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Encapsulation of tetramethylphosphonium cations

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The weak interactions and capsule formation of tetramethylphosphonium (TMP) cation with resorcinarenes **1** and **2** and the corresponding pyrogallarenes **3** and **4** were studied in the solid state by single-crystal X-ray diffraction, in solution by NMR and in the gas phase by mass spectrometry. In methanol-d_4, the NMR titration studies reveal that the association constants for the 1:1 complexes of TMP@**3** and TMP@**4** are much higher (TMP@**4**:390 ± 37 M^{-1}) than for the corresponding TMP@**1** and TMP@**2** (TMP@**2**:130 ± 10 M^{-1}) complexes. In the gas phase both monomeric 1:1 TMP@**1**-TMP@**4** complexes as well as the dimeric 1:2 capsule complexes, TMP@$\mathbf{1}_2$–TMP@$\mathbf{4}_2$ were observed. The 1:1:2 molar mixtures of **1**:**2**:TMP or **3**:**4**:TMP resulted in homo- and heterocapsules TMP@$\mathbf{1}_2$, TMP@**1** + **2** and TMP@$\mathbf{2}_2$, with the expected statistical 1:2:1 ratio. Using the 1:1:2 ratio of **1**:**3**:TMP, **1**:**4**:TMP, **2**:**3**:TMP or **2**:**4**:TMP showed a marked prefence to the homopyrogallarene capsules TMP@$\mathbf{3}_2$ and TMP@$\mathbf{4}_2$, thus supporting the stronger complexation of TMP with **3** and **4** as observed in solution. The X-ray structures[1] confirmed the dimeric capsular structures with only minor structural differences to the corresponding tetramethylammonium (TMA) capsules reported earlier.

Keywords: supramolecular chemistry; resorcinarenes; capsules; X-ray crystallography; mass spectrometry

Introduction

For many years, self-assembling, reversibly hydrogen-bonded capsules (*1*) have contributed a great deal to our current understanding of enzyme action. Considerable interest has been focused on the design and synthesis of biomimetic receptors. In order to achieve convergent arrangement of binding sites, many of these receptors have utilised the cone shape of the resorcinarenes and pyrogallarenes for a variety of applications (*2*). The easy large-scale preparations of these compounds makes them very attractive building blocks in supramolecular chemistry (*3*).

Resorcinarenes and pyrogallarenes have the ability to easily form molecular capsules via hydrogen-bonded networks. Open inclusion complexes (*4*), dimers (*5*), hexamers (*3a*, *6*), larger supramolecular (*2b*) and tubular (*2b*, *7*) assemblies linked together by hydrogen bonding with cavities aimed at trapping cationic (*4b*, *5*) and neutral (*2c*, *8*) guests. Recently, anion complexation using resorcinarene-based cavitand has been reported (*9*). Ammonium cations have proved to be good guest candidates for resorcinarene complexation since they have the possibility to interact via cation$\cdots\pi$ and C—H$\cdots\pi$ interactions as well as advantageously fill the empty space in the hollow cavity of the resorcinarene host (*5*). Under neutral conditions, closer to the biological environment, the binding of quaternary alkyl ammonium cations is significantly weakened compared with complexation in alkaline solvents (*10*). Mass spectrometry (*11*) is an important tool to examine binding interactions of cations in the gas phase. It has the advantage of proving the complexation without solvent interference. Dimeric (*5a*) and hexameric (*6d*) capsules of resorcinarenes, pyrogallarenes and related compounds encapsulating small and large cations have been shown to prevail in the gas phase (*12*) without solvent mediation and have been predicted to be directly hydrogen bonded.

