Electronic Supplementary Information for:

Tetraphosphonate cavitands: Interplay between metal coordination and H-bonding in the formation of dimeric capsules

*By Monica Melegari,[a] Chiara Massera*[b], Franco Ugozzoli[b] and Enrico Dalcanale*[a]*

[a] Dipartimento di Chimica Organica e Industriale and INSTM, UdR Parma, Università di Parma, Viale G. P. Usberti 17/A, 43124 Parma, Italy. Fax: (+) 39-0521-905472. E-mail: enrico.dalcanale@unipr.it. Homepage: www.ssmg.unipr.it

[b] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale G. P. Usberti 17/A, 43124 Parma, Italy. Fax: (+) 39-0521-905557. E-mail: chiara.massera@unipr.it.

a)
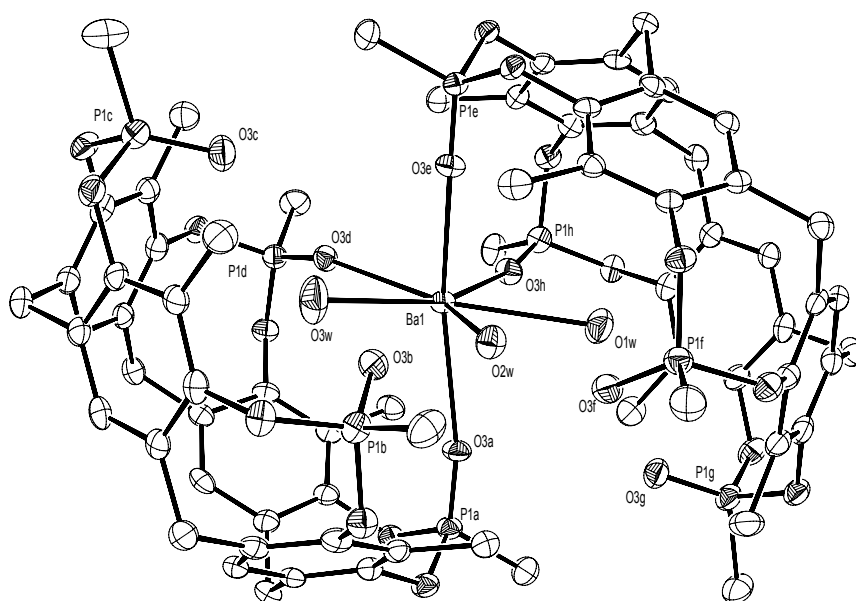
b)
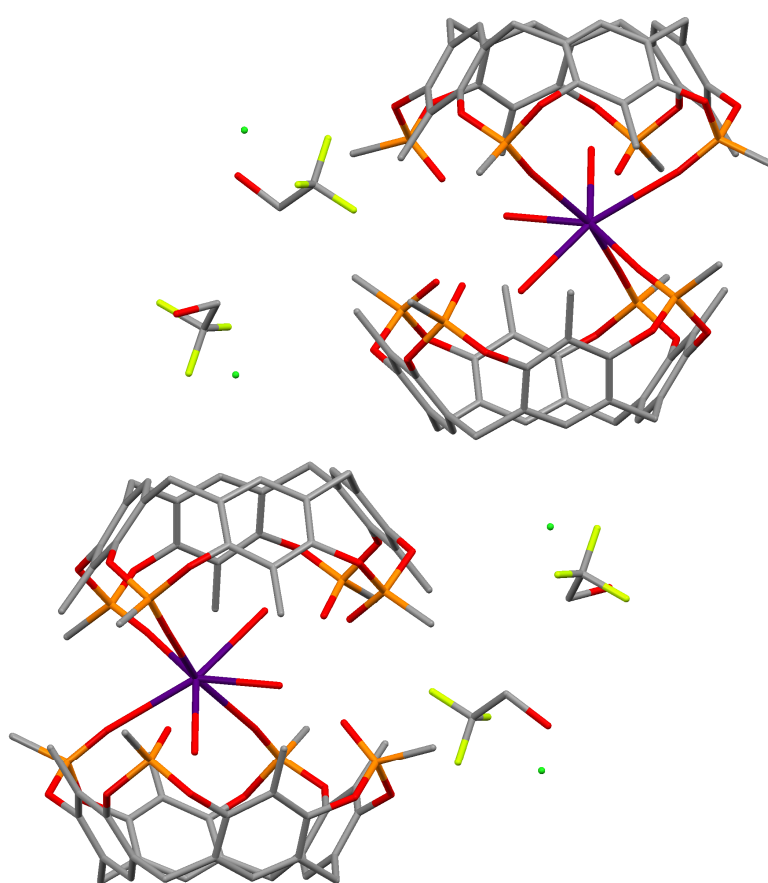
c)

