Formation of tetrameric water clusters driven by a cavitand template

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Figure S1. a) Ortep view (20% ellipsoid probability) of the molecular structure of compound **Tiiii[H, CH₃, CH₃]·4H₂O** (1). Symmetry operations: (2) $\frac{1}{2}$ -x; $\frac{1}{2}$ -y; z. (3) $\frac{1}{2}$ -y; x; z. (4) y; $\frac{1}{2}$ -x; z. Only the hydrogen atoms involved in hydrogen bonds (dotted lines) are drawn; b) CPK top and side views of (1).

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Figure S2. a) Ortep view (10% ellipsoid probability) of the molecular structure of compound **Tiiii[H, CH₃, CH₃]·CH₃OH·4H₂O (2)**. Symmetry operations: (2) $\frac{1}{2}$ -x; $\frac{1}{2}$ -y; z. (3) $\frac{1}{2}$ -y; x; z. (4) y; $\frac{1}{2}$ -x; z. Only one of the four possible orientations of the methanol guest is shown. Hydrogen atoms are omitted for clarity; b) CPK top and side views of (2).





Figure S3. a) Ortep view (20% ellipsoid probability) of the molecular structure of compound Tiiii[H, CH₃, CH₃]·HOCH₂CH₂OH·4H₂O (3). The lattice dichloromethane molecule is omitted for clarity. Only the hydrogen atoms involved in hydrogen bonds (dotted lines) are drawn; b) CPK top and side views of (3).



Figure S4. Self-assembly of the **Tiiii[H, CH₃, CH₃]·CH₃OH·4H₂O** (2) complexes in the infinite up-up columnar arrangement running parallel to the crystallographic **c** axis. Each up-up column is surrounded by four nearest neighboring down-down parallel columns of complexes. Only relevant hydrogen atoms have been reported. Water molecules are represented as red balls.

Materials. The cavitand Tiiii[H,CH₃,CH₃] was prepared following a published procedure.¹

X-ray Crystallographic Studies. Crystal data and experimental details for data collection and structure refinement are reported in Table S1.

The crystal structures of compounds **1**, **2**, and **3** were determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at room temperature for **1** and **2** and at 173 K for **3** (due to the instability of the crystal at room temperature) on a Bruker AXS Smart 1000 single-crystal diffractometer (MoK_{α} radiation) equipped with a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.² The structures was solved by Direct Methods using the SIR97 program³ and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program.⁴

The PLATON SQUEEZE procedure⁵ was used for compound **3** to treat regions of diffuse solvent which could not be sensibly modelled in terms of atomic sites. Their contribution to the diffraction pattern was removed and modified F_o^2 written to a new HKL file. The number of electrons thus located, 80 per unit cell, are included in the formula, formula weight, calculated density, μ and F(000). This residual electron density was assigned to two molecules of dichloromethane solvent per unit cell (two molecules of dichloromethane would give 84 e).

All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry (C-H 0.95 Å) and refined "riding" on the corresponding parent atoms. The hydrogen atoms of the water molecules in compound **1** were found in the difference Fourier map. In compound **2**, the water and methanol hydrogen atoms could neither be found in the difference Fourier map nor calculated. In compound **3**, the hydrogen atoms of the ethylene glycol were calculated using the program implemented in WinGX based on the method of M. Nardelli.⁶ The water hydrogen were partly found in the difference Fourier map and partly calculated using the above mentioned program.

The weighting schemes used in the last cycle of refinement were $w = 1/[\sigma^2 F_o^2 + (0.0180P)^2]$, $w = 1/[\sigma^2 F_o^2 + (0.1008P)^2]$ and $w = 1/[\sigma^2 F_o^2 + (0.0671P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ for **1**, **2** and **3** respectively.

