

Solid-state self-assembly of a complex from 1,3,5-benzenetricarboxylic acid and 1,3,5-trihydroxybenzene: influence of strong O–H···O and C–H···O hydrogen bonds

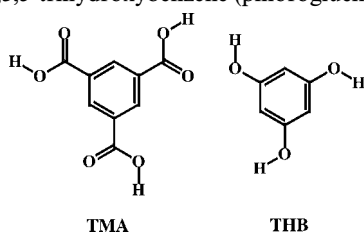
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1,3,5-Benzenetricarboxylic acid (trimesic acid, TMA) was cocrystallized with 0.5 equiv. of 1,3,5-trihydroxybenzene (phloroglucinol, THB) to generate a close-packed non-interpenetrating planar mosaic motif. Both O–H···O and C–H···O hydrogen bonds were observed in the crystal lattice. Each THB molecule is hydrogen bonded to six adjacent TMA molecules to form a planar rosette-shaped structure, which constitutes the repeating units of a layer-type lattice.

1,3,5-Benzenetricarboxylic acid (trimesic acid, TMA) is an important building block in crystal engineering¹ due to its predictable honeycomb formation in the crystal lattice. The α -polymorph crystal structure of TMA contains hexagonal rings made of TMA molecules with a diameter of approximately 14 Å,² which are concatenated to meet the close packing requirement of the crystal lattice. Many elegant approaches have been attempted to remove the concatenation and to fill the cavity at the center of the hexametric rings with organic compounds. Herbststein *et al.* reported³ the first non-catenated TMA structures containing disordered alkane guests. Zimmerman's group incorporated large and relatively non-flexible guest molecules such as pyrene inside the cavity to form an expanded hexamer.⁴ Recently, the same group⁵ observed a series of crystal structures that generate clathrates from substituted TMA. Here, we report a non-penetrating, planar and distorted mosaic structure from a complex of TMA with 1,3,5-trihydroxybenzene (phloroglucinol, THB).⁶



In undertaking this work, we anticipated that THB would be a good partner molecule for preparing TMA clathrates because of its planar rigid structure and the availability of three hydroxyl functional groups, which can form strong hydrogen bonds with the acid groups of TMA. However, it is not large enough to fill the 14 Å cavity in the middle of the TMA ring. These two factors prompted us to investigate the crystal lattice of the TMA·THB complex in detail, with the expectation of creating an interesting 3D crystal lattice. Crystallization from a solution of methanol containing stoichiometric amounts of TMA and THB afforded the desired cocrystals with a 2 : 1 stoichiometry (2TMA·1THB), which were characterized by single crystal X-ray diffraction using a Siemens SMART-CCD diffractometer.

The self-assembly of molecules in the crystal lattice of the 2TMA·1THB complex is shown in Fig. 1. Owing to the

strong hydrogen bonding interaction between TMA and THB, TMA molecules self-assemble in such a manner that typical ring structures involving 6 TMA molecules are not seen in the lattice. Instead, the acid and alcohol functional groups interact to form an interesting planar rosette-type architecture (Fig. 1). Moreover, C–H···O hydrogen bonds between the carbonyl oxygen of TMA molecules and the hydrogen atoms on the THB molecules are seen in the lattice.

In each rosette-type structure, there are two types of crystallographically independent TMA molecules. One type is involved in 6 O–H···O hydrogen bonds and the second is involved in 6 O–H···O and 3 C–H···O hydrogen bonds. They alternate around the central THB molecule. There are nine hydrogen bonds between each THB molecule and the six neighboring TMA molecules (6 O–H···O and 3 C–H···O hydrogen bonds). Each TMA molecule forms hydrogen bonds