Figure S1. a) Ortep view (20% ellipsoid probability) of the molecular structure of the cation **[(Cav)₂Ba(H₂O)₃]²⁺**. (Cav = Tiiii[H, CH₃, CH₃]). Hydrogen atoms are omitted for clarity; b) Stick model of the unit cell content. The two disordered trifluoroethanol (TFE) molecules treated with squeeze are not included; c) Crystal packing of the cation **[(Cav)₂Ba(H₂O)₃]²⁺** showing the two-dimensional layer formed through π-π stacking interactions.
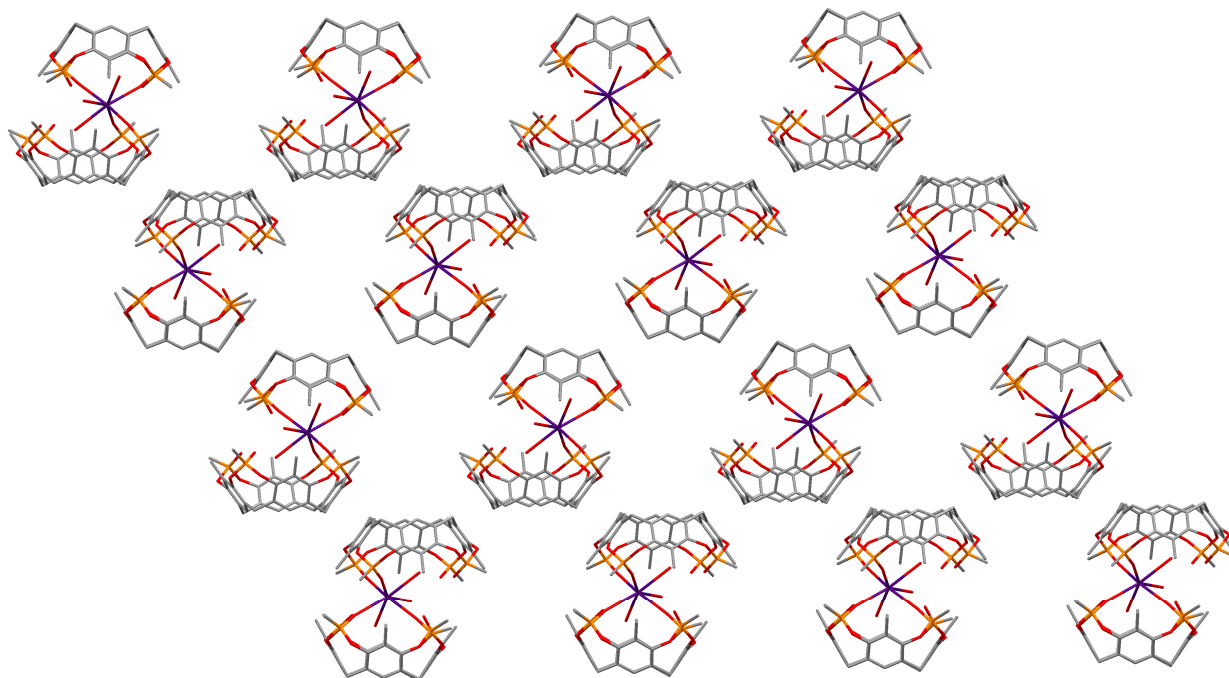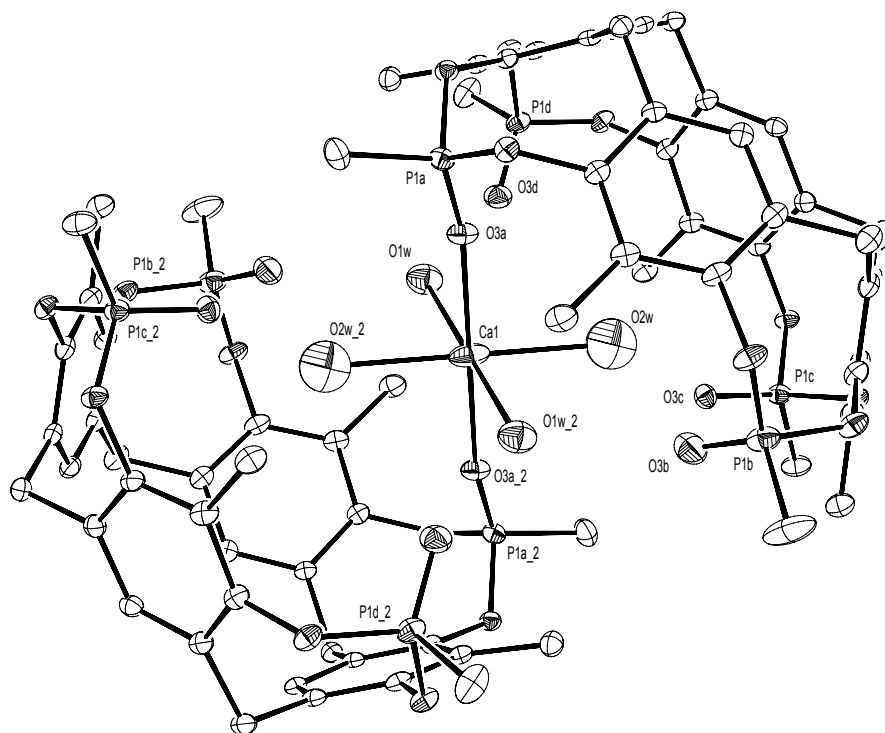
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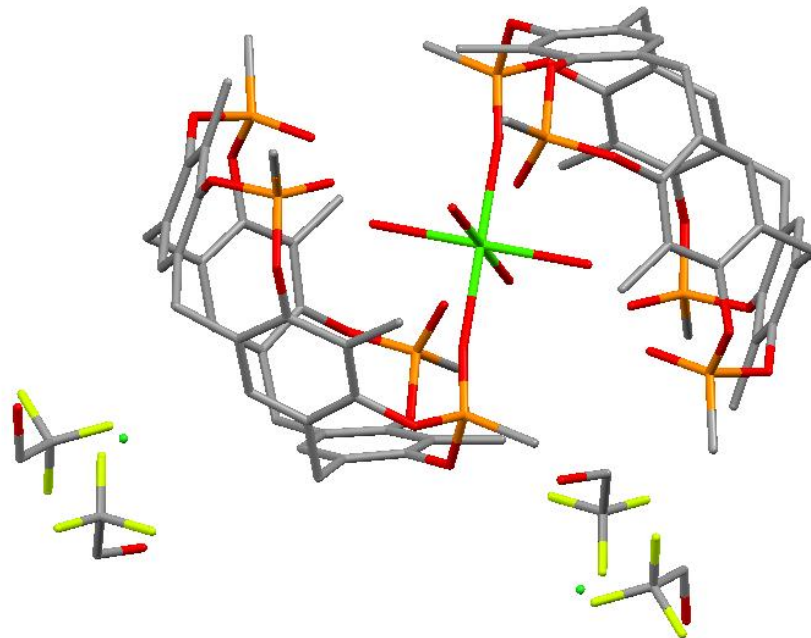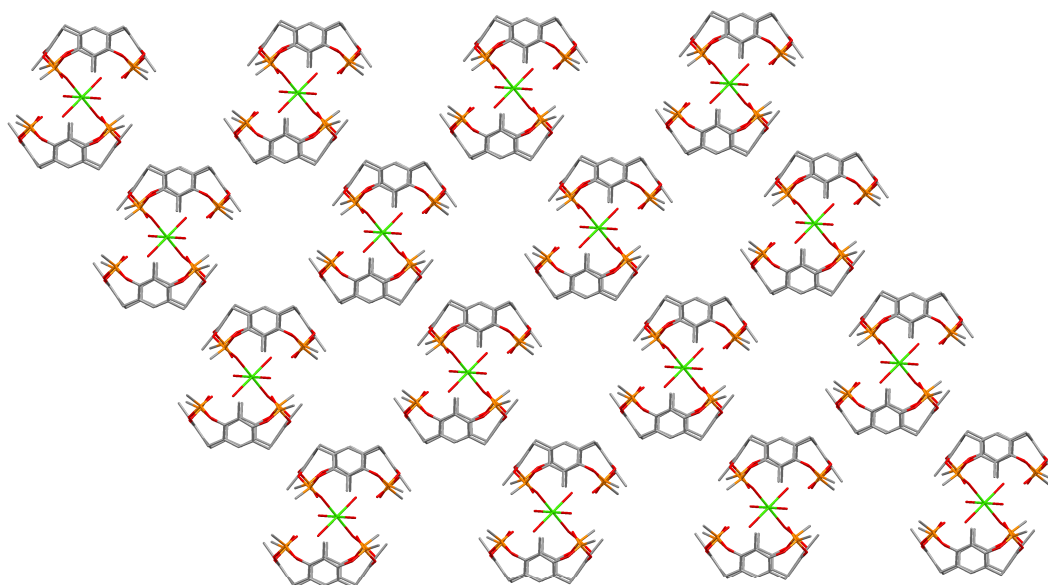

