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ARTICLE

Structural characterization of inclusion complexes of *para*-sulphonato-calix[8]arene with 1,2-bis(4-pyridyl)-ethane and 1,3-bis(4-pyridyl)-propane. New 'double cone' and 'up-flat-down' conformations of *para*-sulphonato-calix[8]arene

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The solid-state structures of two complexes (organic salts) between *para*-sulphonato-calix[8]arene **(C8S)** and bipyridinium derivatives 1,2-bis(4-pyridyl)-ethane **(BPE)** and 1,3-bis(4-pyridyl)-propane **(BPP)**, have been determined. In the **BPE**-*para*-sulphonato-calix[8]arene complex structure a total of six different channels are observed, four wide, along [100], [010], [110] and [101] and two narrow but real, along [001] and [011]. One of the wide channels is partially occupied by a **BPE** cations while the others contain water and co-solvents (methanol and ethanol) molecules. Reversible gas adsorption of propane has been observed at pressures below 1bar.

Introduction

The *para*-sulphonato-calix[n]arenes represent, probably, the most widely studied class of water soluble synthetic organic hosts.[1] In solution they are capable of complexing a vast range of substrates ranging from ions,[2] small organic molecules,[3] Active Pharmaceutical Ingredients (APIs),[4] small biomolecules including nucleic acids,[5] amino acids,[6] and peptides.[7] They have been widely studied for their ability to complex proteins,[8] and to act as pharmacologically active molecules against various proteins.[9] So far, little or no toxicity has been observed either in vitro,[10] or in vivo,[11] for these molecules.

One major point with regard to the study of these molecules is their tendency to crystallise with a wide range of substrates.[12] This is particularly true for the relatively rigid *para*-sulphonato-calix[4]arene, which was for the first time structurally characterized in 1988 by Atwood *et al.*, as a bilayer system resembling an organic clay.[13] Since then the structural diversity of the packing motifs has become recognized. The larger *para*-sulphonato-calix[6]arene and *para*-sulphonato-calix[8]arene present a different problem as their flexibility renders their crystallization more difficult.[14] This is particularly true for *para*-sulphonato-calix[8]arene and for other calix[8]arene derivatives such as the *para*-phosphonato derivatives. In a series of studies by ourselves,[15] and by Raston,[16] our understanding of the solid-state structural nature of these systems is becoming clearer. It is apparent that in the solid-state the previous notions of the number of geometric isomers of calix[8]arene were probably well short of the mark.[17]

It is has been observed that in many of the solid-state complexes of calix[8]arenes, for example that with the butane diammonium cations, channels capable of taking up gases or volatile organic compounds are available.[18] Such behaviour has been observed for *para*-phosphonato-calix[8]arene-O-alkyl ethers with regard to linear alcohols.[19]

In this paper we describe the solid state structures of the complexes of *para*-sulphonato-calix[8]arene, **C8S**, with two flexible ligands 1,2-bis(4-pyridyl)-ethane (**BPE**) and1,3-bis(4-pyridyl)-propane (**BPP**). While there is a difference of a single carbon atom in the bridge between the two pyridyl moieties the two structures are remarkably different. That with 1,2-bis(4-pyridyl)-ethane (**BPE**) is a massively porous system containing six different channels, whereas that with **BPP** shows only apparent porosity.

Results and discussion

The structural formulae of the compounds studied in the current work are given below in Figure 1.

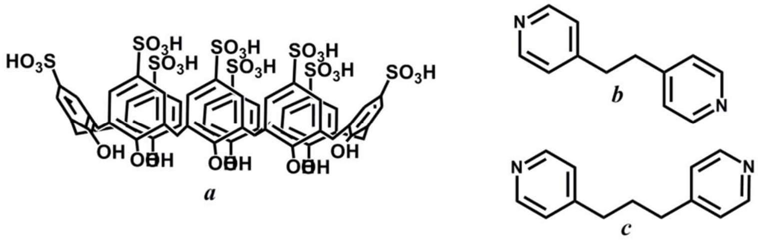

Figure 1. Structural formulae of (a) *para*-sulphonato-calix[8]arene (**C8S**); (b) 1,2-bis(4-pyridyl)-ethane (**BPE**); (c) 1,3-bis(4-pyridyl)-propane (**BPP**).

para-Sulphonato-calix[8]arene, **C8S**, is larger and possesses a more flexible framework than its smaller homologs: *para*-sulphonato-calix[4]arene and *para*-sulphonato-calix[6]arene. **C8S** may adopt many different conformations, for example: pleated loop,[20] distorted pleated loop (‘chalice-like’),[21] double cone,[22] double inverted cone[23] and Gutsche proposed sixteen up-down conformations for the orientation of the aromatic rings.[17] In the current work we obtained two supramolecular compounds where **C8S** molecule adopt two newly observed for sulphonated calix[8]arene conformations which we describe as ‘double cone’ in complex **1** and ‘up-flat-down’ in complex **2**.

