Letter

Synthesis and characterization of a new layered compound of trimesic acid†

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The hydrothermal reaction between 1,3,5-benzenetricarboxylic acid (trimesic acid, H_3BTC) and 1,2-bis(4-pyridyl)ethane (BPE), in the presence of cadmium(II) ions, results in the formation of a novel layered salt, in which the organic cations and water molecules occupy spaces between anionic layers of trimesic acid.

The ultimate goal of crystal engineering is to design and predict the structure and properties of supramolecular frameworks, based only on knowledge of the intermolecular interactions of their basic building blocks.[1] To this end, synthons based on both weak and strong hydrogen bonds have been extensively used, leading to the synthesis of stable open organic frameworks with nonlinear optical properties,[2] and with potential applications in homogeneous and heterogeneous separations, reversible guest exchange[3] and selective organic catalysis.[4]

On account of its robustness and the presence of three exodentate carboxylic groups, trimesic acid is often used in crystal engineering.[5] The compound self-assembles into an infinite interpenetrated framework with a honeycomb motif, through carboxylic acid dimers, with the graph set $R_2^2(8)$.[6] A non-interpenetrated framework can also be synthesized through the inclusion of neutral guests.[7] Extended frameworks of trimesic acid through conjugation with neutral guests[8,9] or organic cations[10,11] have also been found, but large voids usually imply interpenetration to stabilize the structure.[5] Perforated salt tapes of trimesic acid residues (H_xBTC, $x = 1$, 2 or 3) and amines commonly contain weak C–H···O hydrogen bonds, which confer additional robustness to the structure and create new topology.[12,13] In these cases, the organic cations are included in the H_xBTC sheets, directly connected by strong N–H···O and O–H···N hydrogen bonds. We report herein the hydrothermal synthesis and structural characterization of a novel salt, where H_xBTC forms negatively charged sheets, with bipyridinium cations and solvent molecules occupying interlayer spaces, but not directly included in the trimesic acid layers.

Single-crystal X-ray analysis reveals an asymmetric unit containing four trimesic acid residues, one BPE cation ($BPEH_2^{2+}$), and one solvent molecule, corresponding to the empirical formula $(H_2BTC)_2(BPEH_2)(H_3BTC)_2 \cdot H_2O$, **1**. Surprisingly, in **1**, trimesic acid does not induce its typical extended honeycomb topology.[8,14] The structure is layered [Fig. 1(a)] and assembled by both strong and weak hydrogen bonds.

Each H_xBTC sheet is formed by parallel linking of tapes through strong O–H···O$^-$ hydrogen bonds, as described by Gilli *et al.*,[15] with O···O distances of 2.450(3) and 2.481(3) Å [Fig. 1(b)]. The tapes show alternation between two motifs for the carboxylate groups (see ESI). In the first motif, they adopt the *syn–syn* conformation,[16] with the average O···O distance being 2.62 Å, in good agreement with reported results.[17] In the second conformation, the two trimesic acid residues inside each tape are further connected by two O–H···O hydrogen bonds, with *syn*(donor)–*anti*(acceptor) conformations and an average O···O distance of 2.66 Å, within the range expected for tertiary carboxylates.[18] The robustness of this motif may be attributed to the presence of two weak C–H···O hydrogen bonds with the average C···O distance being 3.24 Å [Fig. 1(b)]. Similar behaviour has been reported for $C_{13}H_{15}N_2^+ \cdot C_9H_5O_6^-$.[12] In that structure, however, the amine itself participates in the layered hydrogen bond network. To the best of our knowledge, two-dimensional self-assembly with anionic H_xBTC residues only, as observed for **1**, has not been reported before.

Compound **1** has double layers, formed by H_xBTC sheets connected through $BPEH_2^{2+}$ cations and water molecules. The $BPEH_2^{2+}$ cations with *anti* conformation[19] are perpendicular to the layers [Fig. 1(a–c)], and neutralize the excess of two electrons per H_xBTC asymmetric unit. One of the pyridyl nitrogens in $BPEH_2^{2+}$ is directly connected to one H_xBTC sheet through two N$^+$–H···O$^-$ bonds in which the donor group adopts a bifurcated geometry. Similar bifurcated C–H···O interactions link the same pyridyl ring to the second sheet in the double layer, giving rise to a centrosymmetric hexameric motif (Fig. 2). The other pyridyl nitrogen of the same $BPEH_2^{2+}$ cation is connected *via* an N$^+$–H···O hydrogen bond to a water molecule (Fig. 2). In turn, this water molecule acts as a bridge, forming strong hydrogen bonds with O(3) and O(4) in different H_xBTC sheets (Fig. 2). In this manner, a second centrosymmetric motif is generated within the double layer. Adjacent double layers are stacked in an offset coplanar geometry and additional interlayer C–H···O contacts exist between H_xBTC sheets and the $BPEH_2^{2+}$ cations.