Figure S2. a) Ortep view (20% ellipsoid probability) of the molecular structure of the cation $[(Cav)_2Ca(H_2O)_4]^{2+}$. (Cav = Tiiii[H, CH$_3$, CH$_3$])**.** Symmetry operation _2: 1-x; -y; 1-z. Hydrogen atoms are omitted for clarity; b) Stick model of the unit cell content; c) Crystal packing of the cation $[(Cav)_2Ca(H_2O)_4]^{2+}$ showing the two-dimensional layer formed through π-π stacking interactions.

a)

b)

c)
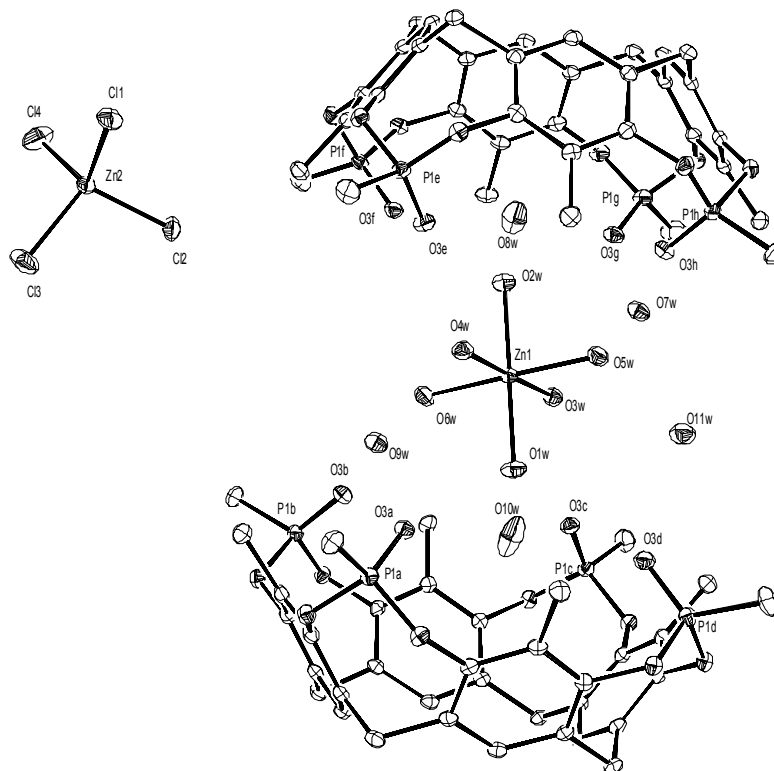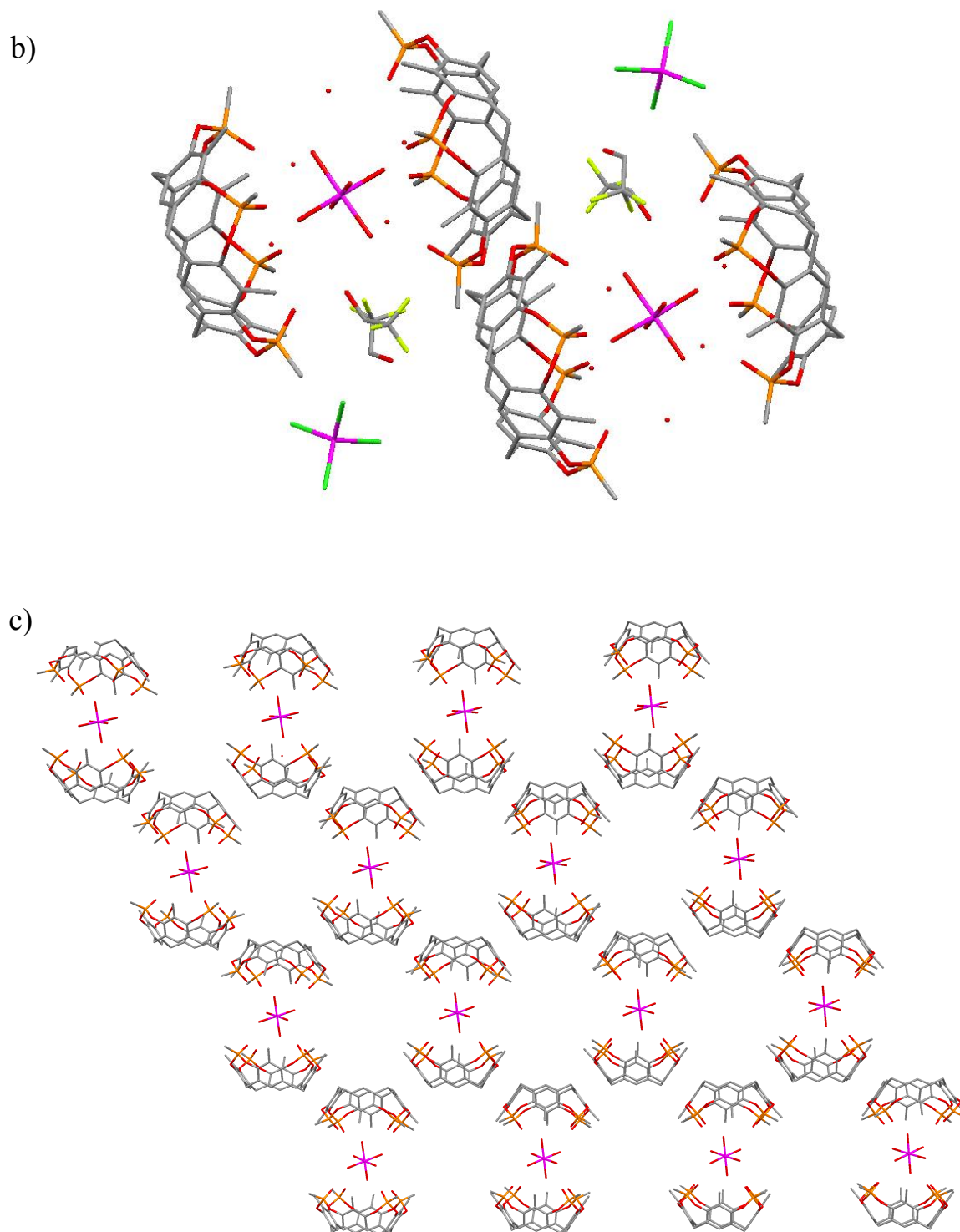
Figure S3. a) Ortep view (20% ellipsoid probability) of the molecular structure of the complex $\{[Zn(H_2O)_6](Cav)_2(H_2O)_5\}ZnCl_4$. (Cav = Tiiii[H, CH_3, CH_3]). Hydrogen atoms and lattice trifluoroethanol molecules are omitted for clarity; b) Stick model of the unit cell content. The three disordered trifluoroethanol (TFE) molecules treated with squeeze are not included; c) Crystal packing of the cation $\{[Zn(H_2O)_6](Cav)_2\}^{2+}$ showing the two-dimensional layer formed through π-π stacking interactions.

