

# Tetrakis(4-sulfophenyl)methane dodecahydrate. Reversible and selective water inclusion and release in an organic host†‡

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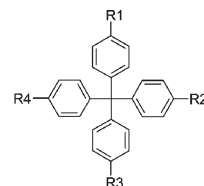
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Infinite water helices and discrete  $\text{H}_2\text{O}-\text{H}_2\text{O}-\text{SO}_3\text{H}$  hydrogen bond aggregates occupy 19% unit cell volume in different channels of the title host tecton. The cooperative nature of  $\text{H}_2\text{O}-\text{SO}_3\text{H}$  H bonds and inter-connected channels correlate with higher  $T_{\text{onset}}$  of O4 and O5 water molecules at 149 °C compared to release of O6 H-bonded water helix from parallel channels at 114 °C. The zeolite-like organic host shows reversible water uptake and dehydration in successive heat-cool-heat cycles.

Tetrahedral tectons<sup>1</sup> are versatile building blocks for the directed organization of host-guest and/or interpenetrated networks.<sup>2</sup> The tetrahedral core is C, Si or the adamantane group<sup>3</sup> with *para*-substituted phenyl rings. Crystal structures of symmetrical molecules are extensively studied (4 identical R groups) but there are a few examples of unsymmetrical molecules as well (different R groups) in crystal engineering.<sup>4</sup> The molecules displayed in Scheme 1 have strong H bonding functional groups, halogens, ethynyl, and various heterocycles at the periphery. Apart from organic tectons tetrahedral ligands coordinated to metal ions are reported.<sup>5</sup> Wuest<sup>1,6</sup> has popularized the concept of molecular tectonics (tecton = builder molecule with sticky functional groups) for over a decade now using tetrahedral molecular scaffolds.

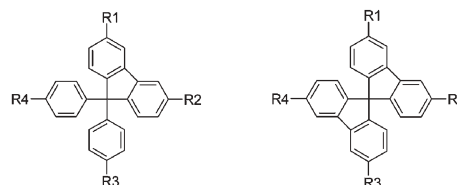
A remarkable structural feature of tetraaryl methanes is that they crystallize in a columnar architecture, usually in tetragonal or monoclinic space groups, *e.g.*  $I4_1/a$ ,  $I-4$ ,  $C2/c$ , *etc.* Tetrahedral tectons organize in predictable packing motifs of diamondoid, rhombohedral or columnar type directed by the molecular node and supramolecular synthon of tetrahedron symmetry,<sup>2</sup> or because the tetrahedrally oriented arms fit into the voids created by the molecular core of the same symmetry. Tetraphenylmethanes and silanes with the boronic acid group include guest species to the extent of 60–65% in inter-connected channels.<sup>3a</sup> However, the structural chemistry of the sulfonic acid group has not been studied in tetrahedral molecules although metal complexes of adamantane sulfonic acid anion were recently reported.<sup>5a,b</sup> Sulfonated calixarenes are well known in host-guest inclusion and supramolecular chemistry.<sup>7</sup>

Tetrakis(4-sulfophenyl)methane (abbreviated as TPM- $\text{SO}_3\text{H}$ ) was synthesized by the *para*-sulfonation<sup>5a</sup> of tetraphenyl methane<sup>8</sup> with chlorosulfonic acid in 93% yield.§ The compound is readily