The $BPEH_2^{2+}$ cations and water molecules are periodically present in only half the trimesic acid interlayer spaces (separation *ca.* 3 Å), arranging themselves into layers separated by *ca.* 10 Å [Fig. 1(a)]. These structural features are directly observed in the reflectance PRXD pattern, which shows only two major reflections, with *d*-spacings of 10.16 and 3.01 Å, attributable to preferential orientation of the crystallites when pressed in the horizontal position.[20] However, this was not observed for **1** randomly distributed in the sample holder, as similar PXRD patterns were obtained in both the reflectance and transmission modes. These latter experimental patterns are in good agreement with theoretical calculations based on single-crystal X-ray diffraction data.

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† Electronic supplementary information (ESI) available: top view of the H_xBTC anionic network (Fig. S1) and detailed hydrogen bond graph sets present in the interactions linking the two H_xBTC sheets within a double layer (Fig. S2). See http://www.rsc.org/suppdata/nj/b1/b108083k/

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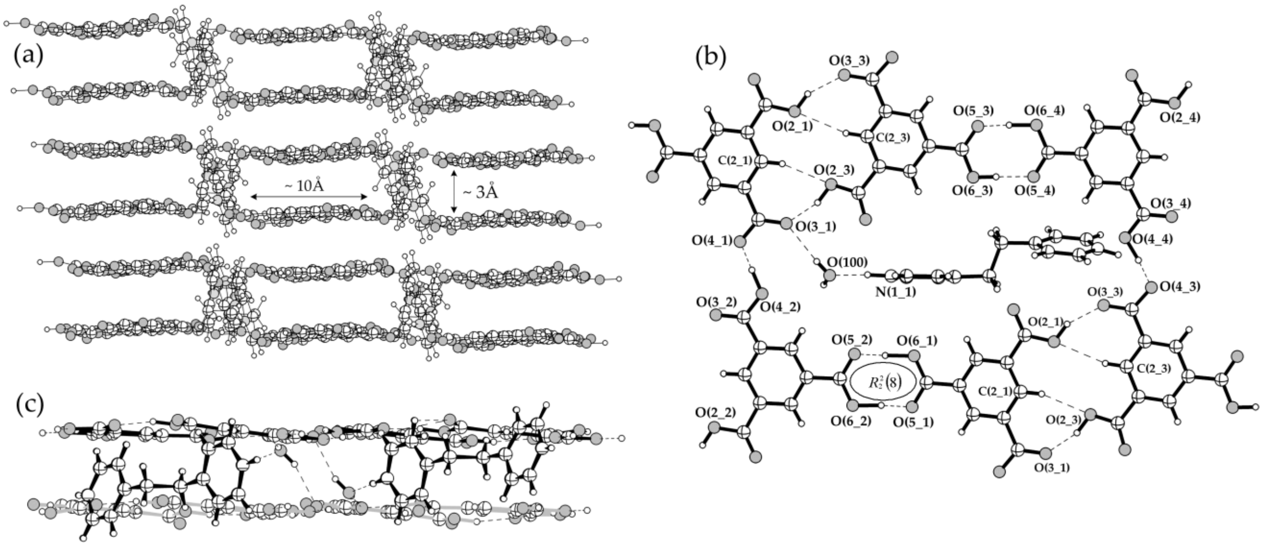

Fig. 1 (a) Perspective view of **1** showing the double layer packing. (b) Top view of the H_xBTC anionic network. Hydrogen bonds within layers are represented by dotted lines. Distances between donors and acceptors: O(6_1)···O(5_2) = 2.628(3); O(6_2)···O(5_1) = 2.594(3); O(2_1)···O(3_3) = 2.717(3); O(2_3)···O(3_1) = 2.592(3); O(6_4)···O(5_3) = 2.583(3); O(6_3)···O(5_4) = 2.676(3); O(4_2)···O(4_1) = 2.481(3); O(2_4)···O(3_2) = 2.648(3); O(2_2)···O(3_4) = 2.666(3); O(4_4)···O(4_3) = 2.450(3); N(1_1)···O(100) = 2.658(3) Å. (c) $BPEH_2^{2+}$ are perpendicular to the layers and H_2O molecules are slightly above them, both connecting the H_xBTC sheets through hydrogen bonding.

