

# Bi-Layer Complexes Incorporating Large Organic Cations and Anionic Tetra-*p*-Sulfonated Calix[4]arene Capsules

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$\text{H}_4\text{TMTAA}^{2+}/18\text{-crown-6}$ ,  $\text{H}_4\text{TMTAA}^{2+}/2\text{-hydroxybenzimidazole}$  and  $\text{cyclamH}_4^{4+}$  self-assemble with sodium tetra-*p*-sulfonated calix[4]arene to form capsules within overall bilayer structures.  $[\text{H}_4\text{TMTAA}^{2+}]_2[\text{trans-}\{\text{Na}^+\text{C}(18\text{-crown-6})(\text{H}_2\text{O})_2\}\text{C}\{(p\text{-O}_3\text{S-calix[4]arene})_2\} + 3\text{H}^+]\cdot 17\text{H}_2\text{O}$  crystallises in the triclinic space group  $P\bar{1}$  and contains the "Russian Doll" assembled superanion capsule,  $\{\text{Na}^+\text{C}(18\text{-crown-6})(\text{OH}_2)_2\}\text{C}\{(p\text{-O}_3\text{S-calix[4]arene})_2\}^{7-}$ .  $[\text{H}_4\text{TMTAA}^{2+}]_2[(\text{C}_7\text{N}_2\text{OH}_7^+)_2\text{C}\{(p\text{-O}_3\text{S-calix[4]arene})_2\} + 2\text{H}^+]\cdot 17\text{H}_2\text{O}$  also crystallises in the

triclinic space group  $P\bar{1}$  and also contains a superanion capsule with two 2-hydroxybenzimidazolium cations as the capsule core.  $[\text{cyclamH}_4^{4+}][\{\text{cyclamH}_4^{4+}\}\text{C}\{(p\text{-O}_3\text{S-calix[4]arene})_2\}]\cdot 18\text{H}_2\text{O}$  crystallises in the space group  $P2_1/n$  and is an example of a slipped capsule, with the slight "mismatch" allowing stronger internal capsule H-bonding. The cations influence the spacing between the bilayers and can span the calixarene layers.

## Introduction

Capsules based on two *p*-sulfonatocalix[*n*]arenes shrouding other molecules including 18-crown-6<sup>[1–4]</sup> and protonated cyclam<sup>[5]</sup> ( $n = 4$ ) and  $\text{H}_2\text{SO}_4$  ( $n = 5$ ),<sup>[6]</sup> have recently been established. In the solid state these capsules ( $n = 4$ ) have host-guest hydrophobic complementarity and hydrogen bonding mediated by a variety of inorganic cationic species including lanthanide cations,<sup>[7]</sup> aluminium(III)/Keggin ions,<sup>[3]</sup> chromium(III)<sup>[1,4]</sup> and rhodium(III)<sup>[3]</sup> polynuclear oxo/hydroxo cations. Some of these complexes take on a bi-layer structure with an adjacent calix[4]arene from different capsules, with alternating H-bonding and  $\pi$ -stacking in opposite directions, as shown in cartoon form for  $\text{trans-}\{\text{Na}^+\text{C}(18\text{-crown-6})(\text{H}_2\text{O})_2\}$  in Figure 1.<sup>[1,8a–8g]</sup> Other examples of the bilayer structures represent "slipped" capsules (a misalignment of the calixarenes), which in some cases allows one sulfonate group to be in or over the cavity of the other calixarene, and vice versa, through to a complete mismatch of the calixarenes in opposing layers. Generally the inorganic ions stabilise the capsule by H-bonding and reside in the hydrophilic layers in the complexes. The 18-crown-6-containing capsules held together by the dimeric and trimeric oxo-chromium cations are located in a considerably distorted bilayer arrangement.<sup>[2]</sup> The Keggin ion complexes completely disrupt the bilayer structure with the presence of two types of calixarenes.<sup>[4]</sup> The large cation,  $\text{La}^{3+}$ , also completely disrupts the bi-layer structure.<sup>[7]</sup> Herein we report the use of large organic cations,  $\text{H}_4\text{TMTAA}^{2+}$  ( $\text{TMTAAH}_2 = 5,7,12,14\text{-tetramethyldibenzo}[b,i][1,4,8,11]\text{tetraazacyclotetradecane}$ ) and  $\text{cyclamH}_4^{4+}$ ,