Materials. The cavitand Tiiii[H,CH$_3$,CH$_3$] was prepared following a published procedure.[1]
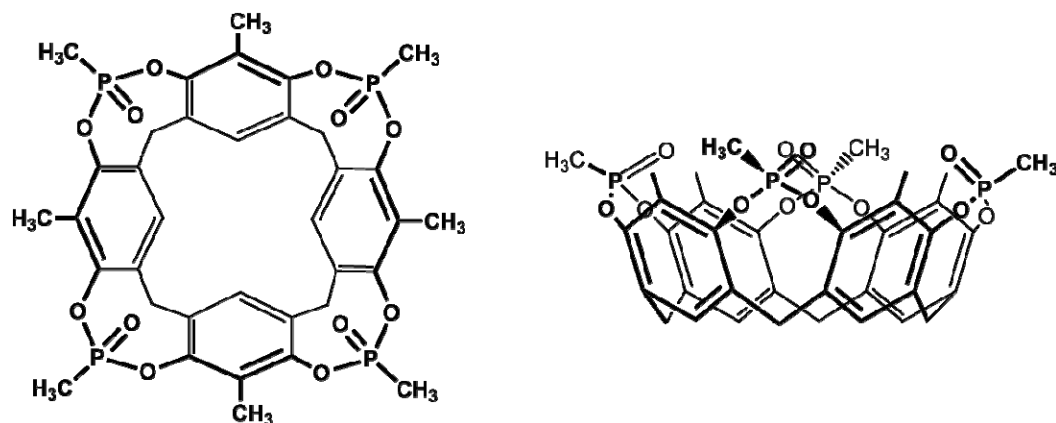
Scheme S1. Top and side views of the Tiiii[H,CH$_3$,CH$_3$] cavitand.

Experimental section.

Crystals of (**1**), (**2**) and (**3**) were obtained from slow evaporation of the corresponding solutions.

[(Cav)$_2$Ba(H$_2$O)$_3$]Cl$_2$·3TFE (1): To a solution of Tiiii[H,CH$_3$,CH$_3$] cavitand (10 mg, 0.0127 mmol) in 0.8 mL of TFE were added: *i*) 6.2 mg (0.0254 mmol) of BaCl$_2$·2H$_2$O dissolved in 0.2 mL of H$_2$O (metal:cavitand ratio 1:2); *ii*) 3.1 mg (0.0127 mmol) of BaCl$_2$·2H$_2$O dissolved in 0.2 mL of H$_2$O (metal:cavitand ratio 1:1); *iii*) 1.6 mg (0.00635 mmol) of BaCl$_2$·2H$_2$O dissolved in 0.2 mL of H$_2$O (metal:cavitand ratio 1:2).

