Hydrothermal synthesis and X-ray structural characterisation of calcium benzene-1,3,5-tricarboxylate

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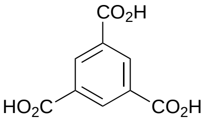
Benzene-1,3,5-tricarboxylic acid (H_3btc) forms a calcium salt of stoichiometry Ca(hbtc)·$2H_2O$ which possesses an infinite layered structure.

The synthesis of novel crystal structures from polar tectons by hydrogen-bond directed self-assembly and metal-ion or ligand-directed assembly has allowed the preparation of networked microporous materials with potential applications as absorbents,[1] ion exchangers,[2] protonic conductors[3] and catalysts. An inherent difficulty in the formation of microporous materials by the hydrogen-bond controlled self-assembly of tectons[4] such as benzene-1,3,5-tricarboxylic acid (H_3btc) **1** or adamantanetetracarboxylic acid (H_4atc) **2** is the tendency for packing to minimise voids and maximise van der Waals contacts in the crystal lattice.[5] Infinite lattice networks of H_3btc[6] and H_4atc stabilised by the hydrogen-bond dimers **3** would possess large micropores but in practice the dimeric hydrogen bonding is too weak to stabilise these open frameworks and a different condensed crystal structure forms. Recently Yaghi *et al.* reported a solution to this problem by preparing divalent metal ion (Co, Ni, Zn) salts of H_3btc which possess a stable networked structure with hydrated divalent metal ions forming strong ionic bonds between the rigid btc tectons.[7] Heating dehydrates the metal ions leaving micropores in the crystal lattice with the metal ions lining the channels.

The work described here is part of an investigation into the hydrothermal synthesis and structural characterisation of the alkaline-earth metal (Ca, Sr, Ba) salts of benzene-1,3,5-tricarboxylic acid with the aim of producing stable microporous materials.† Heating H_3btc with calcium acetate in water in a sealed bomb to 180 °C followed by slow cooling gave colourless crystals whose structure was solved by X-ray analysis.‡ The compound did not have the expected 1 : 2 btc : Ca ratio but instead gave crystals of formula Ca(hbtc)·$2H_2O$.† The IR spectrum also showed a stretch at 1695 cm^{-1} indicative of an aromatic carboxylic acid.



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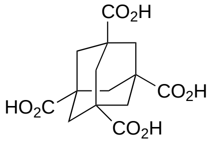

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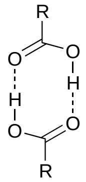

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The structure consists of infinite two-dimensional layers of hbtc dianions alternating with layers of Ca and water molecules in the *c*-axis direction. The proton H(5) bonded to O(5) of one of the carboxylate groups forms a strong hydrogen bond O(5)–H(5)···O(35) linking the hbtc anions in chains perpendicular to (1,1,0) (Fig. 1). The layers of hbtc anions are composed of such chains packed side-by-side and related in pairs and therfore inverted in orientation by crystallographic centres of symmetry as are the layers themselves. As a result the O(1)–C(7)–O(2) carboxylate groups of the anions in a particular hydrogen-bonded chain lie on one side of the layer while the same carboxylate groups of the neighbouring chains lie on the other side of the layer.

In the layers of Ca and water molecules lying between the layers of hbtc anions the Ca cations occur in centrosymmetrically related pairs. Ca is irregularly coordinated by eight oxygens with Ca–O distances in the range 2.4121(18)–2.5701(16) Å (Fig. 2). Seven of these contacts arise from interaction of Ca with five distinct carboxylate anions. Three anions operate as monodentate ligands generating the Ca contacts with O(14), O(23) and O(62). The last two anions coordinate in a bidentate fashion to generate pairs of contacts with Ca [O(1) and O(2) and O(31) and O(41) respectively]. The coordination of Ca is completed by a contact with one of the water molecules [Ca–O(1w) 2.4199(20) Å]. A feature of the Ca coordination is the presence of the Ca–O(14) and Ca–O(23) contacts which involve distinct carboxylate anions which are in the same layer but related by a cell translation along the *a* axis. The contacts then produce linked pairs of chains interleaved with symmetry related and differently oriented linked chain pairs.

The molecular formula and the asymmetric unit both contain two water molecules. The presence of water was shown by the IR spectrum which showed OH stretches at 3542 and 3342 cm^{-1}. One of these [O(1w), H(11w), H(12w)] is not only involved in the coordination of Ca but also forms hydrogen bonds as O(1w)–H(11w)···O(46) to a carboxylate oxygen and