tetra-protonated 1,4,8,11-tetraazacyclotetradecane, to assembly a variety of capsules based on the assembly of two tetra-*p*-sulfonatocalix[4]arenes.

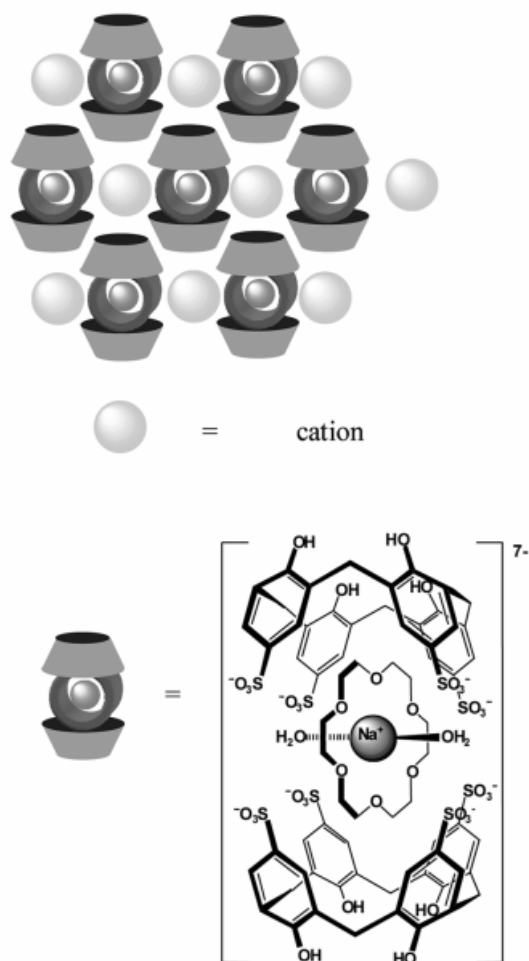


Figure 1. Cartoon of the bi-layer assembly of *p*-sulfonatocalix[4]arene capsules

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## Results and Discussion

The synthesis of the new capsule-type complexes (Figure 2) is summarised in Scheme 1. For compounds  $[\text{H}_4\text{TMTAA}^{2+}]_2[\text{trans-}\{\text{Na}^+\text{C}(\text{18-crown-6})(\text{H}_2\text{O})_2\}\text{C}\{\text{p-O}_3\text{S-calix[4]arene}\}_2\} + 3\text{H}^+\cdot 17\text{H}_2\text{O}$  (**1**) and  $[\text{H}_4\text{TMTAA}^{2+}]_2[(\text{C}_7\text{N}_2\text{OH}_7^+)_2\text{C}\{\text{p-O}_3\text{S-calix[4]arene}\}_2\} + 2\text{H}^+\cdot 17\text{H}_2\text{O}$  (**2**), the products are also contaminated with 2,4-dimethyl-1,5-benzodiazepinium chloride due to acid decomposition of  $\text{H}_4\text{TMTAA}^{2+}$ . Compound **1** crystallises in