[(Cav)$_2$Ca(H$_2$O)$_4$]Cl$_2$·4TFE (2): To a solution of Tiiii[H,CH$_3$,CH$_3$] cavitand (10 mg, 0.0127 mmol) in 0.5 mL of TFE were added: *i*) 5.6 mg (0.0254 mmol) of CaCl$_2$·6H$_2$O dissolved in 0.1 mL of H$_2$O (metal:cavitand ratio 2:1); *ii*) 2.8 mg (0.0127 mmol) of CaCl$_2$·6H$_2$O dissolved in 0.1 mL of H$_2$O (metal:cavitand ratio 1:1); *iii*) 1.4 mg (0.00635 mmol) of CaCl$_2$·6H$_2$O dissolved in 0.1 mL of H$_2$O (metal:cavitand ratio 1:2).

{[Zn(H$_2$O)$_6$](Cav)$_2$(H$_2$O)$_5$}ZnCl$_4$·5TFE (3): To a solution of Tiiii[H,CH$_3$,CH$_3$] cavitand (10 mg, 0.0127 mmol) in 0.8 mL of TFE were added: *i*) 3.5 mg (0.0254 mmol) of ZnCl$_2$ dissolved in 0.2 mL of H$_2$O (metal:cavitand ratio 1:2); *ii*) 1.7 mg (0.0127 mmol) of ZnCl$_2$ dissolved in 0.2 mL of H$_2$O (metal:cavitand ratio 1:1); *iii*) 0.9 mg (0.00635 mmol) of ZnCl$_2$ dissolved in 0.2 mL of H$_2$O (metal:cavitand ratio 1:2).

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 **[(Cav)$_2$Ba(H$_2$O)$_3$]Cl$_2$·3TFE (1)**, **[(Cav)$_2$Ca(H$_2$O)$_4$]Cl$_2$·4TFE (2)**, and **{[Zn(H$_2$O)$_6$](Cav)$_2$(H$_2$O)$_5$}ZnCl$_4$·5TFE (3)** were determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at room temperature for **1** on a Bruker Apex II single crystal diffractometer, and at 173 K for **2** and **3** on a Bruker AXS Smart 1000 single-crystal diffractometer (employing a MoK$_\alpha$ radiation and a CCD area detector in all the three cases). The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[2] The structures were solved by Direct Methods using the SIR97 program[3] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program.[4]

The PLATON SQUEEZE procedure[5] was used for compounds **1** and **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 per unit cell thus located, 130 for compound **1** and 330 for compound **3,** are included in the formula, formula weight, calculated density, μ and F(000). This residual electron density was assigned to two molecules of trifluoroethanol in compound **1** and to six molecules of trifluoroethanol in compound **3**.

All non-hydrogen atoms were refined with anisotropic atomic displacements with the exception of two water molecules in **2** and of some TFE atoms in compounds **1** and **3**. The hydrogen atoms were included in the refinement at idealized geometry (C-H 0.95 Å) and refined "riding" on the corresponding parent atoms. In all the complexes the hydrogen atoms of the water molecules and of the alcoholic group of the TFE solvents could neither be calculated nor located in the difference Fourier map

The weighting schemes used in the last cycle of refinement were $w = 1/ [\sigma^2 F_o^2 + (0.0982P)^2]$, $w = 1/ [\sigma^2 F_o^2 + (0.0857P)^2]$ and $w = 1/ [\sigma^2 F_o^2 + (0.1183P)^2]$, 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.[6] Drawings were obtained using ORTEP3 in the WinGX suite[7] and Mercury.[8]

Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-xxxxxx (**1**) –xxxxxxx (**2**) and –xxxxxx (**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: deposit@ccdc.cam.ac.uk]

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7   ORTEP3 for Windows - L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

8   Mercury CSD 2.2 (Build RC5)

Table S1. Crystal data and structure refinement information for compounds **[(Cav)$_2$Ba(H$_2$O)$_3$]Cl$_2$·3TFE** **(1)**, **[(Cav)$_2$Ca(H$_2$O)$_4$]Cl$_2$·4TFE** **(2)** and **{[Zn(H$_2$O)$_6$](Cav)$_2$(H$_2$O)$_5$}ZnCl$_4$·5TFE** **(3)** (Cav = Tiiii[H, CH$_3$, CH$_3$]; TFE = trifluoroethanol).

