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# Step-wise dis-assembly of trimesic acid: mono- and bis(methanol) solvates

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**Single crystal X-ray structures of methanol solvates of trimesic acid provide an insight into the step-wise dis-assembly of this strongly hydrogen-bonded acid through the disruption of acid–acid head-to-tail dimer motifs by alcohols.**

Trimesic acid (benzene-1,3,5-tricarboxylic acid, $H_3TMA$) is amongst the most used members of the benzenepolycarboxylic acid family, favoured by the supramolecular chemist for their numerous divergent carboxyl groups, useful in the creation of extensive arrays through hydrogen bonding[1] and metal-coordination bonds.[2] The inclusion of solvent molecules into the "chicken wire" solid state structure of $H_3TMA$[1a,3] received interest, notably from Herbstein, in the 1970s and 1980s,[1a,1c,4] with more recent work investigating the formation of channels in $H_3TMA$ solvates utilising poly-aromatic compounds as templates.[5] While the crystallographic study of solvates was initially hindered by rapid desolvation at room temperature,[6] the advent of low temperature systems for X-ray data collection now allows for more precise structural determinations.[4e]

The crystallisation of a methanolic solution of $H_3TMA$ over a period of seven days at −18 °C resulted in a mixture of colourless blocks $H_3TMA{\cdot}MeOH$, **1**, and colourless needles $H_3TMA{\cdot}2MeOH$, **2**, the latter being the major component. Both **1** and **2** were analysed using single-crystal X-ray diffraction† and were found to possess tape structures, maintained by strong O–H···O hydrogen bonding interactions.[7]

Two of the carboxylic acid groups in the $H_3TMA$ molecule in **1** are prevented from forming the prevalent[8] carboxylic acid–carboxylic acid head-to-tail dimer motif, designated $R^2_2(8)$ using Etter's graph set analysis,[9] by the insertion of a molecule of MeOH into the structure. Alcohols are known to disrupt the expected $R^2_2(8)$ motif, forcing the formation of $R^3_3(10)$ singly-bridged or $R^4_4(12)$ doubly-bridged dimer motifs.[5a] In the case of **1**, the MeOH molecule hydrogen bonds to the carbonyl *O* of one $H_3TMA$ molecule and the O*H* of another, forming the $R^3_3(10)$ motif. The $R^2_2(8)$ motif utilising the third carboxyl group of the tri-acid does remain intact, producing one-dimensional tapes (Fig. 1).

The network of strong hydrogen bonds creates cavities with dimensions of 11 × 7.5 Å, comparable in the greatest dimension with those observed in pure $H_3TMA$.[3] The $R^4_4(32)$ hydrogen bonding pattern surrounding the cavity is identical to that seen in $H_3TMA{\cdot}MeOH{\cdot}H_2O$ (crystallised from a 1 : 1 mixture of MeOH and benzene),[4b] except in this literature example the water molecules (rather than MeOH in the case of **1**) disrupt two of the $R^2_2(8)$ acid–acid synthons in each $H_3TMA$ molecule, while the MeOH molecules form a polymeric chain within the cavity. The three-fold interpenetration[3] observed in the solid state structure of $H_3TMA$ is not seen in **1**, as π-stacking and electronic repulsions maintain a distance of 3.55 Å between adjacent tapes, with Me groups of the solvent molecules from adjacent tapes lying just above and below the cavity (Fig. 2).

The crystal structure of **2**, $H_3TMA{\cdot}2MeOH$, shows further disruption of the acid–acid hydrogen bonding through the inclusion of a second equivalent of MeOH. All acid–acid head-to-tail interactions are disrupted in **2** (Fig. 3a), with two carboxyl groups interacting with one MeOH molecule in the same $R^3_3(10)$ motif observed in **1**. In contrast to **1**, the third carboxyl group of each $H_3TMA$ molecule does not interact directly with any other $H_3TMA$ molecule. Instead it hydrogen bonds only with two symmetry-equivalent molecules of MeOH as part of a $R^4_4(8)$ motif formed by two carboxyl OH and two MeOH, creating hydrogen-bonded chains bridged by pairs of MeOH molecules (Fig. 3b). This second unique MeOH molecule is disordered equally over two positions, with complementary disorder of the *H* atom in the carboxyl group.