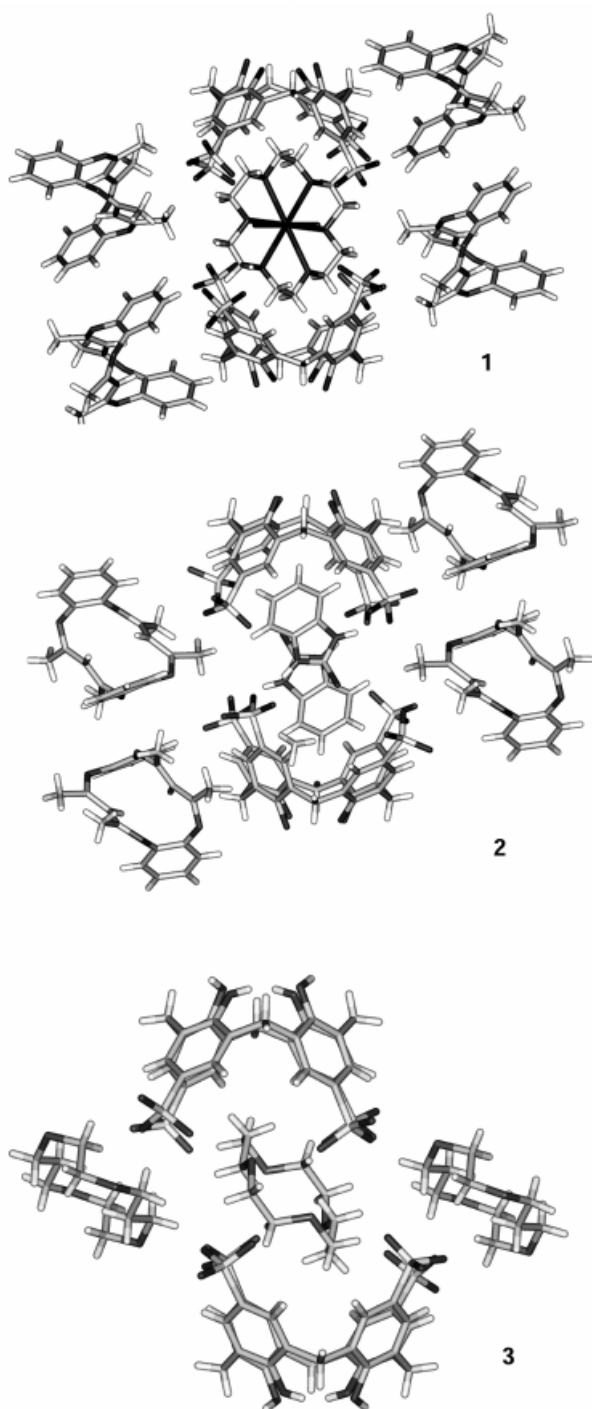


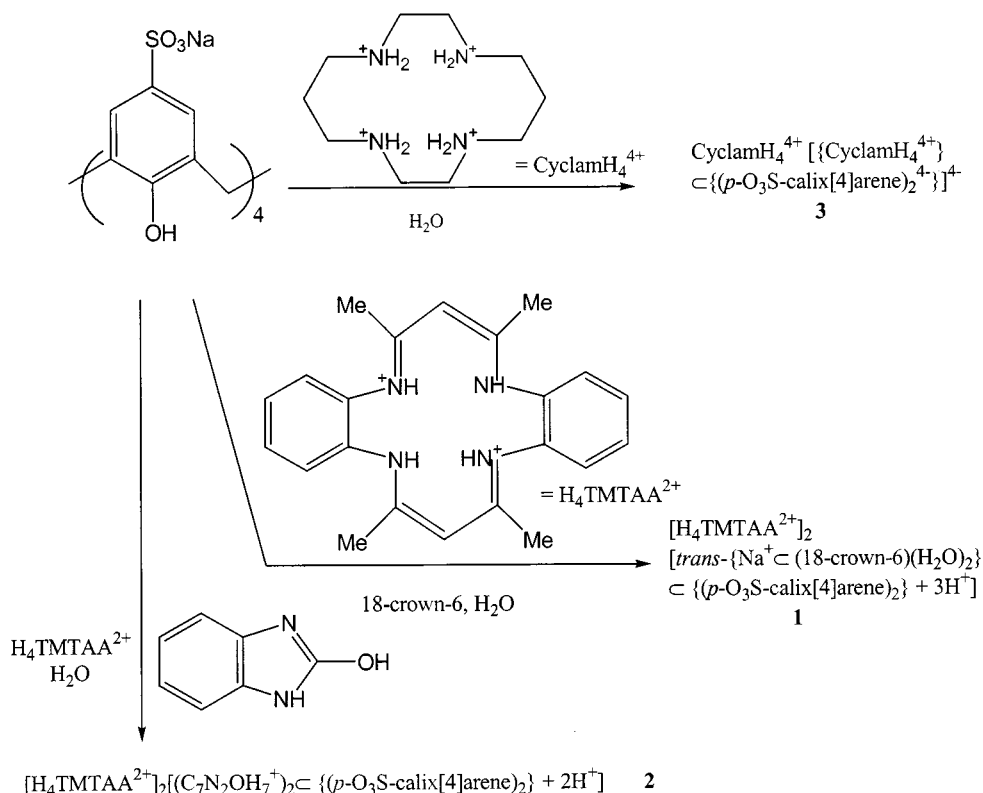
Figure 2. Comparison of the structures of compounds **1**–**3**

