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Water and tris(5-acetyl-3-thienyl)methane (TATM) assemble into a one-dimensional channel compound

Paul S. Sidhu,[ab] Konstantin A. Udachin[a] and John A. Ripmeester[ab]

[a] *Steacie Institute for Molecular Sciences, National Research Council of Canada Ottawa, Ontario K1A 0R6. E-mail: john.ripmeester@nrc-cnrc-gc.ca; Fax: +1 613 998-7833; Tel: +1 613 993-201*

[b] *Department of Chemistry, Ottawa-Carleton Chemistry Institute, Carleton Campus, Ottawa K1S 5B6*

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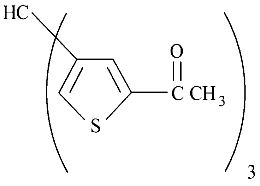
Tris(5-acetyl-3-thienyl)methane (TATM), a well known hydrophobic host compound, assembles with water molecules into a material with one-dimensional channels that also contain water.

Water transport is a fundamental requirement for all life processes, and its elucidation in biological systems has captured much attention in recent years.[1–3] Two types of pore systems that have been studied extensively are the transmembrane proteins gramicidin A and the aquaporins, each forming essentially hydrophobic pore systems capable of varying degrees of specialized functional transport.[1–3] Because of the complexity of these systems, their study is a difficult and time consuming process.[4] Hence much can be learned by studying simpler model systems[5,6] that may display some degree of related functionality. For instance, some work[6] on one-dimensional water channels in simple dipeptides has shown some unusual properties, *e.g.* negative thermal expansion related to the ordering of water in the peptide nanotubes. Here, we show that tris(5-acetyl-3-thienyl)methane (TATM), a well-known host system, is an example of a very simple hydrophobic molecule that assembles with water into a one-dimensional channel system that should also be capable of water transport.

TATM is a much-studied tripodal host molecule[7–12] related to the triphenylmethane group of hosts.[13] In the initial study,[8] inclusion compounds resulted for every solvent from which the host was recrystallized. TATM guest–host materials show a variety of stoichiometries and structural motif;[10,11] they also have demonstrated some propensity for polymorphism.[12] Upon guest removal by heating, the host material usually becomes an oil or an amorphous solid, the latter melting at ~50–58 °C. Similarly, sublimation produces only an amorphous form, and, so far, a crystalline form of the guest-free host has not been reported. Likely reasons are that the molecules lack the ability to interact with each other *via* strong directional interactions, as there are only acetyl oxygens and weakly acidic hydrogens. Also, the absence of strongly preferred orientations of the thienyl rings is likely to give a variety of conformational isomers in the liquid or vapour, thus making efficient packing difficult upon solidification. In almost all structural studies the observed host and guest interact weakly through van der Waals' forces, so, the energy gained by crystallization appears to be significant only when a suitable guest is present to organize the host for efficient packing. During attempts to produce a crystalline guest-free host we have discovered a novel crystalline form of TATM where long-range order is induced by connecting the individual molecules with strongly directional linkers, namely water molecules.

Guest-free amorphous TATM was dissolved in liquid SO_2 in a Pyrex tube immersed in a Dewar cooled to −78 °C with dry ice. The SO_2 was allowed to evaporate as the sample warmed to room temperature in air. The material turned out to be a hydrated form of TATM (**1**) as revealed by crystallographic analysis† of a suitable single crystal. There was no evidence of SO_2 being incorporated into the structure.



Scheme 1 Schematic of tris(5-acetyl-3-thienyl)methane (TATM)

The compound was shown (Fig. 1) to be TATM·$2H_2O$ (**1**) which has a triclinic $P\bar{1}$ structure. The material has a novel one-dimensional channel structure formed from pairs of TATM molecules linked through a water molecule that H-bonds to an acetyl oxygen in each. The channel is oriented along the *a* axis of the structure and contains water molecules (Figs. 1,2).

There are four water molecules in the asymmetric unit of the structure. Two sites, O1A and O2A, are fully occupied by water molecules and form hydrogen bonds with oxygen molecules of the

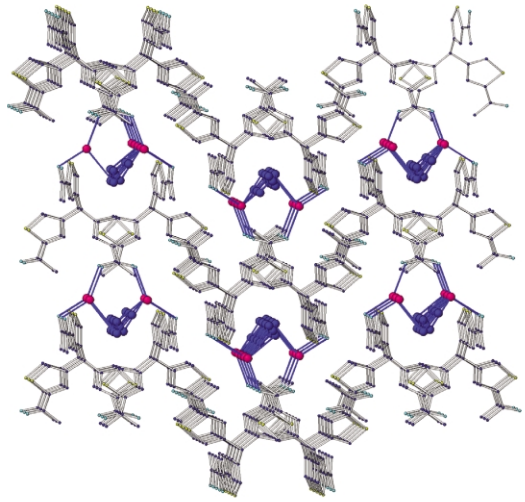


Fig. 1 View of **1** approximately along the channel (*a* axis). Ordered water molecules that form part of the channel wall are shown in red, disordered water molecules as blue circles. Hydrogen bonds are shown as blue lines.