Our aim was to probe other cationic species that could act in a way similar to the tetraalkylammonium cations extensively studied by us (*5a–g*). Previously, Rebek et al. (*13*) showed the complexation of tetramethylphosphonium (TMP) cation by resorcinarenes and pyrogallarenes in solution. The longer P—C bond length compared to the C—N bond increases the volume of the TMP cation to 115 Å^3 from the 105 Å^3 of that of tetramethyl ammonium (TMA) cation. The softer nature of the phosphorous atom and the slightly larger size could lead to different complexation behaviour with resorcinarenes and pyrogallarenes. Thus, we report herein the examples of the complexation and capsule formation of TMP cation with core resorcinarenes and pyrogallarenes in the solid state supplemented by complexation studies in solution by NMR and in the gas phase by MS. In the gas phase, competition studies reveals the formation of heterodimers

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and showed that the complexation/encapsulation of TMP with pyrogallarenes is markedly more efficient than with resorcinarenes.

Results and discussion

X-ray structures

The solid-state complexation and encapsulation properties of the alkyl resorcinarenes **1** and **2,** as well as pyrogallarenes **3** and **4**, with TMP cation **5** (Figure 1) were investigated in crystallisation studies from aqueous methanol solution using a 1:2 guest to host molar ratio. We were able to obtain capsules for single-crystal X-ray determination from resorcinarenes **1** and **2** with tetramethylphosphonium bromide **5b**. All solid-state complexation experiments with pyrogallarenes **3** and **4** or with the tetramethylphosphonium chloride **5a** resulted in a microcrystalline powder precipitate.

In the capsule, $\mathbf{5}^{+}@\mathbf{1}_2 \cdot Br^{-} \cdot 16H_2O$, two molecules of **1** are linked via water molecules and, as expected, the cation $\mathbf{5}^{+}$ is encapsulated inside the cavity formed by the two resorcinarene hosts (Figure 2). However, the disorder of the TMP is very severe that definite conclusions about its orientation and possible interactions with the host could not be made. As with other C2 resorcinarene capsules (*5d*), the bromide anion is found to reside in the small pocket between the ethyl groups of the host via weak C—H···anion interactions. The encapsulation of the spherical cation and the location of the anion is very similar to that observed by us within the eclipsed $TMA@\mathbf{1}_2 \cdot Br^{-} \cdot 8MeOH$ (*5d*) capsule complex. The dimensions of the corresponding TMA capsule are very similar to the TMP capsule reported here. Table 1 lists the values of the capsular dimensions for four TMP and TMA capsules.

As in $\mathbf{5}^{+}@\mathbf{1}_2 \cdot Br^{-} \cdot 16H_2O$, the methanol molecules in the capsule $\mathbf{5}^{+}@\mathbf{2}_2 \cdot Br^{-} \cdot 4MeOH$ mediated the capsule formation (Figure 3). The encapsulated TMP cation inside

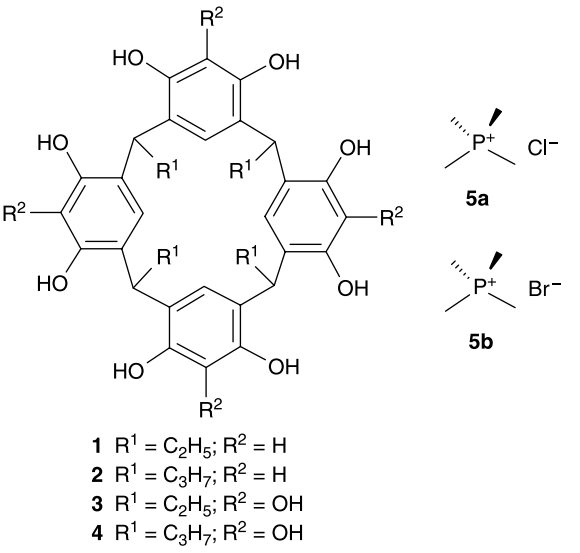

Figure 1. Hosts **1–4** and cationic guests **5a** and **5b**.