the triclinic space group  $P\bar{1}$  and contains the “Russian Doll”-assembled superanion capsule  $\{\text{Na}^+\text{C}(\text{18-crown-6})(\text{H}_2\text{O})_2\}\text{C}\{\text{p-O}_3\text{S-calix[4]arene}\}_2\}^{7-}$ . The capsule has internal H-bonding (axially bound water molecules; sulfonate to water  $\text{O}\cdots\text{O}$  distance: 2.78 Å) and external H-bonding through  $\text{H}_4\text{TMTAA}^{2+}$  interactions (sulfonate to imine  $\text{O}\cdots\text{N}$  distance: 2.77 Å) as well as H-bonding through waters of crystallisation ( $\text{O}\cdots\text{O}$  distance: 2.82 Å).

Remarkably a bilayer structure is formed in the presence of the large organic cation  $\text{H}_4\text{TMTAA}^{2+}$ , which has similar dimensions to  $\text{p-O}_3\text{S-calix[4]arene}$  and essentially substitutes alternate calix[4]arenes in the usual bilayer found in  $\text{p-O}_3\text{S-calix[4]arene}^{4-}$  complexes that consist of columns of “up”/“down” calix[4]arenes.<sup>[8a–8g]</sup> Within each column an “up” calix[4]arene is in close proximity to two other “down” calix[4]arenes with each interacting through aromatic ring  $\pi$ -stacking and two sulfonate-to-hydroxy H-bonds associated with the stacked rings. Four other calix[4]arene molecules in the two adjacent columns are then associated through sulfonate-to-sulfonate H-bonds possibly mediated by water. In the present structure,  $\text{H}_4\text{TMTAA}^{2+}$  cations are interspersed between columns of “up”/“down” calix[4]arenes. Within each calix[4]arene column an “up” calix[4]arene is in close proximity to two other “down” calix[4]arenes with each interacting through aromatic ring  $\pi$ -stacking (offset, coplanar with shortest  $\text{C}\cdots\text{C}$  contacts of 3.40 Å) and two sulfonate-to-hydroxy H bonds ( $\text{O}\cdots\text{O}$  distance: 3.02 Å) associated with the stacked rings. The  $\text{H}_4\text{TMTAA}^{2+}$  cations interact with calix[4]arenes through a non-classical H bond (a methyl hydrogen pointing to the centre of the calix[4]arene aromatic ring; methyl carbon to ring carbons:  $\text{C}\cdots\text{C}$  distances = 3.54–3.62 Å, with a  $\text{C}\cdots$ ring centroid distance of 3.31 Å) and the imine hydrogen to sulfonate H bond described above. Two other  $\text{H}_4\text{TMTAA}^{2+}$  cations pack close to each calix[4]arene with no obvious interactions: the phenyl- or methyl-lined concave surfaces are seemingly too steep to accommodate the concave-convex supramolecular interaction seen in many  $\text{Ni}(\text{TMTAA})$  complexes.<sup>[9a–9e]</sup> Water also permeates the  $\text{H}_4\text{TMTAA}^{2+}$  and calix[4]arene layer, with H-bonding to both calix[4]arenes and  $\text{H}_4\text{TMTAA}^{2+}$  cations.