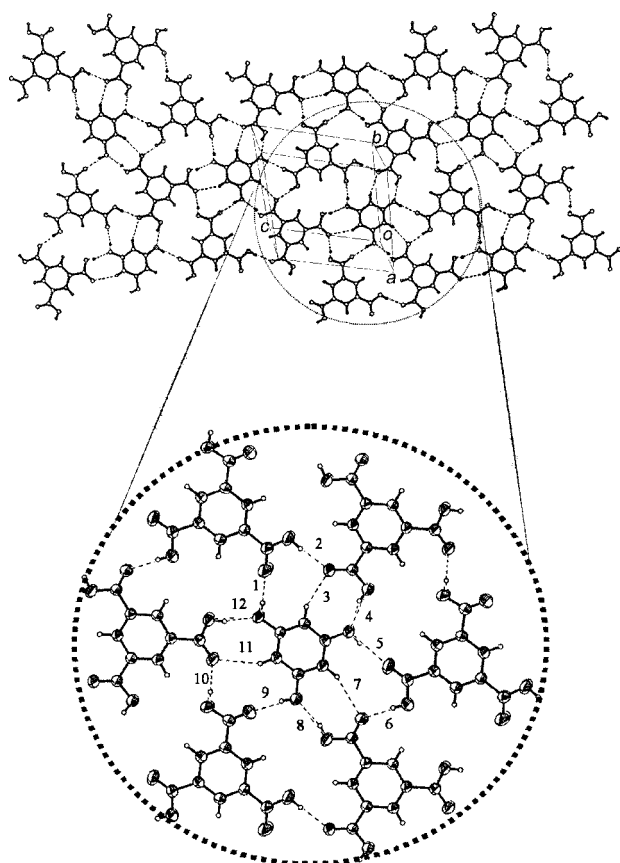


Fig. 1 Crystal structure of 2TMA·1THB showing one planar lamella and enlarged rosette: the hydrogen bonding graph sets between THB and the surrounding TMA molecules are $R_2^2(8)$ and $R_3^2(10)$.

with neighboring TMA molecules and the THB molecules; however, each THB molecule forms hydrogen bonds with adjacent TMA molecules only (Fig. 1). The distances of a few hydrogen bonds around a THB molecule are given in Table 1. All O–H...O bond distances are close to 1.9 Å (O...O distance of 2.7 Å) and all C–H...O bond distances are close to 2.6 Å (C...O distance of 3.4 Å).

There are two different types of hydrogen bond graph sets: $R_2^2(8)$ (formed by bonds 3 and 4; 7 and 8; 11 and 12) and $R_3^2(10)$ (formed by bonds 1, 2 and 3; 5, 6 and 7; 9, 10 and 11) (see Fig. 1). No acid dimer [$R_2^2(8)$] was observed in the lattice, however, there are six TMA molecules surrounding the central THB molecule to form a rosette-type structure. Such an organization could be due to the close packing requirement of the crystal lattice. Since the guest molecule (THB) is relatively small compared with the 14 Å diameter of the central cavity of a typical TMA hexamer, the ring is puckered to accommodate the THB molecule. All TMA and THB molecules in the layer-type lattice are coplanar (Fig. 2). A side view of the crystal lattice, given in Fig. 2, shows the planarity of the layers.

Adjacent layers do not stack on top of each other, but are shifted slightly from one another. The packing relationship between the different layers is illustrated in Fig. 3. The distance between the adjacent layers is about 3.3 Å. Two ellipses (black and grey) representing the rosettes present in the adjacent layers have a rotational relationship of about 60°. The reason for the slight shift and staggered packing of the rosettes may be due to optimization of the packing interactions to achieve a stable lattice.

In conclusion, investigation of the complex of 2TMA·1THB revealed rosette-shaped repeating units of a planar layer-type crystal lattice with many hydrogen bonds. Both TMA and THB molecules form multiple hydrogen bonds with neighboring molecules, resulting in mosaic-type architecture for the crystal lattice. The planar layers packed to

Table 1 Length (Å) and angles (°) of hydrogen bonds indicated in Fig. 1

HB ^a	<i>d</i> (D–H)	<i>d</i> (H...A)	∠DHA	<i>d</i> (D...A)
1	0.820	1.882	170.3	2.694
2	0.820	1.863	173.0	2.679
3	0.930	2.551	155.5	3.420
4	0.820	1.849	164.8	2.649
5	0.820	1.899	170.0	2.710
6	0.820	1.850	173.1	2.666
7	0.930	2.554	157.2	3.430
8	0.820	1.858	164.4	2.657
9	0.820	1.899	170.3	2.711
10	0.820	1.865	171.2	2.678
11	0.930	2.560	155.7	3.429
12	0.820	1.850	164.2	2.648

^a Hydrogen bond numbering given in Fig. 1.