Compound	**1**	**2**	**3**
Formula	C$_{78}$H$_{87}$O$_{30}$P$_8$F$_9$Cl$_2$Ba	C$_{80}$H$_{92}$O$_{32}$P$_8$F$_{12}$Cl$_2$Ca	C$_{82}$H$_{109}$O$_{40}$P$_8$F$_{15}$Cl$_4$Zn$_2$
Molecular weight	2131.48	2152.28	2539.99
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a / Å	12.695(3)	12.664(2)	12.784(1)
b / Å	17.501(5)	13.967(2)	18.154(1)
c / Å	23.862(6)	16.164(2)	26.277(1)
α / °	89.857(5)	106.558(2)	78.801(1)
β / °	77.873(5)	112.004(2)	83.730(1)
γ / °	69.836(5)	97.153(3)	70.891(1)
V / Å^3	4813(2)	2453.5(6)	5645.6(5)
Z	2	1	2
T / K	293(2)	173(2)	173(2)
ρ / g cm^{-3}	1.471	1.457	1.526
μ / mm^{-1}	0.693	0.349	0.737
F(000)	2172	1110	2608
Data / parameters	13929 / 1051	11663 / 611	26852 / 1209
Total reflections	45305	30502	71418
Unique reflections (R$_{int}$)	1051 (0.0813)	11663 (0.0629)	26852(0.0304)
Observed reflections [$I>2\sigma(I)$]	8821	5815	17102
Goodness–of–fit on F^{2a}	1.003	1.001	0.998
R indices [$I>2\sigma(I)$]^b R1, wR2	0.0642, 0.1642	0.0730, 0.1974	0.0516, 0.1460
Largest diff. peak and hole / eÅ^{-3}	0.940, -0.608	1.383, -0.905	1.833, -0.955

[a]Goodness-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. [b]R1 = $\Sigma \|F_o\|-\|F_c\|/\Sigma\|F_o\|$, wR2 = $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2. H-bonding in (**1**) **[(Cav)$_2$Ba(H$_2$O)$_3$]Cl$_2$·3TFE**

	Donor···Acceptor (Å)
O1W···O3G	2.850(9)
O2W···O3B	2.726(7)
O2W···O3F	2.813(7)
O3W···O3B	3.001(8)
Cl1···O2S	3.096(9)
Cl2···O1S	2.962(9)

Table S3. H-bonding in (**2**) **[(Cav)$_2$Ca(H$_2$O)$_4$]Cl$_2$·4TFE**

	Donor···Acceptor (Å)
O1W···O3D	2.667(6)
O1W···O3B[a]	2.718(7)
O2W···O3C	2.826(7)
Cl1···O1S	2.967(6)
Cl1···O2S	3.013(5)

[a]: 1-x, -y, 1-z

Table S4. H-bonding in **{[Zn(H₂O)₆](Cav)₂(H₂O)₅}ZnCl₄·5TFE (3)**

	Donor···Acceptor (Å)
O1W···O3C	2.744(3)
O1W···O10W	2.598(5)
O2W···O3E	2.833(3)
O2W···O8W	2.603(5)
O3W···O3C	2.856(3)
O3W···O7W	2.735(3)
O4W···O3E	2.822(4)
O4W···O9W	2.664(3)
O5W···O3H	2.768(3)
O5W···O11W	2.808(5)
O6W···O3B	2.850(3)
O6W···O1S	2.732(4)
O7W···O3G	2.820(4)
O7W···O3H	2.824(3)
O8W···O3F	2.893(4)
O8W···O3G	2.911(4)
O9W···O3A	2.841(4)
O9W···O3B	2.872(3)
O10W···O3A	2.807(6)
O10W···O3D	2.768(4)
O11W···O3D	2.780(4)
O11W[a]···Cl4	3.187(3)
O1S···O3F	2.685(4)
O2S···Cl2	3.233(6)

[a]: x, 1+y, z