1.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{R}_4=\text{CN}$ ;  $\text{NH}_2$ ;  $\text{N}=\text{C}=\text{S}$ ;  $\text{NHCOOR}$ ;  $\text{I}$ ;  $\text{Br}$ ;  $\text{NHCONH}_2$ ;  $\text{NHCONHR}$ ;  $\text{C}_6(\text{Ph})_5$ ;  $\text{N}(2'\text{-Pyridone})_2$ ;  $\text{OH}$ ;  $\text{COOH}$ ;  $\text{C}^*\text{CH}$ ;  $\text{H}$ ;  $\text{CH}_2\text{Cl}$ ;  $\text{NO}_2$ ;  $\text{NHCOMe}$ ;  $\text{C}^*\text{CPh}$ ;  $\text{CH}=\text{CHPh}$ ;  $\text{C}^*\text{C}-\text{C}^*\text{C}-\text{C}(\text{Me}_2)(\text{OH})$ ;  $\text{C}^*\text{CBr}$ ;  $\text{I}(\text{OCOMe})_2$
2.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{C}_6\text{H}_2(2'\text{-OH}-3'\text{-t-Bu}-5'\text{-Me})$ ,  $\text{R}_4=\text{H}$
3.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{H}$ ,  $\text{R}_4=\text{CONH}_2$
4.  $\text{R}_1=\text{R}_2=\text{NO}_2$ ,  $\text{R}_3=\text{R}_4=\text{H}$
5.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{H}$ ,  $\text{R}_4=\text{OH}$
6.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{CH}_3$ ,  $\text{R}_4=\text{H}$
7.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{COOH}$ ,  $\text{R}_4=\text{H}$
8.  $\text{R}_1=\text{R}_2=\text{C}^*\text{CH}$ ,  $\text{R}_3=\text{R}_4=\text{Br}$
9.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{C}^*\text{CH}$ ,  $\text{R}_4=\text{Br}$
10.  $\text{R}_1=\text{R}_2=\text{R}_3=\text{H}$ ,  $\text{R}_4=\text{OH}$
11.  $\text{R}_1=\text{R}_2=\text{NO}_2$ ,  $\text{R}_3=\text{R}_4=\text{I}$

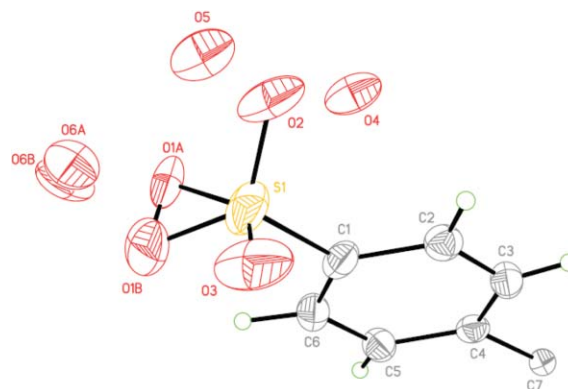
where \* = triple bond  
 $\text{R}_1=\text{R}_2=\text{R}_3=\text{R}_4=\text{SO}_3\text{H}$ , this paper



$\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$  are functional groups such as  $\text{OH}$ ;  $\text{NO}(\text{t-Bu})$ ;  $\text{CH}_2\text{OH}$ ;  $\text{COOH}$ ;  $\text{H}$ ;  $\text{CN}$ ;  $\text{NHCOMe}$ ;  $\text{CHO}$ ;  $\text{CH}=\text{C}(\text{CN})_2$ ;  $\text{Br}$ ;  $\text{NH}_2$ ;  $\text{t-Bu}$ ;  $\text{NO}_2$

**Scheme 1** List of tetrahedral tectons having the tetraphenylmethane aromatic core and diverse R groups.

soluble in alcoholic solvents and water. Recrystallization from MeOH at room temperature afforded needle-shaped crystals for X-ray diffraction.†¶ Structure solution and refinement in the  $I4_1/a$  space group showed  $\frac{1}{4}$  TPM- $\text{SO}_3\text{H}$  molecule and 3 water molecules in the asymmetric unit (Fig. 1), giving a host : guest ratio