Molecular geometry calculations were carried out using the PARST97 program.⁷ Drawings were obtained by ORTEP3 in the WinGX suite.⁸

Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-737537 (1) -737538 (2) and -737539 (3) and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: <u>deposit@ccdc.cam.ac.uk</u>]

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Table S1. Crystal data and structure refinement information for compounds Tiiii[H, CH3, CH_3]· $4H_2O$ (1), Tiiii[H, CH3, CH_3]· CH_3OH · $4H_2O$ (2) and Tiiii[H, CH3, CH_3]· $HOCH_2CH_2OH$ · $4H_2O$ (3)

Compound	1	2	3
Formula	$C_{36}H_{44}O_{16}P_4$	$C_{37}H_{48}O_{17}P_4$	$C_{40}H_{54}O_{18}P_4Cl_4$
Molecular weight	856.59	888.63	1088.51
Crystal system	Tetragonal	Tetragonal	Triclinic
Space group	P4/n	<i>P</i> 4/n	<i>P</i> –1
<i>a</i> / Å	14.396(8)	14.352(2)	10.3676(4)
b / Å	-	-	13.1307(5)
<i>c</i> / Å	9.799(5)	9.822(2)	19.1132(8)
α / °	-	-	69.980(1)
β / °	-	-	88.713(1)
γ / °	-	-	82.935(1)
$V / Å^3$	2031(2)	2023.2(6)	2425.6(2)
Ζ	2	2	2
T / K	293(2)	293(2)	173(2)
ρ / g cm ⁻³	1.401	1.459	1.490
μ / mm^{-1}	0.256	0.262	0.448
<i>F</i> (000)	896	932	1132
Data / parameters	2354 / 140	2626 / 144	11553 / 611
Total reflections	11151	12598	25175
Unique reflections (R _{int})	2354 (0.0994)	2626 (0.0260)	11553 (0.0385)
Observed reflections $[I \ge 2\sigma(I)]$	1187	1836	7160
Goodness–of–fit on F^{2a}	1.006	1.008	0.998
R indices $[I \ge 2\sigma(I)]^{b}$ R1, wR2	0.0481, 0.0765	0.0467, 0.1417	0.0515, 0.1288
Largest diff. peak and hole / $e \hat{A}^{-3}$	0.423, -0.288	0.549, -0.228	0.709, -0.415

^aGoodness-of-fit S = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p the number of parameters. ^bR1 = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, wR2 = $[\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.

	H…Acceptor (Å)	Donor-H (Å)	Donor…Acceptor (Å)	Donor-H…Acceptor (°)
water/P=O	1.85(4)	0.99(4)	2.801(5)	159.4(9)
Water/water	2.05(4)	0.98(3)	2.858(5)	138.9(9)

Table S2. H-bonding in Tiiii[H, CH₃, CH₃]·4H₂O (1)

Table S3. H-bonding in Tiiii[H, CH₃, CH₃]·CH₃OH·4H₂O (2)

	H…Acceptor (Å)	Donor-H (Å)	Donor…Acceptor (Å)	Donor-H…Acceptor (°)
water/P=O			2.807(3)	
Water/water			2.916(5)	
guest/P=O			2.958(8)	
guest/water			2.796(9)	

Table S4. H-bonding in Tiiii[H, CH₃, CH₃]·HOCH₂CH₂OH·4H₂O (3)

	H…Acceptor (Å)	Donor-H (Å)	Donor…Acceptor (Å)	Donor-H…Acceptor (°)
water/P=O	1.97(3), 1.87(2)	0.90(3); 0.90(2)	2.817(3), 2.762(3)	154.7(9), 168.3(9)
water/water	1.85(1), 1.92(3), 1.93(5), 1.93(3)	0.91(1), 0.90(3) 0.90(5), 0.91(3)	2.758(4), 2.786(3), 2.820(5), 2.831(6)	175.2(9), 160.1(9), 166.2(9), 177.8(9)
guest/P=O	1.77(4), 1.72(5)	0.95(3), 0.96(5)	2.683(4), 2.662(3)	160.0(9), 168.8(9)
guest/water	1.79(1), 1.83(2)	0.91(1), 0.91(2)	2.692(4), 2.660(4)	172.2(9), 150.4(9)