The hydrophilic layer consists of the di-aqua sodium/18-crown-6 complex and water of crystallisation, with the 18-crown-6 complex within the capsule thus spanning the layers.  $\text{H}_4\text{TMTAA}^{2+}$  cations form “up”/“down” columns perpendicular to the calix[4]arene columns and interacting across the layers through aromatic ring  $\pi$ -stacking. Within the calix[4]arene layer there are offset, coplanar aromatic rings with shortest  $\text{C}\cdots\text{C}$  distances of 3.42 Å. Within the hydrophilic layer there are offset, coplanar aromatic rings with shortest  $\text{C}\cdots\text{C}$  distances of 3.31 Å. The calix[4]arene separation across the capsules (or layers) is characterised by pairs of sulfonate groups with a shortest  $\text{O}\cdots\text{O}$  distance of 4.27 Å.

Compound **2** also crystallises in the triclinic space group  $P\bar{1}$  and also contains a superanion,  $\{(\text{C}_7\text{N}_2\text{OH}_7^+)_2\text{C}\{\text{p-O}_3\text{S-calix[4]arene}\}_2\}^{6-}$ . The capsule also has internal H-bonding (2-hydroxybenzimidazol-N and -O to sulfonate



Scheme 1

oxygen interactions:  $\text{N} \cdots \text{O} = 2.75, 2.81 \text{ \AA}$ ;  $\text{O} \cdots \text{O} = 3.36, 3.44 \text{ \AA}$ ) and external H-bonding through waters of crystallisation (distances  $2.61 \text{ \AA}$ ). H-bonding for  $\text{H}_4\text{TMTAA}^{2+}$  to calix[4]arene in this complex is weaker than in compound **1** (sulfonate to imine:  $\text{O} \cdots \text{N}$  distance =  $3.10 \text{ \AA}$ ). The guest molecules form an aromatic ring  $\pi$ -stacked dimer (coplanar; closest contacts:  $\text{O} \cdots \text{C} = 3.42 \text{ \AA}$ ;  $\text{C} \cdots \text{N} = 3.41 \text{ \AA}$ ;  $\text{C} \cdots \text{C} = 3.37 \text{ \AA}$ ) with the monomers *anti* to each other.

The calix[4]arene layer again consists of  $\text{H}_4\text{TMTAA}^{2+}$  interspersed between columns of calix[4]arenes. The “up”/“down” calix[4]arene columns exhibiting the usual sulfonated phenol  $\pi$ -stacking/H-bonding interactions (coplanar rings;  $\text{C} \cdots \text{C}$  distances =  $3.61\text{--}3.64 \text{ \AA}$ ; sulfonate oxygen to phenolic oxygen distance:  $3.22 \text{ \AA}$ ). Across the columns the calix[4]arenes interact with  $\text{H}_4\text{TMTAA}^{2+}$  through “non-classical” H-bonding interactions ( $\text{C} \cdots \text{ring centroid} = 3.46 \text{ \AA}$ ). Columns of  $\text{H}_4\text{TMTAA}^{2+}$  cations, perpendicular to the calix[4]arene columns, again transverse the calix[4]arene layer. The  $\text{H}_4\text{TMTAA}^{2+}$  columns therefore span the bilayer by aromatic ring  $\pi$ -stacking (well aligned; coplanar aromatic rings with  $\text{C} \cdots \text{C}$  distances of  $3.40\text{--}3.58 \text{ \AA}$  and  $3.55\text{--}3.62 \text{ \AA}$  for the stacking in and out of the hydrophilic layer, respectively). The calix[4]arene separation across the capsules (or layers) is characterised by sulfur-to-sulfur distances of  $5.42$  and  $6.70 \text{ \AA}$  (closest  $\text{O} \cdots \text{O}$  contact:  $4.00 \text{ \AA}$ ).