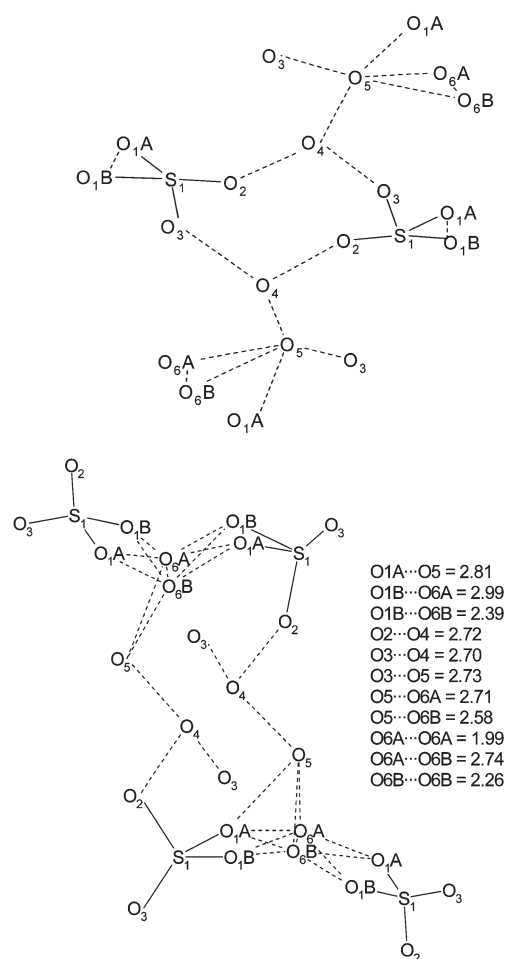
**Fig. 1** ORTEP of TPM- $\text{SO}_3\text{H}$  ( $\frac{1}{4}$  molecule) and water (3 molecules).

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 † CCDC reference number 644921. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706194c

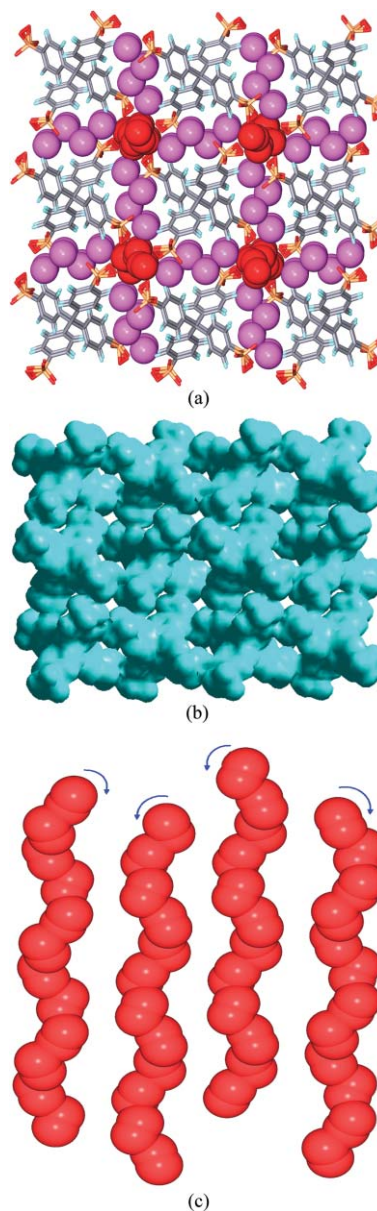
‡ Electronic supplementary information (ESI) available: Thermal and powder XRD plots, tables of H bonds and CSD refcodes. See DOI: 10.1039/b706194c

of 1 : 12. The aromatic hydrocarbon core is ordered in the crystal structure except one of the SO<sub>3</sub> oxygen atoms (s.o.f. O1A 0.30, O1B 0.70; O2 and O3 are fully ordered). S–O bond distances indicate that S–O1 is a single bond (S–O1A, 1.546(4) Å; S–O1B, 1.48(7) Å) whereas S=O2 and S=O3 are double bonds (1.426(4) Å, 1.446(4) Å) in the sulfonic acid group. Of the three water molecules, two O atoms have full occupancy (O4, O5) while the third water is distributed over two positions (O6A, O6B, s.o.f. 0.25 each). Hydrogen atoms of neither the SO<sub>3</sub>H group nor water molecules could be located in the difference electron density map.