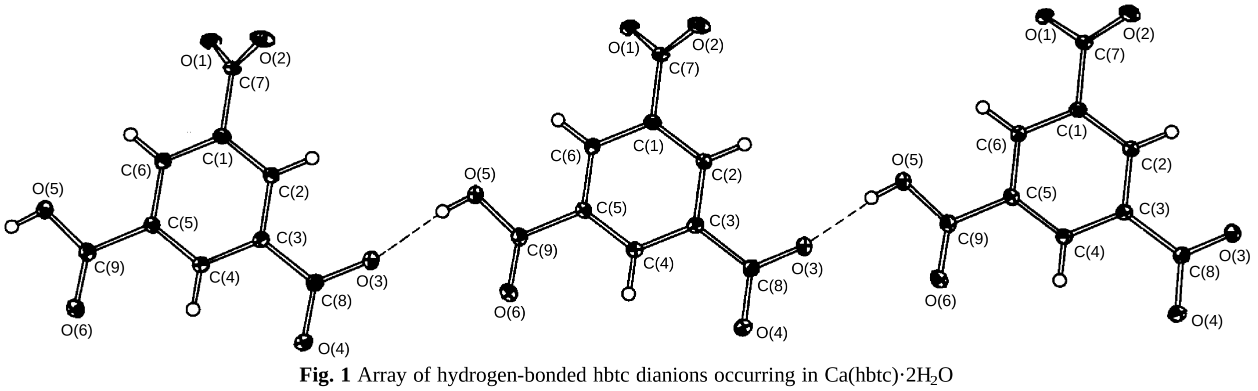

Fig. 1 Array of hydrogen-bonded hbtc dianions occurring in Ca(hbtc)·$2H_2O$

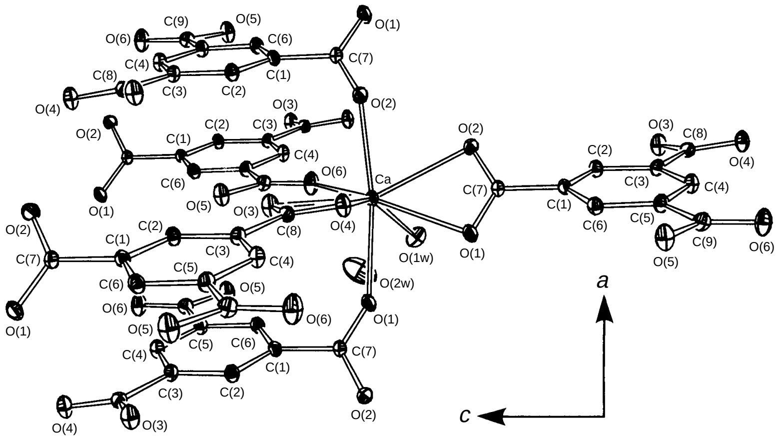

Fig. 2 The coordination of Ca^{2+} by two bidentate and three monodentate carboxylates and one water molecule

O(1w)–H(12w)···O(2w) to the second water molecule. The hydrogens of the second water molecule involving O(2w) are disordered and have been modelled in terms of three sites two of which, H(21w) and H(23w), have been assigned fixed site occupancy factors of 0.5 while the third, H(22w), is fully occupied. H(22w) participates in the formation of the hydrogen bond O(2w)–H(22w)···O(1w) complementing the O(1w)–H(12w)···O(2w) bond described. Whereas H(23w) is involved in the formation of the O(2w)–H(23w)···O(47) hydrogen bond H(21w) does not participate in hydrogen-bond formation.

Thermal gravimetric analysis from room temperature to 230 °C showed a gradual mass loss finally corresponding to the loss of two water molecules per formula unit showing that both the loosely bound and calcium coordinated water can be eliminated. Upon rehydration the X-ray powder diffraction pattern was virtually identical to that of the hydrated material suggesting that the polymeric anion layers and high Ca carboxylate coordination stabilises micropores after removal of water from the lattice. Further detailed studies on these and related materials will be reported shortly.

Footnotes

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† Prior to the publication of ref. 7 our independent attempts to characterise a calcium salt of H_3btc by single-crystal X-ray crystallography were unsuccessful. We were naively following hydrothermal synthesis procedures without slow cooling of the sample which gave poor quality crystals.

Typical procedure: H_3btc (400 mg, 1.9 mmol) and $Ca(O_2CMe)_2$ (301 mg, 1.9 mmol) in water (25 ml) were sealed in a 45 ml Teflon-lined safety bomb[8] and placed in an oven at 180 °C. After about 10 h the oven temperature was slowly reduced over a 36 h period to 80 °C and then allowed to cool to room temp. Colourless crystals were collected and washed with distilled water (494 mg, 91%). The homogeneity of the sample was shown by satisfactory carbon and hydrogen microanalysis and by the X-ray powder diffraction pattern which was identical to the calculated pattern.

‡ *Crystal data*: **2**: $C_9H_8CaO_8$, triclinic, space group $P1$ (no. 1), a = 6.853(5), b = 9.007(9), c = 9.987(6) Å, α = 102.23(6), β = 100.53(5), γ = 110.21(7), U = 543.2(8) Å^3, Z = 2, D_c = 1.737 g cm^{-3}, data collection and cell refinement: Nicolet P3 diffractometer using a graphite monochromator with μ(Mo-Kα) = 0.063 mm^{-1}, T = 293 K. Data collection used ω scan rates of 5.33 (I_p < 150) to 58.6 (I_p > 2500)° min^{-1}, where I_p was the prescan intensity. Scan widths ω were 2.4–2.8°. Data reduction *via* RDNIC.[9] The structure was solved by direct methods to yield positions for all non-hydrogens except the oxygens of the water molecules which were obtained later from difference maps as were the positions of hydrogens attached to oxygens. The final R value was 0.041 (R_w = 0.048). Refinement was by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. For the anion the acid hydrogen H(5) was refined isotropically in the usual manner but the hydrogen attached to carbons were placed in calculated positions with C–H = 0.95 Å and refined with a riding model and common group U_{iso}. Hydrogens of the water molecules were also refined with group U_{iso} values, one for each molecule. The disorder of the hydrogen associated with O(2w) has already been described in the text. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/421.

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