Single crystal X-ray data has been previously used to investigate the dis-assembly of polymeric ladder structures,[10] for example,

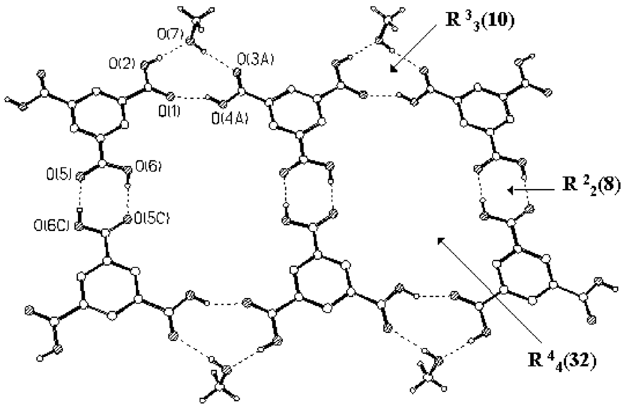

**Fig. 1** Tape structure of **1**, viewed along the crystallographic [5 5 3] direction and maintained by $R^2_2(8)$ and $R^3_3(10)$ hydrogen-bonded motifs. Aromatic hydrogen atoms have been removed for clarity and hydrogen-bonding interactions are shown by dashed lines. Symmetry equivalent atoms appended A are generated by the symmetry operation $-x+1, -y+2, -z+2$; C by the symmetry operation $x+1, y+1, z$. Selected hydrogen bonding parameters (Å) O(2)···O(7) 2.6037(13), O(4A)···O(1) 2.5941(13), O(7)···O(3A) 2.7979(14), O(6)···O(5C) 2.6208(13).

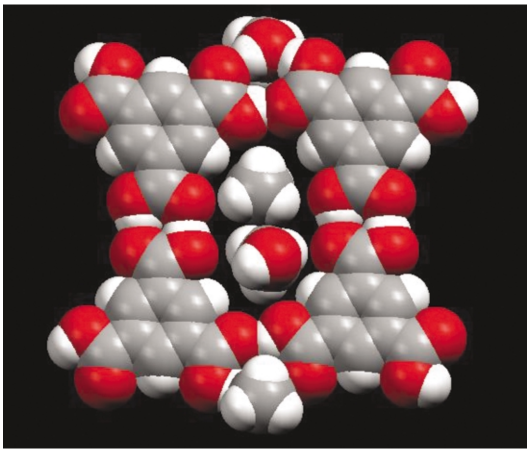

**Fig. 2** Space-filling plot of **1**, viewed along the crystallographic [5 5 3] direction, showing the cavity (11 × 7.5 Å) produced within the tapes and the pendant Me groups of MeOH molecules protruding up and down from adjacent tapes. Carbon atoms are shown in dark grey, oxygen atoms in red and hydrogen atoms in white.

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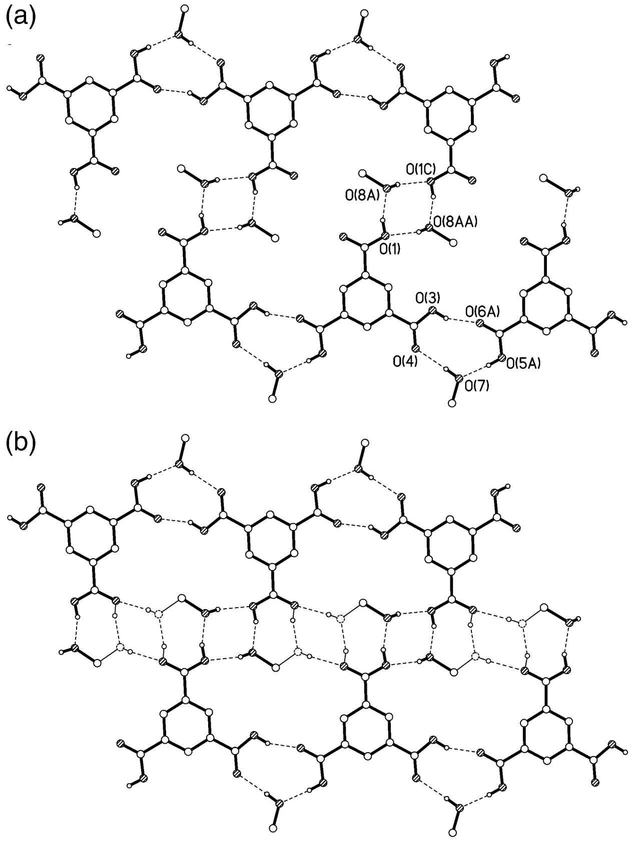