There are no direct SO<sub>3</sub>H⋯SO<sub>3</sub>H hydrogen bonds in the crystal structure. The inclusion of three symmetry-independent water molecules and strong SO<sub>3</sub>H group produce an extended network of O–H⋯O hydrogen bonds shown in Scheme 2. O⋯O distances are in the typical range (2.4–3.0 Å) for strong, cooperative H bonds<sup>9</sup> (see Table S1 for a list of O⋯O and C–H⋯O distances, ESI†). Disordered S–O1 groups make square channels of 3.5 Å on each side that include O6 water molecules which are arranged in a helix down [001]. The four helices at the corners of TPM–SO<sub>3</sub>H host (O6 water) have opposite handedness<sup>10</sup> (Fig. 2). O4 and O5 waters are present in irregular-shaped but inter-connected channels (see Fig. 2b) surrounded by SO1A/B and SO2 polar groups and hydrophobic phenyl CH walls. A difference between O4, O5 and O6 water molecules is that the cooperative network of H bonds to



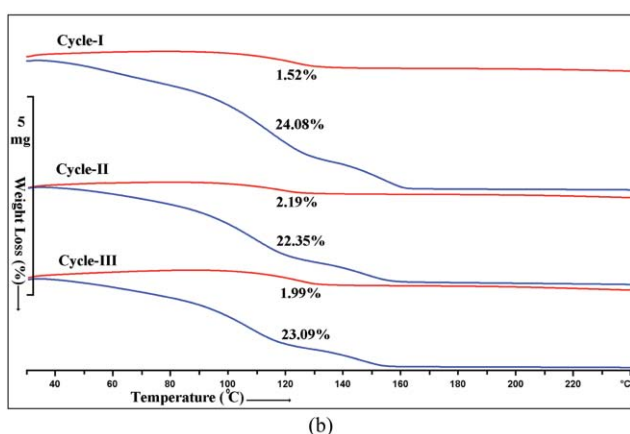
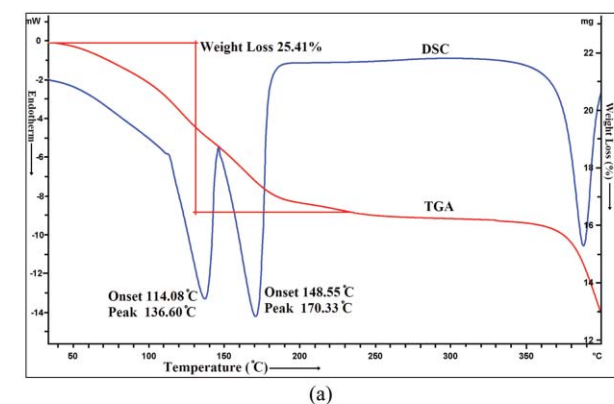
**Scheme 2** Hydrogen bonded networks of SO<sub>3</sub>H group and H<sub>2</sub>O molecules. O⋯O distances are given in Å.



**Fig. 2** (a) A slice of the host layer to show two types of channels. Square channels accommodate O6 water helices (red) and irregular-shaped channels have H-bonded water molecules O4 and O5 (magenta). (b) A uniform pore of 3.5 Å in square channels at the vertices and irregular, interconnected channels along the sides of the host molecule. (c) Water helices down [001] at the four vertices have opposite handedness. O6 of partial occupancy at both sites are shown.

ordered O4 and O5 waters is more extended compared to that of disordered O6 water. Whereas O6 forms 1D helical chains,<sup>11</sup> O4 and O5 are engaged in 2D H bond networks. The total available free volume in the crystal is 46.5% of which guest water molecules occupy 19.1%. This value compares well with water occupancy (by volume) in recently reported hydrates<sup>12</sup> (Table S2, ESI†).

Structural and H bonding differences between guest molecules mentioned above are manifested during water release. Water is lost in two endothermic steps—one water molecule escapes at 120–150 °C ( $T_{\text{peak}}$  140 °C) and two water molecules are lost at 150–185 °C ( $T_{\text{peak}}$  165 °C). The total weight loss between 100–200 °C



**Fig. 3** Thermograms of TPM-SO<sub>3</sub>H dodecahydrate. (a) DSC shows weight loss in two steps corresponding to O6 and O4 + O5 water molecules in TG. (b) TGA exhibits complete water uptake after dehydration and release in three successive heat-cool-heat cycles.