It would appear that shape of the guest has the capacity to influence the shape of the **C8S** cavity and shape of **C8S** has the capacity to influence the shape of **BPE** and **BPP** cations. The mutually induced fit in host-guest complexes between conformationally flexible *para*-sulphonato-calix[8]arene and photolabile cholinergic ligands has been observed in solution.[24].

C8S-BPE complex (1)

The asymmetric unit comprises one half of a **C8S** anion, 1.25 diprotonated **BPE** cations, half of an ethanol molecule, half of a methanol molecule, 2.8 water molecules and 1.5 hydronium ions. The **C8S** anion adopts a novel conformation, which is significantly different from those for previously reported structures of **C8S**[20-23,25,26,27] which is a twofold double cone conformation (Figure 2) previously unknown for **C8S** (the twofold symmetry is crystallographically imposed). Such a conformation was previously observed only for *tert*-butylcalix[8]arene with lanthanides.[28]

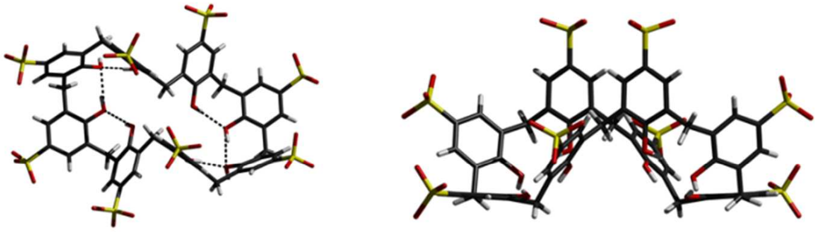

Figure 2. *para*-Sulphonato-calix[8]arene twofold double cone conformation in complex **1**: (left) the **C8S** molecule showing intramolecular hydrogen bonding between oxygen atoms of the hydroxyl groups (dotted lines); (right) side view.

This conformation provides two identical binding sites which mimic the calix[4]arene cone cavity and are capable to bind **BPE** cations and one distinct binding site for an ethanol molecule. Indeed, in each of the two cavities one **BPE** cation is included with one of the ethylenic carbon atom sitting deeply (Figure 3). The included **BPE** cation is a V-shaped and is slightly disordered over two close one to each other positions with site occupancy factors 0.6 and 0.4. Additionally, such a conformation of the **C8S** anion provides another cavity which accommodates an ethanol molecule. The second **BPE** cation with site occupancy factor of 0.25 is located in the channels existing in the crystal lattice, and it was found to be in substitutional disorder with three water molecules also with site occupancy factors equal to 0.25. The channels are also filled with ethanol, methanol and remaining water molecules.

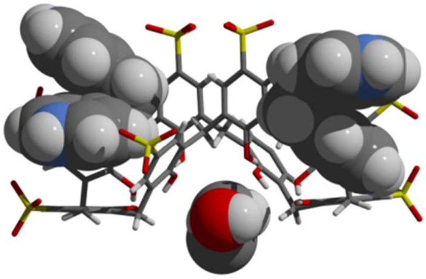

Figure 3. Supramolecular assembly of *para*-sulphonato-calix[8]arene with two **BPE** molecules and an ethanol molecule.

The included **BPE** cation is retained in the calixarene cavity primarily through a C–H···O interaction (C···O distance: 3.345 Å) between the carbon atom of the aromatic ring of **BPE** and the sulphonate oxygen atom of the **C8S**, π–π interaction between aromatic ring of **BPE** and of **C8S** with a 'parallel-displaced' geometry (centroid···centroid distance: 3.930 Å), and C–H···π interaction with an 'edge-to-face' geometry: C_{arom}···centroid distance: 3.291 Å, and also two C–H···π interactions (H···centroid distances: 2.850 and 2.886 Å) between C–H atoms in methylene groups in **BPE** and aromatic rings of **C8S**. Inclusion of the ethanol molecule is stabilized by C–H···O interaction (C···O distance: 3.222 Å) between C–H atoms of the methylene group from ethanol molecule and oxygen atom of a hydroxyl group belonging to the **C8S** anion. Due to the symmetry (2-fold axis) the ethanol molecule is disordered with s.o.f. = 0.5. It should be noted that the ethanol, methanol and **BPE** molecules as well as the disordered sulphonate groups were adequately modeled (see ESI).