the cavity is also severely disordered. In addition to solvent molecules, the capsule is also mediated by Br^{-} anions. This is similar to the eclipsed $TMA@\mathbf{2}_2 \cdot Cl^{-} \cdot 4MeOH$, $TMA@\mathbf{2}_2 \cdot Cl^{-} \cdot 4EtOH$ and $TMA@\mathbf{2}_2 \cdot Br^{-} \cdot 4EtOH$ capsules reported earlier by us (*5d*). The capsule $\mathbf{5}^{+}@\mathbf{2}_2 \cdot Br^{-} \cdot 4MeOH$ resembles more the previously reported ethanol-mediated capsules having similar crystallographic parameters (space group, cell dimensions, etc.) than the C2 resorcinarene TMP capsule $\mathbf{5}^{+}@\mathbf{1}_2 \cdot Br^{-} \cdot 16H_2O$ shown in Figure 2. The distance between resorcinarene moieties in $\mathbf{5}^{+}@\mathbf{2}_2 \cdot Br^{-} \cdot 4MeOH$ is also slightly longer (0.25–0.51 Å) when compared with the mentioned TMA capsules, but otherwise the capsule dimensions are similar (Table 1). Due to the different location of the bromine anions within the capsules, the ion pair (TMP^{+} and Br^{-}) is slightly more separated in the C2 than in the C3 capsule (Table 1).

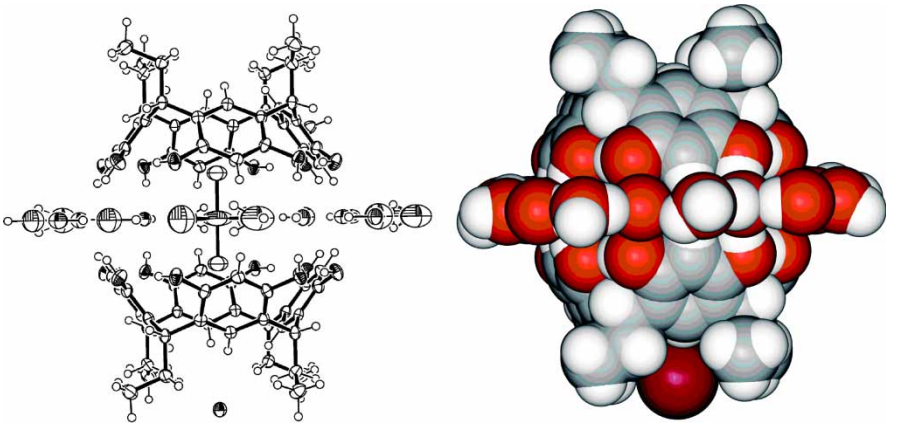

Figure 2. Ortep and CPK plots of the X-ray structure of hydrogen-bonded solvent–anion-mediated resorcinarene capsule $\mathbf{5}^{+}@\mathbf{1}_2 \cdot Br^{-} \cdot 16H_2O$.

Table 1. The dimension for TMP and TMA (*5d*) capsules.

Capsule	TMP@ $\mathbf{1}_2 \cdot Br^- \cdot 16H_2O$	TMA@ $\mathbf{1}_2 \cdot Br^- \cdot 8MeOH$	TMP@ $\mathbf{2}_2 \cdot Br^- \cdot 4MeOH$	TMA@ $\mathbf{2}_2 \cdot Br^- \cdot 4EtOH$
Capsule mediating hydrogen bonds to solvents (Å)	2.68–2.72	2.67–2.69	2.68–2.96	2.66–2.75
Capsule mediating hydrogen bonds to Br^- (Å)	–	–	3.15	3.23, 3.25
Distance between the capsule halves (Å)[a]	9.00	8.86	8.85	8.59
Distance between the centroids of opposite aromatic rings of a resorcinarene molecule (Å)	6.85	6.87	6.84/6.94	6.79/6.97
Capsule conformation	Eclipsed	Eclipsed	Eclipsed	Eclipsed
Closest P/N···Br distance (Å)	7.69	7.76	6.47	7.07

[a] Defined as a distance between the planes formed by the methine bridges of the resorcinarenes.