(Fig. 3a) is consistent with a 1 : 12 host : guest stoichiometry from the X-ray crystal structure (obs. 25.41%, calc. 25.23%). We ascribe loss of the O6 water helix first from the parallel channels at the vertices followed by the loss of strongly bonded O4 and O5 waters from the inter-connected channels along the sides of the host molecule. Heat-cool-heat cycle in DSC showed that water is completely lost below 200 °C. The sample does not absorb moisture within the DSC sample chamber, and there is no weight loss in the second heating cycle up to 280 °C (Fig. S1, ESI†). The loss and uptake of water<sup>13</sup> is quantitative in three successive cycles (Fig. 3b). Powder X-ray diffraction patterns of the solid after heating under vacuum matched with the original dodecahydrate, suggesting that the material absorbs moisture during handling and data collection. When the dehydrated solid was immediately coated with wax and the powder XRD recorded, it showed a different crystalline phase (Fig. S2, ESI†). Full structural characterization of this apohost material is pending for want of single crystals.

A ratio of 1 : 12 host : water is not so common in organic crystal hydrates. There are 32 refcodes for dodecahydrates in the CSD<sup>12</sup> (Table S3, ESI†) among which 16 structures are fully ordered. Water H atoms were located in 6 structures. Three crystal structures have an hydrated sulfonic acid dimer motif similar to that shown in Scheme 2 (see earlier)—they are refcodes EBIFIE, NIQHOK and YENQOX.<sup>14</sup>

To summarize, we show novel and interesting structural chemistry of the sulfonic acid group in a tetrahedral tecton. Hydrogen bonding in water helices and clusters of TPM-SO<sub>3</sub>H host channels are described. Water uptake is selective, because TPM-SO<sub>3</sub>H does not include alcoholic co-solvents, guest release is reversible, and re-uptake of water from the atmosphere is immediate. These properties have potential application in organic zeolites and/or as dehydrating reagents.

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## Notes and references

§ Tetraphenylmethane<sup>8</sup> 640 mg (2.0 mmol) was dissolved in 25–30 mL of dry CH<sub>2</sub>Cl<sub>2</sub> under an inert N<sub>2</sub> atmosphere. Freshly distilled chlorosulfonic acid<sup>5a</sup> (660 µL, 10.0 mmol) dissolved in 12 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise over 1 h to the stirred reaction mixture at 5–10 °C. The reaction was continued for another 3 h. The precipitate was filtered and washed thoroughly using CH<sub>2</sub>Cl<sub>2</sub> in which it is practically insoluble. The product was recrystallized from MeOH. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 7.38 (d, *J* = 8 Hz, 2 H); 7.12 (d, *J* = 8 Hz, 2 H). <sup>13</sup>C NMR (D<sub>2</sub>O): δ 148.70, 140.66, 131.28 (× 2), 125.18 (× 2), 64.78. IR (KBr): ν/cm<sup>−1</sup> 3650–3000 (br, O–H), 1685, 1487, 1367 (SO<sub>3</sub>H), 1285 (SO<sub>3</sub>H), 1192 (hydrated SO<sub>3</sub>H), 1006, 873. TPM-SO<sub>3</sub>H is readily soluble in alcoholic solvents and water. Colorless needle-shaped crystals suitable for X-ray diffraction were crystallized after evaporation of the solvent over a few days.

¶ Crystal data were collected on a Bruker SMART APEX CCD X-ray diffractometer with graphite-monochromator Mo-Kα radiation (*λ* = 0.71073 Å) at 100 K. TPM-SO<sub>3</sub>H: C<sub>25</sub>H<sub>16</sub>O<sub>22</sub>, *M*<sub>r</sub> = 796.62, tetragonal, *I*<sub>4</sub>/a, *a* = 21.8492(12), *b* = 21.8492(12), *c* = 7.3635(9) Å, α = β = γ = 90°, *V* = 3515.2 (5) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.505 g cm<sup>−3</sup>, *R*<sub>1</sub> = 0.0818, *wR*<sub>2</sub> = 0.1272. Intensities were collected for absorption effects using the multi-scan technique SADABS. All non-hydrogen atoms were refined anisotropically and H atoms were located from difference electron density maps. Structure solution and refinement were carried out in Bruker SHELX-TL. Packing fraction and solvent accessible volume was calculated in PLATON.

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