We note that syntheses under the same conditions but in the absence of the cadmium(II) ions, or under ambient conditions, did not result in the formation of **1**, suggesting that the presence of these ions is important to obtain the structure. We have recently synthesized the compound **1** in the presence of Sn^{2+} and Zn^{2+} cations, although the role of the metal ions in the system remains unclear. In addition, $^{13}C\{^1H\}$ CP/MAS NMR confirms the presence of BTC and BPE units in the structure. Detailed solid-state NMR studies focusing on the dynamics of the structure are in progress. Infrared spectro-

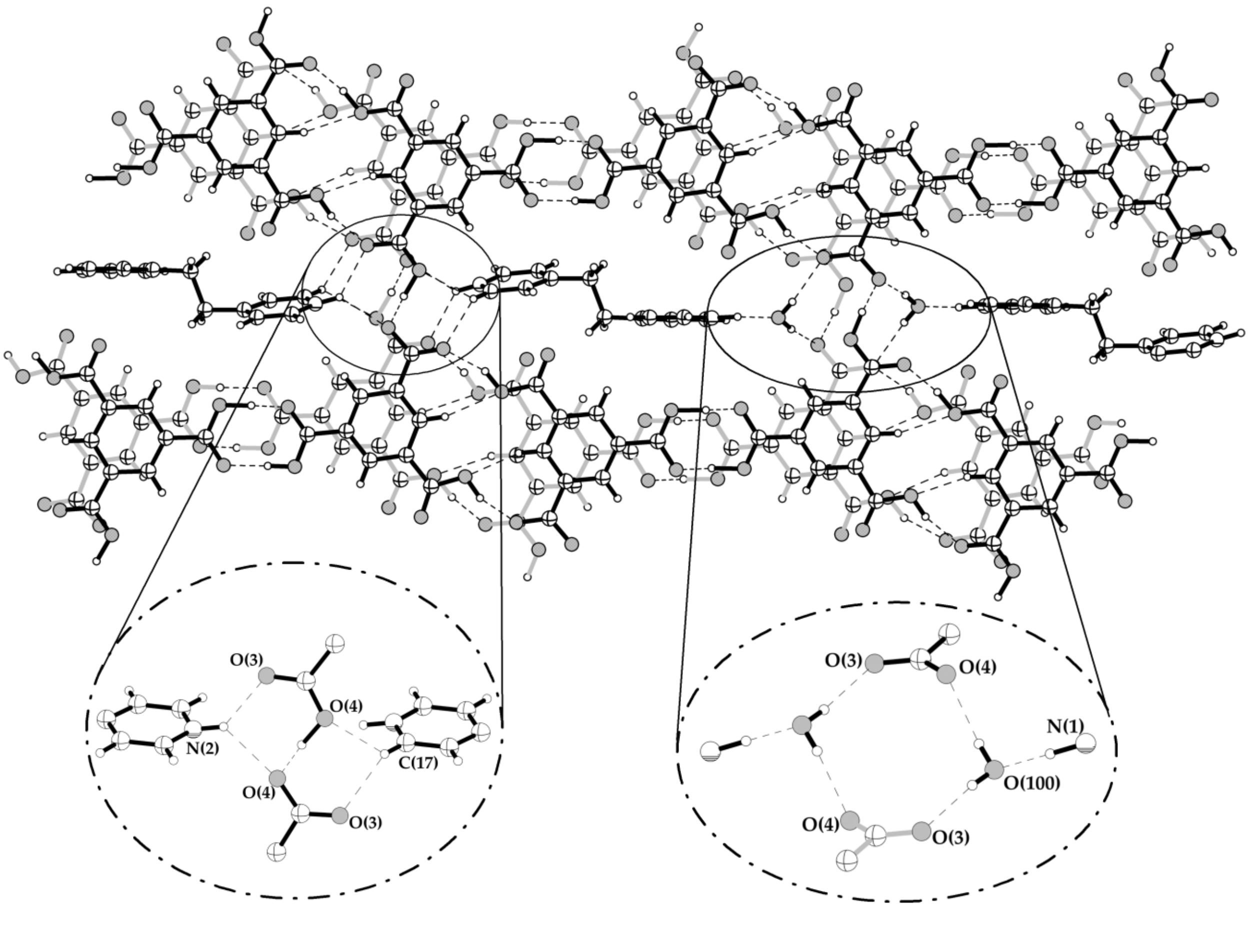

Fig. 2 Top view of a section from a double layer (black carbon network corresponds to the top layer; the grey network corresponds to the one below). Interactions linking the two H_xBTC sheets within a double layer are highlighted. Distances between donors and acceptors:

metry confirms the presence of the hydrogen bond network. Thermogravimetric analysis shows the release of one water molecule per asymmetric unit in the 200–250 °C temperature range, consistent with the crystal structure of **1**.

A new hydrogen bond topology for trimesic acid has been found in the layered salt of this compound with BPE, synthesised under hydrothermal conditions. Several types of weak and strong hydrogen bonds are found in the structure. Metal ions seem to play a structure-directing role in the overall process, although the origin of this effect is unclear.