$[\text{cyclamH}_4^{4+}][\{\text{cyclamH}_4^{4+}\} \subset \{(p\text{-O}_3\text{S-calix[4]arene})_2\}] \cdot 18\text{H}_2\text{O}$  (**3**) crystallises in the space group  $P2_1/n$  and is an example of a slipped capsule, with the slight “mismatch” allowing stronger internal H-bonding interactions. A sim-

ilar capsule has been observed in  $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8][\{\text{cyclamH}_4^{4+}\} \subset \{(p\text{-O}_3\text{S-calix[4]arene})_2\}]$ .<sup>[4]</sup> The capsule in compound **3** is characterised by internal H bond interactions ( $\text{N} \cdots \text{O}$  distances:  $2.73, 2.78$  and  $2.90 \text{ \AA}$ ) with the shortest  $\text{O} \cdots \text{O}$  calix[4]arene separations at  $5.21 \text{ \AA}$ . The capsule also features external H-bonding through the *exo*-cyclam $\text{H}_4^{4+}$  interactions ( $\text{N} \cdots \text{O}$  distance:  $2.79 \text{ \AA}$ ) as well as H-bonding through waters of crystallisation (shortest  $\text{O} \cdots \text{O}$  distance:  $2.58 \text{ \AA}$ ).

The overall structure is characterised by the bilayer arrangement with the cyclam cations located in the hydrophilic layer. Each calix[4]arene molecule is in close proximity to two other calix[4]arenes through sulfonated phenol  $\pi$ -stacking/H-bonding interactions (coplanar rings;  $\text{C} \cdots \text{C}$  distances:  $3.67\text{--}3.79 \text{ \AA}$ ; sulfonate oxygen to phenolic oxygen distance:  $3.16 \text{ \AA}$ ). Four other calix[4]arene molecules in the two adjacent columns are associated through sulfonate-to-sulfonate  $\text{O} \cdots \text{H}$  bonds, some mediated by water. The cyclam cations are well separated (shortest  $\text{C} \cdots \text{C}$  distance:  $4.03 \text{ \AA}$ ) but are H-bonded to water molecules in the hydrophilic layer.

## Conclusion

The sulfonated phenol  $\pi$ -stacking/H-bonding interaction in tetra-*p*-sulfonatocalix[4]arene complexes leading to columns of alternating “up”/“down” calix[4]arenes dominates in the overall assembly of calix[4]arene complexes. As seen

in the results presented in this study, the presence of charge-balancing cations *exo* and *endo* to the calix[4]arenes can influence the overall structures in two major ways: they can determine the calix[4]arene layer separation and they can act to separate columns of calix[4]arenes within the calix[4]arene layer. The alignment of calix[4]arene columns to allow capsule formation and the subsequent efficient internal and external H-bonding leads to more tightly bound structures. The encapsulation of guest molecules within the superanions offers the possibility of arranging molecules to permit subsequent stereospecific reaction, and, in view of the dimer observed in the 2-hydroxybenzimidazole capsule, offers the possibility to study  $\pi$ -stacking in amino acid pairs. The  $\text{H}_4\text{TMTAA}^{2+}$  complexes contain columns of the cations running transverse to the columns of the calix[4]arene anions and thus spanning the calix[4]arene layers, which is of current interest with respect to understanding transport across bilayer structures.<sup>[8b]</sup>