NMR and mass spectrometric studies

Significant complexation-induced upfield shifts of the guest signals were observed when resorcinarene **2** and pyrogallarene **4** were mixed with **5a** or **5b** in methanol-d_4 similar to that reported by Rebek et al. (*13*). The titration data clearly support a fast guest exchange compared with the NMR time scale at 303 K with a 1:1 complexation model in methanol-d_4 determined by Job plot (*14*) experiments. The efficiency with which the solvent competes with the hydrogen bonding system of the host, how it competes with the TMP cation in the inclusion to the host cavity and the fact that methanol very efficiently solvates the ion pair explains well why the possible 1:2 dimeric capsule complex is not formed in dilute solutions at 303 K. The association constants for $\mathbf{5}^+$ at 303 K for hosts **2** and **4** were determined to be 130 ± 10 and $390 \pm 37\,M^{-1}$, respectively, by the nonlinear least-squares fitting of the titration curve (*15*). The association constants of the pyrogallarene were much higher than that with the respective resorcinarene as expected due to the more π-basic character of the pyrogallarenes.

Mass spectrometric studies of complexes of resorcinarenes with singly charged alkyl ammonium cations showed that the dimeric molecular capsules of resorcinarene also exist in the gas phase (*5d*, *f*). For electrospray ionisation, solution of **5a** and **5b** with the corresponding resorcinarenes and pyrogallarenes were used. The base peaks corresponding to the open monomeric inclusion complexes of resorcinarene $[\mathbf{5@1}]^+$ (*m*/*z* 691), $[\mathbf{5@2}]^+$ (*m*/*z* 747) and pyrogallarenes $[\mathbf{5@3}]^+$ (*m*/*z* 755), $[\mathbf{5@4}]^+$ (*m*/*z* 811) were easily detected. Without solvent interference in the ion source of the instrument, dimeric capsules containing the TMP guests as $[\mathbf{5@1}_2]^+$ (*m*/*z* 1291) and $[\mathbf{5@2}_2]^+$ (*m*/*z* 1403) for the resorcinarenes and $[\mathbf{5@3}_2]^+$ (*m*/*z* 1419) and $[\mathbf{5@4}_2]^+$ (*m*/*z* 1531) for the pyrogallarenes were also observed. This is in line with earlier results using tetraalkylated ammonium cations (*5*) and TMP cation (*13*).

Upon mixing a 1:1 molar solution of **1** and **2**, heterodimers are quickly formed with $\mathbf{5}^+$ as the guest. Figure 4 depicts the region of the spectra in which the charged dimeric complexes $[\mathbf{5@1}_2]^+$ (*m*/*z* 691) and $[\mathbf{5@2}_2]^+$ (*m*/*z* 1291) appears. The spectra (a) and

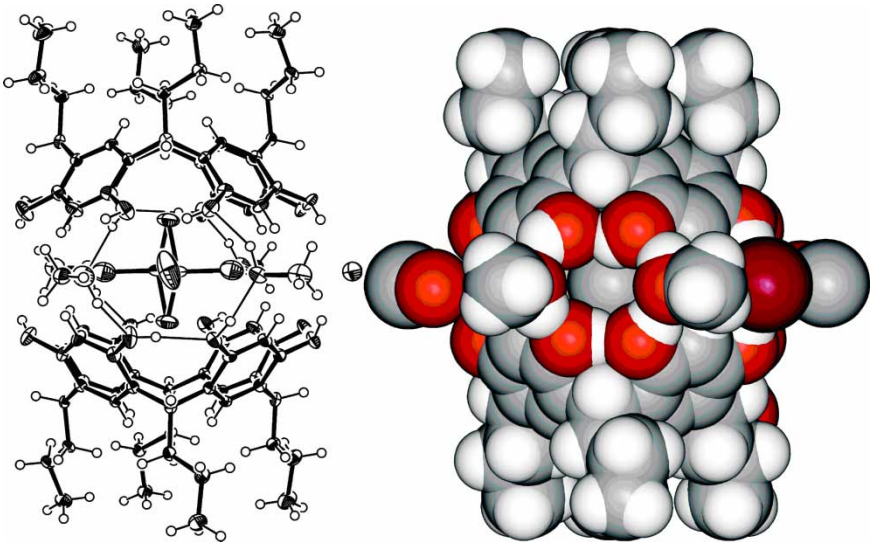

Figure 3. Ortep and CPK plots of the X-ray structure of hydrogen-bonded solvent–anion-mediated resorcinarene **2** capsule $\mathbf{5}^+@\mathbf{2}_2 \cdot Br^- \cdot 4MeOH$.