Experimental

All chemicals were used as purchased from Aldrich without further purification. Elemental analysis was performed on an Exeter Analytical CE-440 elemental analyser. Thermogravimetric measurements were carried out using a Polymer Laboratories TGA 1500 (heating rate 10 °C min^{-1}). The FTIR spectrum was collected from KBr pellets on a Mattson Genesis II FTIR spectrometer. $^{13}C\{^{1}H\}$ CP/MAS NMR spectra were recorded at 9.4 T (100 MHz for ^{13}C and 399.89 MHz for ^{1}H) using a Chemagnetics CMX-400 spectrometer with zirconia rotors 4 mm in diameter spun in nitrogen at 8.0 kHz. ^{13}C chemical shifts are quoted in ppm with respect to TMS.

Synthesis

To a solution of $Cd(NO_3)_2\cdot 4H_2O$ (0.934 g, 3.03 mmol) in water (18.0 g, 1.0 mol), BPE (0.180 g, 0.977 mmol) was added and the mixture was stirred for 15 min. H_3BTC was added (2.03 g, 9.64 mmol) and the mixture stirred thoroughly for 1 h at ambient temperature. The final suspension was placed inside a Teflon-lined Parr autoclave (8 cm^3, filling rate 70%). The reaction was carried out at 145 °C under autogenous pressure for 48 h. The autoclave was removed and left at ambient temperature for 12 h before opening. A white crystalline product was found and crystals suitable for single-crystal X-ray diffraction were separated. The powder was washed with water and ethanol, and air-dried at 70 °C. Selected FTIR data (cm^{-1}): ν(OH) 3108m, 2548m, 2349w, 2159w, 1894w, ν(C=O) 1734m, 1716s, 1677s, 1636m, 1613m, 1554m, 1506w, 1437m, δ(OH) 1395m, 1329m, ν(C–O) 1229s, γ(OH) 834m, δ(C=O) 747m, γ(C=O) 678m, 530m. $^{13}C\{^{1}H\}$ CP/MAS (ppm): 173.0 (H_3BTC), 171.7 (H_3BTC), 166.9 (H_3BTC), 159.1 (BPE), 155.6 (BPE), 142.0 (H_3BTC), 136.0 (H_3BTC), 130.2 (H_3BTC), 123.7 (BPE), 29.5 (BPE). TGA: 200–250 °C 1.72%; 250–600 °C 82.9%. Found: C 54.44, H 3.64, N 2.63%. Calculated: C 55.29, H 3.67, N 2.69%.

X-Ray crystallography

Powder X-ray diffraction patterns were measured either on a STOE STADI-P high resolution diffractometer with Ge(111)-monochromated Cu-Kα radiation ($\lambda = 1.5406$ Å) and a position-sensitive detector covering a 6° 2θ angle (40 kV, 40 mA), or a Philips 1720 powder diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å; 40 kV, 40 mA). Single-crystal data were collected on a Nonius KappaCCD diffractometer with Mo-Kα monochromated radiation ($\lambda = 0.7107$ Å). The structure was solved by direct methods and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms.[21,22] Multi-scan absorption corrections were applied.[23] Hydrogen atoms bound to carbon were placed geometrically and refined using a riding model with an isotropic displacement parameter fixed at 1.2 times U_{eq} for the atom to which they are attached. All hydrogens bound to N and O were located in difference Fourier maps and refined with a single isotropic displacement parameter common to all of these hydrogens. Bond distance restraints were not applied, except for H(100) and H(101), associated with the water molecule, for which the O–H distances were restrained to be 0.84(1) Å. Note that this treatment of the hydrogen atoms is intended to provide the best fit to the X-ray data and does not necessarily facilitate absolute discrimination of the hydrogen atom positions. While it can be said, for example, that H(4O) lies between O(4_2) and O(4_1), its absolute position is not definitive.

Crystal data for **1**: $C_{48}H_{38}N_2O_{25}$, $M = 1042.80$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 12.4048(8)$, $b = 12.9345(7)$, $c = 15.5773(10)$ Å, $\alpha = 93.282(3)$, $\beta = 107.930(3)$, $\gamma = 106.375(3)°$, $V = 2252.9(2)$ Å^3, Density (calculated) = 1.537 g cm^{-3}, $T = 180(2)$ K, μ(Mo-Kα) = 0.127 mm^{-1}, $\theta_{min} = 3.52$ and $\theta_{max} = 24.97°$. Data were collected from colourless crystal plates, with dimensions $0.42 \times 0.12 \times 0.02$ mm. From the 16999 reflections collected, 7712 were independent ($R_{int} = 0.0757$). Final $R1 = 0.0584$ [$I > 2\sigma(I)$] from 4364 reflections, and $wR2 = 0.1557$ (all data).

CCDC reference number 176116. See http://www.rsc.org/suppdata/nj/b1/b108083k/ for crystallographic data in CIF or other electronic format.

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