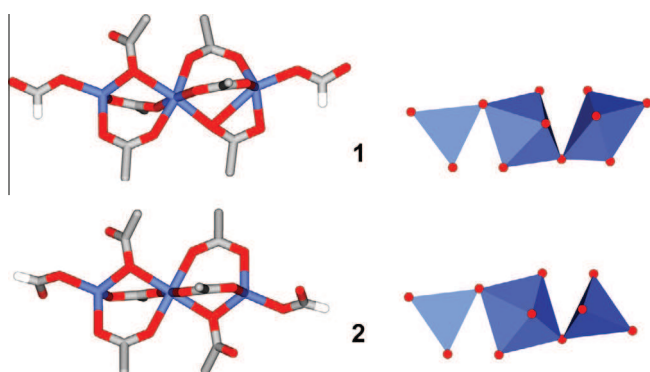


Fig. 2. The trimetallic zinc secondary building units (SBUs) involved in frameworks **1** and **2**. Hydrogen atoms, except for formate ligands, have been omitted.

of **1** consist of a single octahedrally coordinated zinc center surrounded by two peripheral tetrahedrally coordinated zinc centers. One peripheral zinc center is bound to the central zinc atom through three bridging carboxylate groups. The other peripheral zinc center is bound to the central zinc atom through two bridging

carboxylate groups and a single μ_2 -bridging carboxylate oxygen atom. Such trimeric SBUs have already been described in a number of zinc-carboxylate MOF structures [17]. However, instead of being capped by solvent molecules that act as terminal ligands, the zinc-terephthalate layers of **1** are linked into a 3D framework by bridging formate ligands that occupy a coordination site on each of the peripheral zinc centers of the trimetallic units (Fig. 3). The 3D structure of **1** is comparable with that of (H₂NEt₂)₂[Zn₃(BDC)₄] previously described by Burrows [14] and Stock [18] in which the zinc-terephthalate sheets are linked by terephthalate dianions instead of formate monoanions.

Thermogravimetric analysis (TGA) performed on a sample of as-synthesized **1** showed a first weight loss of 29.5% in multiple, not well separated steps in the range 60–275 °C (Fig. S3). This weight loss can be assigned to the removal of 1.5DEF and one diethylammonium formate per formula unit (calc: 28.2%). The lack of well defined steps between 60 and 275 °C suggests that hydrogen-bonded DEF molecules may be crucial to the stability of **1**. One method to confirm the crystallographic aperture of **1** (Fig. 1) is to measure the BET (Brunauer–Emmett–Teller) surface area from a desolvated sample. For activating **1**, we therefore opted for the recently reported flowing supercritical CO₂ (SC-CO₂) procedure [19] which is often the only possibility to desolvate fragile

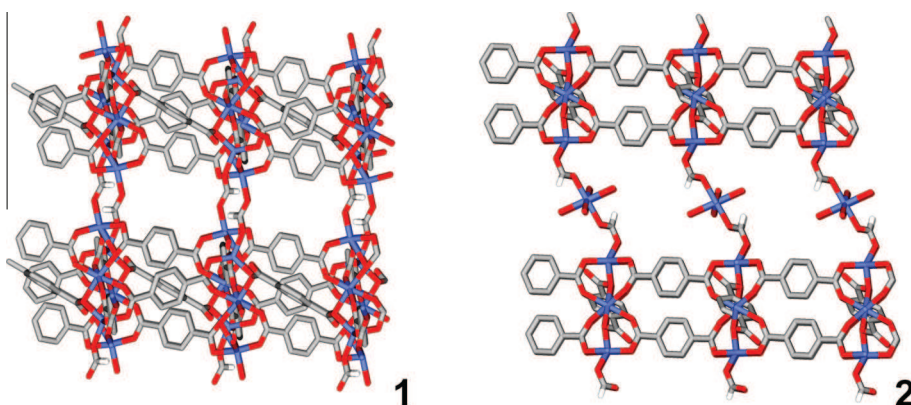


Fig. 3. Inter-layer linkages involved in frameworks **1** and **2**. The diethylammonium cations and DEF molecules have been omitted in **1**. In structure **2**, only the oxygen atoms of coordinated DEF molecules are shown. Hydrogen atoms, except for formate ligands, have been omitted in both structures.

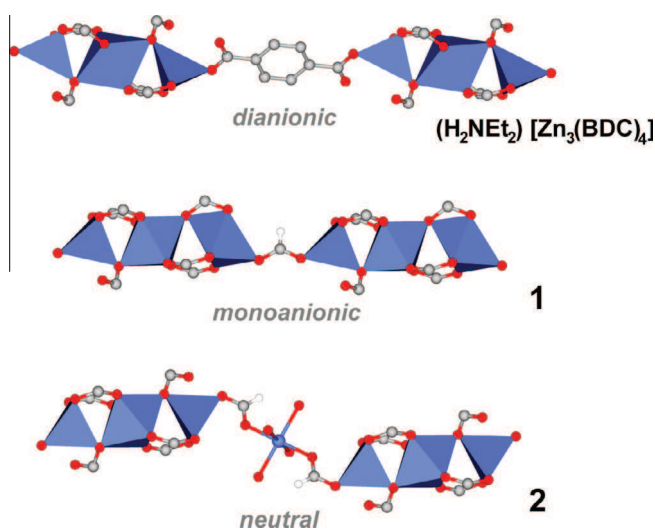


Fig. 4. Dianionic $[\text{BDC}^{2-}]$ [14,18], monoanionic $[\text{HCO}_2^-]$, and neutral $[\text{Zn}(\text{HCO}_2)_2(\text{DEF})_4]$ bridging units involved in the trinuclear $\text{Zn}_3(\text{O}_2\text{CR})_6$ -based zinc-terephthalate 3D frameworks. Only the oxygen atoms of coordinated DEF molecules are shown in the bridging unit of **2**.