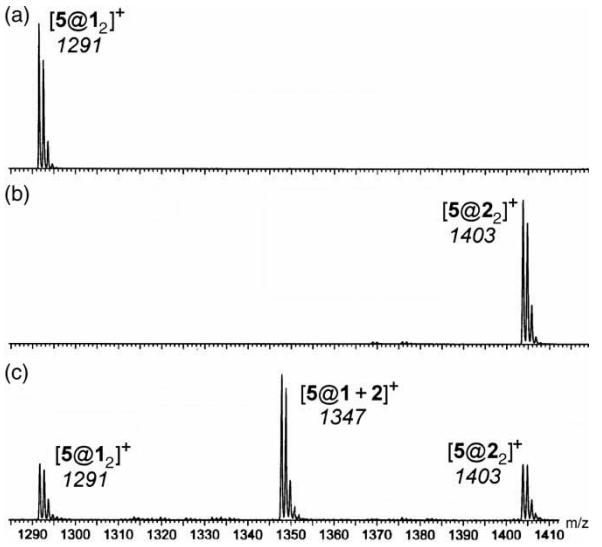

Figure 4. Partial ESI mass spectra of (a) $\mathbf{5}^+@\mathbf{1}_2$, (b) $\mathbf{5}^+@\mathbf{2}_2$ and (c) $\mathbf{5}^+$ with a 1:1 mixture of **1** and **2** in methanol. Heterodimer formation is clearly observed in the statistical 1:2:1 ratio.

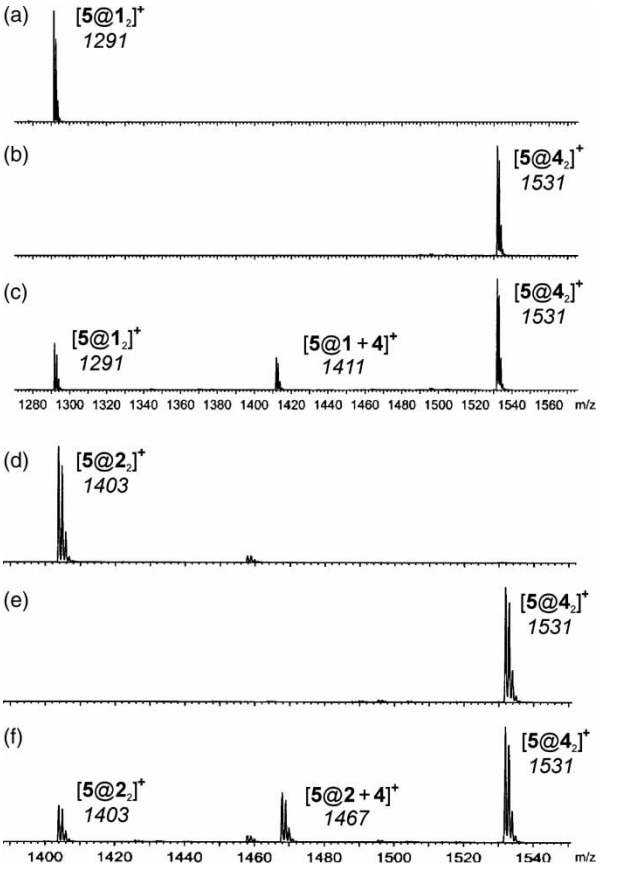

Figure 5. Partial ESI mass spectra of (a) $\mathbf{5}^+@\mathbf{1}_2$, (b) $\mathbf{5}^+@\mathbf{4}_2$ and (c) $\mathbf{5}^+$ with a 1:1 mixture of **1** and **4**, (d) $\mathbf{5}^+@\mathbf{2}_2$, (e) $\mathbf{5}^+@\mathbf{4}_2$ and (f) $\mathbf{5}^+$ with a 1:1 mixture of **2** and **4**. Heterodimer formation is clearly observed and it is seen that the dimer formation with pure pyrogallarene is more favoured.