The **BPE** cations adopt two different conformations in complex **1**. These which are located within the *pseudo* calix[4]arene cavities adopt V-shaped conformation due to the *gauche* conformation around the central ethylenic bond and with an angle between the planes of aromatic rings equal to 34.26°. This conformation may be compared to the Z isomers of substituted ethylene systems. **BPE** molecules which are located *exo* to the inclusion complex and occupy the void space within the channels show an *anti* conformation around the central ethylenic bond and an angle between planes of the **BPE** aromatic rings is equal to 69.15°. This generates a classical lock-key fit between host and guest molecules in the complex.

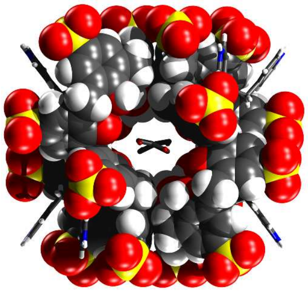

Figure 4. Molecular assembly formed by two *para*-sulphonato-calix[8]arene anions four included **BPE** cations and two disordered ethanol molecules inside capsule, **C8S** and **BPE** ions mutually mould to each other.

Two calix[8]arene anions form ‘circular’ dimeric assemblies which are straightway provided by π–π ‘eclipsed face-to-face’ stacking between aromatic rings of two calixarenes (centroid–centroid distance: 3.650 Å). The void formed in the centre of such assembly has the approximate dimensions 9.0 × 6.4 Å, and is occupied by two disordered ethanol molecules, Figure 4. Neighbouring dimeric assemblies, are connected by π–π interactions (centroid···centroid distance: 3.611 Å) and O–H···O hydrogen bonds (O···O distance: 2.560 Å) and they form ribbons as shown in Figure 5.

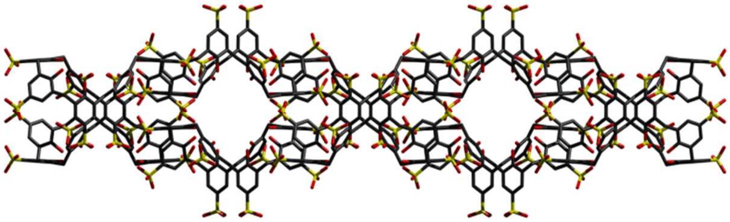

Figure 5. Ribbons formed by supramolecular dimeric assemblies, only *para*-sulphonato-calix[8]arene anions are shown.

The sulphonate groups (–SO_3H) of neighbouring calixarenes are placed very close to each other. Distance between the closest oxygen atoms in neighbouring sulphonate groups is 4.298 Å. We suppose that some of this neighbouring sulphonate groups or more likely water molecules could be protonated. This assumption allows the charge neutrality of the complex to be satisfied. The crystals were of poor quality, leading to a low number of 'observed' reflections so we are not able establish in a sure way where protonation occurs. All sulphonate groups, **BPE**, ethanol, methanol and water molecules are disordered.

The packing of all the ionic and molecular species in the crystal is extremely complex with formation of a 3D network of channels which are interconnected and diverge in many directions (Figure 6). Distinct channels are observed for example along [100] (approximate diameter 11.4 × 15.2 Å), [010] (approximate diameter 4.1 × 8.2 Å), [110] (approximate diameter 8.3 × 7.1 Å), or [101] (approximate diameter 6.5 × 11.7 Å). Channels are occupied by solvent molecules(ethanol, methanol and water) and by the **BPE** cations which are located *exo* to the supramolecular complex. Additional channels in the [001] and [011] directions may be also distinguished but are very narrow. Nevertheless, there is still some free space in the crystal in these directions. The total calculated free volume is 3915 Å^3 and this is about 7% of unit cell volume.