## Experimental Section

**Synthesis of  $[\text{H}_4\text{TMTAA}^{2+}]_2[\text{trans-}\{\text{Na}^+\text{C}(\text{18-crown-6})\text{-(H}_2\text{O)}_2\}]_2\text{C}\{(p\text{-O}_3\text{S-calix[4]arene)}_2\} + 3\text{H}^+\cdot 17\text{H}_2\text{O}$  (1):** Equimolar amounts of  $\text{TMTAAH}_2$ , 18-crown-6 and tetrasodium tetra-*p*-sulfonatocalix[4]arene (0.038 mmol) were mixed in a 50/50 mix of water and ethanol (overall 20 mL) to which 4 mL of 1 M HCl had been added. The solution soon changed from colourless to orange. On slow evaporation crystalline material deposited, the bulk of which (ca. 48 mg; 90%) consisted of clear, colourless crystals of  $[\text{H}_4\text{TMTAA}^{2+}]_2[\text{trans-}\{\text{Na}^+\text{C}(\text{18-crown-6})\text{-(H}_2\text{O)}_2\}]_2\text{C}\{(p\text{-O}_3\text{S-calix[4]arene)}_2\} + 3\text{H}^+\cdot 17\text{H}_2\text{O}$  (1). Purple/yellow dichroic crystals of 2,4-dimethyl-1,5-benzodiazepinium chloride were also present. The colour change on mixing and subsequent isolation of the 2,4-dimethyl-1,5-benzodiazepinium chloride are a result of the aqueous-acid instability of  $\text{TMTAAH}_2$ . The presence of multiple products in these reactions as well as the general rapid loss of water from the complex hydrates meant that good microanalyses could not be obtained.

**Synthesis of  $[\text{H}_4\text{TMTAA}^{2+}]_2[(\text{C}_7\text{N}_2\text{OH}_7^+)_2]\text{C}\{(p\text{-O}_3\text{S-calix[4]arene)}_2\} + 2\text{H}^+\cdot 17\text{H}_2\text{O}$  (2):** Reaction of equimolar amounts of  $\text{TMTAAH}_2$ , tetrasodium tetra-*p*-sulfonatocalix[4]arene and 2-hydroxybenzimidazole (0.038 mmol) in acidic aqueous acid solution resulted in a coloured solution which, on evaporation of the solvents, gave  $[\text{H}_4\text{TMTAA}^{2+}]_2[(\text{C}_7\text{N}_2\text{OH}_7^+)_2]\text{C}\{(p\text{-O}_3\text{S-calix[4]arene)}_2\} + 2\text{H}^+\cdot 17\text{H}_2\text{O}$  (2; ca. 38 mg; 72%) and 2,4-dimethyl-1,5-benzodiazepinium chloride. The presence of multiple products in these reactions as well as the rapid loss of water from the complex hydrates meant that good microanalyses could not be obtained.

**Synthesis of  $[\text{cyclamH}_4^{4+}][\{\text{cyclamH}_4^{4+}\}\text{C}\{(p\text{-O}_3\text{S-calix[4]arene)}_2\}]\cdot 18\text{H}_2\text{O}$  (3):** Reaction of cyclam (6.3 mg, 0.031 mmol), tetrasodium tetra-*p*-O<sub>3</sub>S-calix[4]arene (6.3 mg, 0.076 mmol) and  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (7.0 mg, 0.17 mmol) in aqueous solution, with the pH adjusted to 0.99 using  $\text{HClO}_4$ , followed by slow evaporation of the yellow solution gave pale yellow crystals of  $[\text{cyclamH}_4^{4+}][\{\text{cyclamH}_4^{4+}\}\text{C}\{(p\text{-O}_3\text{S-calix[4]arene)}_2\}]\cdot 18\text{H}_2\text{O}$ , (ca. 20 mg; 60%). Due to loss of solvent from the crystals, satisfactory results from microanalysis were unobtainable.

**X-ray Crystallographic Study:** Crystals were mounted onto glass capillaries under oil. X-ray data were collected at 123(1) K on an Enraf–Nonius KappaCCD single crystal diffractometer with  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data was corrected for Lorentzian and polarisation effects, but not absorption. The non-hydrogen atoms (except oxygen atoms in waters of crystallisation) were refined anisotropically and hydrogen atoms were included at geometrically estimated positions but not refined.