(b) correspond to the two solutions before mixing and (c) corresponds to the two solutions after mixing. In (c), the two homodimers and the heterodimer $\mathbf{5}^+@\mathbf{1}+\mathbf{2}$ are formed with intensity distribution close to the statistically 1:2:1 ratio as expected. This is also similar when pyrogallarenes **3** and **4** are mixed in a 1:1 ratio (S6, supplementary material).

The difference in the complexation strength is evident when resorcinarene **1** or **2** is mixed together with pyrogallarene **3** or **4**, respectively, in the presence of **5a** or **5b**. The pyrogallarene homodimers $\mathbf{5}^+@\mathbf{3}_2$ and $\mathbf{5}^+@\mathbf{4}_2$ are markedly more favoured than the resorcinarene homodimers $\mathbf{5}^+@\mathbf{1}_2$ and $\mathbf{5}^+@\mathbf{2}_2$ or the heterodimers $\mathbf{5}^+@\mathbf{1}+\mathbf{4}$ and $\mathbf{5}^+@\mathbf{2}+\mathbf{4}$ (Figure 5). The biased equilibrium reflecting the difference in the stabilities of the 1:1 complexes is reached before the first MS spectrum can be recorded (ca. 30 s after mixing the two solutions of the resorcinarene and pyrogallarene complexes).

Conclusion

In conclusion, we have demonstrated that the complexation of TMP cation with resorcinarenes and pyrogallarenes behaves very similarly as the corresponding tetramethylammonium cation. The structural studies in the solid state, in solution and in the gas phase confirm the structures of the 1:1 open complexes in solution and gas phase and 1:2 dimeric capsules in solid state and in the gas phase. The complexation studies with NMR in methanol-d_4 revealed ca. three times more stable 1:1 complexes with pyrogallarenes when compared with corresponding resorcinarenes. The complexes in solution are all 1:1 at 303 K due to the fast exchange of the complexed guest and free guest at the NMR time scale. The 1:1 complex is the prerequisite for the capsule formation observed in the solid state and in the gas phase. Experiments aiming at the formation of heterodimers from two different homodimers in the gas phase clearly show the monomer exchange to be fast on the human time scale. It was also seen in the gas phase that the complexations with pyrogallarenes are more favoured.

General remarks

The resorcinarenes and pyrogallarenes were synthesised according to the reported procedures (*16*). The TMP salts were commercially available.

NMR titration

^{1}H NMR titrations were performed in methanol-d_4 by titrating 0.5 ml of a 0.002 M solution of the tetramethylphosphonium chloride or bromide salt with a 0.02 M solution of the resorcinarene or pyrogallarene. The ^{1}H NMR spectra of each titration step was measured on a 500 MHz Bruker Avance DRX spectrometer. Binding

constants were obtained by the nonlinear least-squares fitting of the titration curve.

ESI–TOF mass spectroscopy

The mass spectrometric experiments were performed with a Micromass LCT ESI–TOF instrument equipped with a *Z* geometry electrospray ion source. For positive ion spectra, the samples were introduced into the source as methanol solution mixtures of **1** (0.5 mM) and the salts of charged cations $\mathbf{5}^+$(0.5 mM) at flow rates of 30 μl min^{-1}. Constant spray and the highest intensities were achieved with a capillary voltage of 3885 V at a source temperature of 80°C and a dissolvation temperature of 120°C. Other selected source parameters were as follows: sample cone voltage 40–60 V; extraction cone voltage 5–6 V; flow of cone gas 101 h^{-1} and flow of dissolvation gas 1501 h^{-1}. Other parameters did not influence much the ion intensities. For the examination of heterodimer formation, two of the sample solutions were mixed in a 1:1 molar ratio and then subjected to the same experiments. Multiple scans (50–200) were recorded and averaged for each spectrum in order to improve the signal-to-noise ratio.