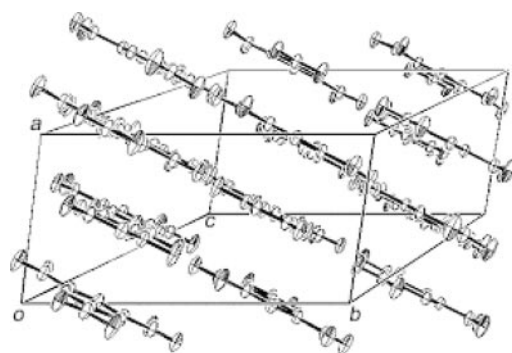


Fig. 2 A side view of the crystal structure showing coplanar layers in the lattice.

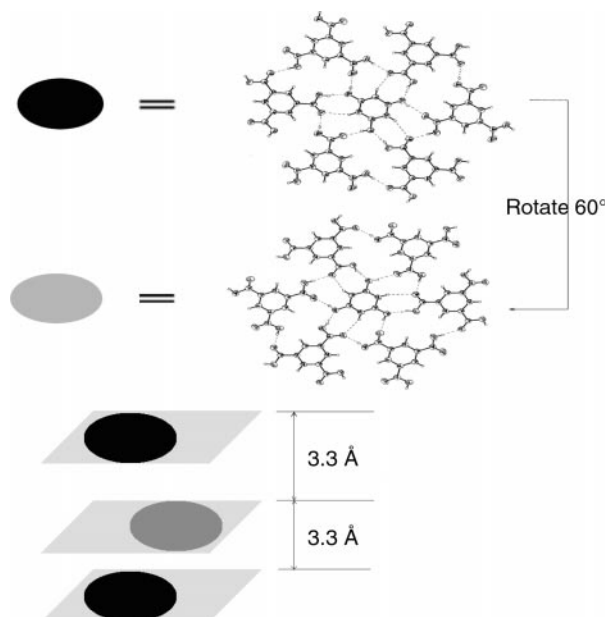


Fig. 3 A diagram showing the layer packing and the relative position of the rosettes in the adjacent layers.

give a stable crystal lattice. Thus the results presented here clearly show that strong interactions between THB and TMA warrant considerable reorganization of the well-established and stable concatenated structures of TMA. Currently, we are trying to develop this concept further to accommodate other multifunctional guests inside the planar TMA lattice.

Experimental

Single crystals suitable for X-ray diffraction studies were grown from methanol by slow evaporation at room temperature in air. In a typical crystallization experiment, TMA (135.1 mg, 0.8 mmol) and THB (100 mg, 0.8 mmol) were dissolved in 8 ml of methanol in a small test tube, which was sealed with Parafilm. Colorless crystals appeared after 3 days and these were collected for single crystal X-ray analysis. The crystals were sealed in a quartz capillary and data collection was carried out on a Siemens CCD SMART system using the ω -scan mode. The structure of the complex was solved by direct methods and the remaining non-hydrogen atoms located in difference Fourier maps. Full-matrix least-squares refinements were carried out with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were placed on calculated positions (C–H 0.96 Å) and assigned isotropic thermal parameters riding on their parent atoms. Initial calculations were carried out on a PC using the SHELXTL PC software package; SHELXL-93⁷ was used for the final refinement.

Crystal data for **1**: $C_{24}H_{18}O_{15}$, triclinic, space group $P\bar{1}$, $a = 7.1504(1)$, $b = 13.5209(2)$, $c = 13.5587(2)$ Å, $\alpha = 63.756(1)$, $\beta = 80.888(1)$, $\gamma = 81.243(1)^\circ$, $u = 1156.39(3)$ Å³, $Z = 2$, $\lambda = 0.71073$, $F(000) = 564$. 4453 reflections out of 5447 unique reflections with $I_{\text{net}} > 2\sigma(I)$ measured at 293(2) K for a crystal of $0.36 \times 0.26 \times 0.18$ mm dimensions afforded on convergence final R factors of $R_f = 0.0368$ and $R_w = 0.1069$.

CCDC reference number 164336. See <http://www.rsc.org/suppdata/nj/b1/b102098f/> for crystallographic data in CIF or other electronic format.

Acknowledgements

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