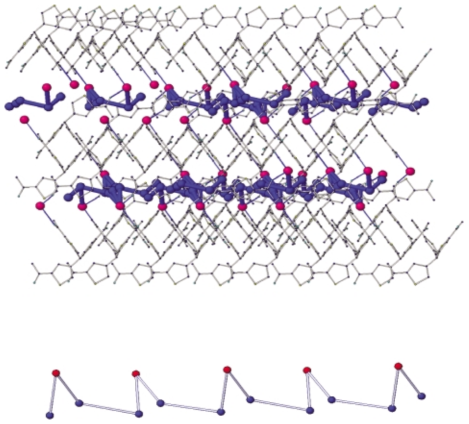


Fig. 2 (top) View of **1** along the *c* axis (perpendicular to the channel) (bottom) Hydrogen bonding of water molecules along the channel. The water molecules bound to TATM in fully occupied positions are red, the water molecules bound only to other water molecules in partially occupied positions are blue.

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TATM acetyl groups. (O ···O distances are 2.85–2.88 Å). Two other water molecules are each disordered over two positions with site occupancies of 78–22% and 57–43%. The disordered molecules form hydrogen bonds only with water in the fully occupied positions (O···O distances are 2.73–2.82 Å) but not with TATM.

The crystalline product is stable at room temperature. The material was studied by DSC and TGA, and this showed that the material holds on to its water quite tenaciously considering that the water molecules are bound only through H-bonds to acetyl oxygens and that they reside in an open channel. Rapid water loss starts only on heating to temperatures above ~ 100 °C, and the compound melts at ~128 °C. An isothermal TGA experiment at 100 °C showed that two-thirds of the water was released in the first 30–40 min, with the remainder taking another 5 h.

Transport of water is not likely to be very efficient, as the channel is filled with H-bonded molecules. The TATM-bound waters are ordered (Fig. 2) and the other water molecules are disordered over pairs of positions because of two possibilities for hydrogen bond formation. Each of the disordered waters has one perfect distance (2.75–2.79 Å) for hydrogen bonding to one TATM-bound water molecule. There is another reasonable distance (3.15 Å) for hydrogen bonding with one of the other disordered pairs of molecules, but too long a distance (4.3–4.6 Å) to the second position for this pair. If we put one fully occupied water position in an intermediate position, all distances, except to the TATM-bound water molecule, will be too long. So these molecules are distributed over two possible flip-flop positions. Water transport therefore must depend on the movement of vacancies down the channel. In order to assess the general mobility of water in the channel, a ^{2}H NMR experiment was carried out on a deuteriated version of the compound. This was prepared by repeating the preparative procedure where a few drops of D_2O were added to the cold SO_2 solution, and the SO_2 was evaporated through a drying tube to prevent the condensation of atmospheric water. The ^{2}H NMR spectrum[‡] is shown in Fig 3, and consists of a sharp line superimposed on a typical ^{2}H doublet. The sharp line is a relatively small proportion of the total, and we attribute it to D_2O on the outside of the crystals. The doublet can be characterized by a quadrupole coupling constant of 53.1(1) kHz with an asymmetry parameter of 0.27(1) The rigid-lattice quadrupole coupling constant for a hydrogen-bonded water molecule is ~200 kHz, so that the reduced value observed indicates that there is extensive motional averaging. Also, the observation of a single doublet means that exchange between the ordered and disordered water molecules is fast on the scale of the quadrupolar splitting. This suggests that a vacancy-mediated mechanism would indeed be effective for water transport.

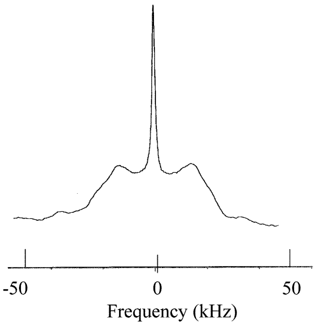

Fig. 3 ^{2}H NMR spectrum of TATM·$2D_2O$

Notes and references

[†] Structural information for **1**. The diffraction data were collected with $Mo_{K\alpha}$ radiation, ω scan mode and a graphite monochromator on a Bruker SMART diffractometer equipped with a CCD detector. The structure was solved by direct method using the SHELXTL suite of programs.[14] A multiscan absorption correction was made with program SADABS.[14] All hydrogen atoms were put in calculated positions. The crystal structure is twinned triclinic (twin law $\bar{1}00\ 0\bar{1}0\ 001$, twin fraction 0.181), $P\bar{1}$; (crystal size 0.3 × 0.3 × 0.2 mm) $a = 8.761(1)$, $b = 10.793(2)$, $c = 21.794(3)$ Å, $\alpha = 88.980(3)$, $\beta = 89.572(3)$, $\gamma = 80.703(3)$; $V = 2033.3(5)$; Å^3, $Z = 4$, $\rho_{calc} = 1.384$ mg m^{-3}, $2\theta_{Max} = 50°$, GoF on $F^2 = 0.956$, residual electron density max. 0.85, min. -0.60 e Å^{-3}. Final R indices ($I > 2\sigma(I)$): $R_1 = 0.074$, $wR_2 = 0.18$ (18435 reflections total, 7156 unique, $4373 > 2\sigma$). Upon the suggestion of one of the reviewers, the space group $P21/c$ was checked as well, however, the structure did not refine to R values below 0.086. CCDC 217092. See http://www.rsc.org/suppdata/cc/b3/b315603f/ for crystallographic data in .cif or other electronic format.

[‡] Experimental details: ^{2}H NMR spectra were obtained on a Bruker AMX 300 spectrometer at a frequency of 46.07 MHz. A quadrupole echo sequence ($\tau = 20$ μs) was used, with a 90° pulse length of 4 μs and a repetition time of 2 s. TGA and DSC traces were obtained on a TA Instruments system, with temperature scanning rates of 5 or 10 °C min^{-1}.

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