Crystal structures

Suitable single crystals for X-ray analysis were obtained from slow evaporation of resorcinarenes **1** or **2** and TMP bromide **5b** in water/methanol mixture. The X-ray crystallographic data for complexes were collected with Bruker Nonius Kappa APEX-II diffractometer at 123.0 ± 0.1 K using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). COLLECT (*17*) data collection software was utilised and data were processed with DENZO-SMN (*18*). The structures were solved by direct methods, using SIR-2002 (*19*), and refined on F^2, using SHELXL-97 (*20*). The reflections were corrected for Lorenz polarisation effects but absorption correction was not applied. Geometrical restraints (DFIX, DANG) were used to fix O—H distances and H—O—H angles in the refinement. The figures were drawn with ORTEP-3 for Windows (*21*) and MERCURY (*22*). The crystal data and other parameters are presented in Table 2.

The cation $\mathbf{5}^+$ in both structures is severely disordered and the determination of exact orientation of the cation inside the capsule was not possible. The hydrogen atoms were not determined for the cation. In $\mathbf{5}^+@\mathbf{1}_2 \cdot Br^- \cdot 16H_2O$, some water molecules are disordered over two sites. In $\mathbf{5}^+@\mathbf{2}_2 \cdot Br^- \cdot 4MeOH$, methanol molecules are also disordered. Half of the methanol molecules have two different orientations and the less occupied oxygen position was treated isotropically. Hydrogens located for water molecules and methanol hydroxyls were fixed to distances of 0.975 Å from oxygens with isotropic temperature factors (1.2 or 1.5 times the O temperature factor). All hydrogens for water and methanol molecules could not be determined. The other hydrogen atoms were calculated to their idealised positions with isotropic temperature factors (1.2 or 1.5 times the parent atom temperature factor) and refined as riding atoms.

Table 2. Crystal data and structure refinement parameters.

Capsule	$\mathbf{5}^+@\mathbf{1}_2 \cdot Br^- \cdot 16H_2O$	$\mathbf{5}^+@\mathbf{2}_2 \cdot Br^- \cdot 4MeOH$
Empirical formula	$C_{75}H_{96}BrO_{32}P$	$C_{27}H_{47}NO_4$
Formula weight	1620.40	449.66
Crystal system	Tetragonal	Triclinic
Space group	I4/m	$P-1$
a (Å), α (°)	14.2933(5), 90	13.2134(3), 105.766(1)
b (Å), β (°)	14.2933(5), 90	13.4323(2), 90.667(1)
c (Å), γ (°)	21.1417(8), 90	14.6404(3), 118.526(1)
Volume ($Å^3$)	4319.2(3)	2166.11(7)
Z	2	1
$Density_{calc}$ (mg/m^3)	1.246	1.218
Absorption coefficient (mm^{-1})	0.573	0.560
F(000)	1704	844
θ range (°)	3.22–25.01	2.49–25.00
Index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-22 \le l \le 25$	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	13356	13432
R_{int}	0.0841	0.0331
Data/restraints/parameters	1954/8/152	7603/2/530
Goodness of fit on F^2	1.061	1.034
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0728$, $wR_2 = 0.1870$	$R_1 = 0.1031$, $wR_2 = 0.2947$
R indices (all data)	$R_1 = 0.0980$, $wR_2 = 0.2069$	$R_1 = 0.1273$, $wR_2 = 0.3180$
Largest diffraction peak and hole ($eÅ^{-3}$)	0.73 and −0.53	0.84 and −2.71[a]

[a] Close to Br1.

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Note

1. Crystallographic data for structures $\mathbf{5}^{+}@\mathbf{1}_2 \cdot Br^{-} \cdot 16H_2O$ and $\mathbf{5}^{+}@\mathbf{2}_2 \cdot Br^{-} \cdot 4MeOH$ have been deposited with the Cambridge Crystallographic Data Centre as CCDC 687169 and 687170. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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