**Fig. 3 (a) and (b)** Tape structure of **2**, viewed along the crystallographic [1 0 3] direction. All hydrogen atoms not involved in hydrogen bonding have been removed for clarity and hydrogen-bonding interactions shown by dashed lines. In (b), alternative positions for disordered groups are denoted by thinner bonds and dotted circles. Selected hydrogen bonding parameters (Å) O(1)···O(8A) 2.521(7), O(2)···O(8B) 2.531(7), O(3)···O(6A) 2.594(4), O(5A)···O(7) 2.572(4), O(7)···O(4) 2.777(4).

through the disruption of lithium amide $(NLi)_2$ dimer interactions by solvent molecules, leading to the fragmentation of the structure.

Similarly, the solid state structures of **1** and **2** provide an insight into the mechanism of the gradual dis-assembly of trimesic acid (and perhaps carboxylic acids in general) in alcohols, suggesting a step-wise disruption of the $R_2^2(8)$ acid–acid dimer motifs until dissolution is achieved.

The positioning of the pendant Me groups of adjacent tapes in **1** (Fig. 1) indicates the space available for the accommodation of the alkyl chains of higher alcohols. Further studies have been carried out into the insertion of the higher homologues, extending to the linking of the tapes through the use of diols. Further details will be published shortly.

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## Notes and references

† Crystal data for **1**: $C_{10}H_{10}O_7$, $M$ = 242.18, triclinic, $a$ = 7.8770(10), $b$ = 8.9629(11), $c$ = 8.9562(11) Å, $\alpha$ = 111.926(3)°, $\beta$ = 96.722(3)°, $\gamma$ = 110.575(3)°, $U$ = 526.24(11) Å$^3$, $T$ = 160(2) K, space group $P\bar{1}$, $Z$ = 2, $\mu$(Mo-K$_\alpha$) = 0.133 mm$^{-1}$, data were collected in the range 2.56 to 28.79° (ω scan), 3969 reflections measured, 2380 unique ($R_{\text{int}}$ = 0.0173) which were used in all calculations. Final $R_1$ 0.0388 ($F^2 > 2\sigma$) and $wR(F^2)$ 0.1140 (all data).

Crystal data for **2**: $C_{11}H_{14}O_8$, $M$ = 274.22, triclinic, $a$ = 3.7519(9), $b$ = 9.579(2), $c$ = 17.732(4) Å, $\alpha$ = 91.206(6)°, $\beta$ = 91.881(6)°, $\gamma$ = 93.998(5)°, $U$ = 635.2(3) Å$^3$, $T$ = 173(2) K, space group $P\bar{1}$, $Z$ = 2, $\mu$(Mo-K$_\alpha$) = 0.124 mm$^{-1}$, data were collected in the range 1.15 to 24.99° (ω scan), 3936 reflections measured, 2215 unique ($R_{\text{int}}$ = 0.0238) which were used in all calculations. Final $R_1$ 0.0780 ($F^2 > 2\sigma$) and $wR(F^2)$ 0.1816 (all data).

Crystal data were collected on a Siemens SMART 1K CCD diffractometer. Programs: Siemens SMART (control) and SAINT (integration), Bruker AXS SHELXTL (structure solution and refinement) and local programs. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 233070–233071. See http://www.rsc.org/suppdata/cc/b4/b402922d/ for crystallographic data in .cif or other electronic format.

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