**1:** Colourless, prismatic crystal of dimensions  $0.20 \times 0.20 \times 0.15 \text{ mm}$ . The structure was solved using direct methods ( $\text{teXsan}^{[10]}$ ) and refined by full-matrix least-squares on  $F$  ( $\text{teXsan}^{[10]}$ ):  $\text{C}_{112}\text{H}_{157}\text{N}_8\text{Na}_1\text{O}_{57}\text{S}_8$ ,  $M_r = 2806.96 \text{ g mol}^{-1}$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 14.3711(5)$ ,  $b = 17.3467(6)$ ,  $c = 17.5191(4) \text{ \AA}$ ,  $\alpha = 115.261(1)^\circ$ ,  $\beta = 95.759(2)^\circ$ ,  $\gamma = 112.623(1)^\circ$ ,  $V = 3498.0(0.2) \text{ \AA}^3$ ,  $\rho_{\text{calc}} = 1.36 \text{ g dm}^{-3}$ ,  $\mu = 2.24 \text{ cm}^{-1}$  (no correction),  $Z = 1$ , 50839 reflections (17557 unique),  $2\theta_{\text{max}} = 60.2^\circ$  [9102 observed,  $I > 2\sigma(I)$ ,  $R = 0.148$ ,  $R_w = 0.155$ ].

**2:** Clear, orange, prismatic crystal of dimensions  $0.25 \times 0.20 \times 0.15 \text{ mm}$ . The structure was solved using direct methods ( $\text{teXsan}^{[10]}$ ) and refined by full-matrix least-squares on  $F$  ( $\text{teXsan}^{[10]}$ ):  $\text{C}_{57}\text{H}_{78}\text{N}_6\text{O}_{25.5}\text{S}_4$ ,  $M_r = 1383.51 \text{ g mol}^{-1}$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 14.6516(5)$ ,  $b = 15.8265(6)$ ,  $c = 16.3448(4) \text{ \AA}$ ,  $\alpha = 108.430(2)^\circ$ ,  $\beta = 105.402(2)^\circ$ ,  $\gamma = 108.984(1)^\circ$ ,  $V = 2929.9(0.1) \text{ \AA}^3$ ,  $\rho_{\text{calc}} = 1.475 \text{ g dm}^{-3}$ ,  $\mu = 2.44 \text{ cm}^{-1}$  (no correction),  $Z = 2$ , 45397 reflections (15658 unique),  $2\theta_{\text{max}} = 60.0^\circ$  [8516 observed,  $I > 2\sigma(I)$ ,  $R = 0.090$ ,  $R_w = 0.070$ ].

**3:** Prismatic crystal of dimensions  $0.5 \times 0.3 \times 0.2 \text{ mm}$ . The structure was solved using direct methods ( $\text{XSEED/SHELXL-97}^{[10]}$ ) and refined by full-matrix least-squares on  $F^2$  ( $\text{XSEED/SHELXL-97}^{[10]}$ ):  $\text{C}_{76}\text{H}_{80}\text{N}_8\text{O}_{50}\text{S}_8$ ,  $M_r = 2161.96 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 10.841(2)$ ,  $b = 28.092(6)$ ,  $c = 15.740(3) \text{ \AA}$ ,  $\beta = 96.29(3)^\circ$ ,  $V = 4764.6(1.6) \text{ \AA}^3$ ,  $\rho_{\text{calc}} = 1.507 \text{ g dm}^{-3}$ ,  $\mu = 2.92 \text{ cm}^{-1}$  (no correction),  $Z = 2$ , 29563 reflections (11988 unique),  $2\theta_{\text{max}} = 52^\circ$  [8088 observed,  $I > 2\sigma(I)$ ,  $R = 0.060$ ,  $R_w = 0.127$ ].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149551 (1), CCDC-149552 (2), and CCDC-149553 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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