frameworks without network transformation [20]. However, as suggested by elemental analysis and TGA, activation of **1** by flowing SC- CO_2 affords only a partially (~80%) desolvated sample, referred to as **1-SC**, which exhibits a negligible BET surface area of $38 \text{ m}^2 \text{ g}^{-1}$ (Fig. S4), suggesting a structural collapse of the network even upon incomplete DEF removal.

The sensitivity of the solvothermal reaction to added formic acid was also investigated as a function of the starting zinc(II) source. Different zinc(II) salts have been successfully used in the preparation of MOF-5 [21,22]. In particular, it has been reported that heating a DEF solution of zinc acetate dihydrate and H_2BDC at 110°C yields pure MOF-5 in microcrystalline form [22]. We have repeated this MOF-5 synthesis and confirmed the formation of MOF-5.² However, when the latter synthesis is conducted in the presence of ca. $\geq 5.4\%$ added formic acid, compound **1** was again identified by PXRD as the unique crystalline product. Interestingly, a slightly lower percentage (ca. 2.7%) of added formic acid (molar ratio $\text{Zn}:\text{H}_2\text{BDC}:\text{HCO}_2\text{H}:\text{DEF} = 2.5:1:6:224$) led, under otherwise identical conditions, to the appearance of an additional phase **2**, identified by PXRD as distinct from MOF-5. By employing a mixture of zinc acetate and zinc nitrate at various molar ratios while keeping the total amount of Zn^{2+} ions constant at the concentration used in the background reaction, we were able, in the presence of ca. 2.7% added formic acid, to produce suitable single crystals of **2** for X-ray structural determination.

The crystal structure of **2** reveals a framework of composition $\text{Zn}_4(\text{BDC})_3(\text{HCO}_2)_2(\text{DEF})_4$. As **1** and $(\text{H}_2\text{NEt}_2)_2[\text{Zn}_3(\text{BDC})_4]$, **2** is a 3D network built from the trinuclear $\text{Zn}_3(\text{O}_2\text{CR})_6$ SBU. The overall architecture of **2**, however, differs from that of **1** and $(\text{H}_2\text{NEt}_2)_2[\text{Zn}_3(\text{BDC})_4]$ in that the 3^6 tessellated zinc-terephthalate 2D sheets are linked to each other by an unusual, neutral bridging unit which consists of an octahedrally coordinated zinc center with two axially bonded bridging formates and four apically bonded terminal DEF molecules (Fig. 4). Thus, in contrast to the cases of **1** and $(\text{H}_2\text{NEt}_2)_2[\text{Zn}_3(\text{BDC})_4]$, **2** is a neutral metal carboxylate framework whose production does not require the presence of the diethylammonium cation. Its formation demonstrates that extended 3D networks may be produced by the involvement of *in situ* generated

bridging units of the type $\text{Zn}(\text{O}_2\text{CR})_2$. The latter units have the clear advantage of being capable of linking perforated layers through robust metal/carboxylate linkages without requiring the presence of counter-cations that would otherwise occupy the space available in any channels obtained in the 3D structure.

4. Conclusion

In summary, two new zinc-terephthalate MOFs **1** and **2** based on the trinuclear $\text{Zn}_3(\text{O}_2\text{CR})_6$ SBU have been solvothermally synthesized from the well-studied MOF-5 system $\text{Zn}-\text{H}_2\text{BDC}-\text{DEF}$. We have shown that a small amount of added formic acid is crucially important in influencing MOF phase selection within this system. In both compounds the formate ion, either alone as in **1**, or coordinated to zinc as in **2**, plays a significant role in linking, into 3D networks, the 2D-layered structures which result from the trinuclear $\text{Zn}_3(\text{O}_2\text{CR})_6$ SBUs. Studies are ongoing to determine the general scope and importance of these findings in the discovery of new MOF structures derived from this and related systems. Activation (flowing supercritical- CO_2) and N_2 adsorption studies show that **1** cannot be fully desolvated without collapse of its 3D-framework suggesting that hydrogen-bonded DEF molecules may be crucial for maintaining the structural integrity of this compound.

Appendix A. Supplementary data

Powder X-ray diffraction patterns, FTIR spectra, TGA, N_2 adsorption isotherm and further crystallographic data. CCDC 948871 and 948872 contains the supplementary crystallographic data for **1** and **2** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jica.2014.11.004>.

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² While capable of yielding pure MOF-5, in our case this reaction also sometimes produced a small amount of $(\text{H}_2\text{NEt}_2)_2[\text{Zn}_3(\text{BDC})_4]$ as observed by PXRD.

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