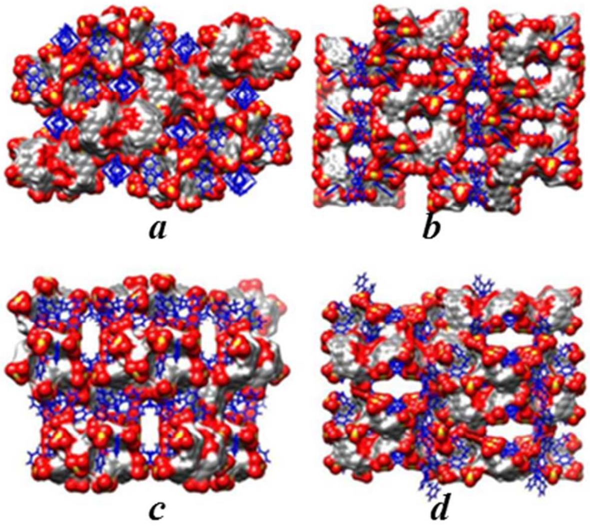

Figure 6. Packing of *para*-sulphonato-calix[8]arene anions in **C8S-BPE** showing the network of channels within the crystal: (a) view along [100] axis; (b) view along [010] axis; (c) view along [101] axis; (d) view along [110]. Solvent molecules which occupy the channels are omitted to show the solvent-accessible area.

C8S-BPP complex (2)

The asymmetric unit comprises two halves of **C8S** anions, four diprotonated fully occupied and two half occupied **BPP** dications of which two are ordered and the remaining ones show positional disorder, and 29 water molecules of which 15 are disordered. The disorder of some sulphonate groups, **BPP** dications and some water molecules were adequately modeled (see ESI).Charge balance for this system implies that all eight sulphonate groups of **C8S** and two hydroxyl groups are deprotonated.

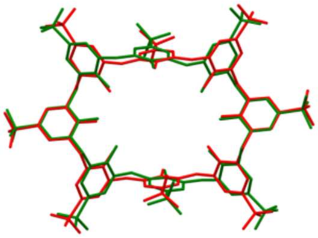

Figure 7. Superposition of two distinct *para*-sulphonato-calix[8]arene anions in complex **2**.

The two symmetrically independent **C8S** anions adopt very similar conformation with only slight differences (Figure 7). Both **C8S** anions lie about inversion centres and adopt a novel for this molecule centrosymmetric ‘up-flat-down’ conformation in which two oppositely located phenolic rings are almost perpendicular to the main plain of the macrocyclic ring (77.4 and 80.9° for the two symmetry independent anions) and point up and down, and the other six phenolic rings lie in the plane of the macrocyclic ring The hydroxyl groups which from these last phenolic rings take part in hydrogen bonding and are stabilising the conformation of **C8S** (Figure 8a). Like in the complex 1, also here the observed conformation was never reported for *para*-sulphonato-calix[8]arene; similar centrosymmetric ‘up-flat-down’ conformation was only observed for unsubstituted calix[8]arenes.[29,30]

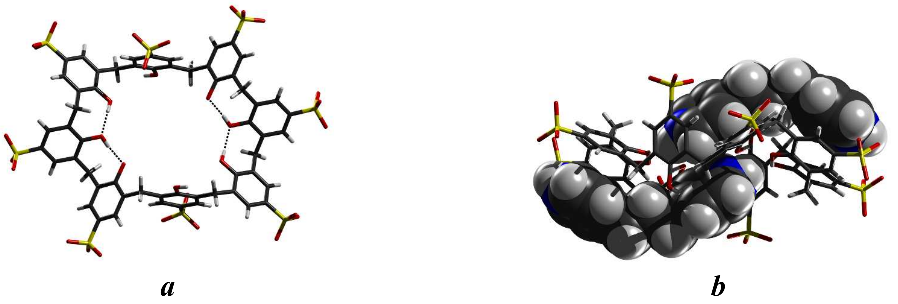

Figure 8. Centrosymmetric 'up-flat-down' conformation of *para*-sulphonato-calix[8]arene in complex **2**: (a) top view, the **C8S** molecule showing intramolecular hydrogen bonding between oxygen atoms of hydroxyl groups (dotted lines); (b) supramolecular complex formed with two **BPP** cations.

Each *para*-sulphonato-calix[8]arene anion is surrounded by four neighbouring crystallographically distinct **C8S** anions and interacts with each one with O–H···O hydrogen bonds (2.637 and 2.721 Å) formed between oxygen atoms of sulphonate and hydroxyl groups (a ***b***

Figure 9a).

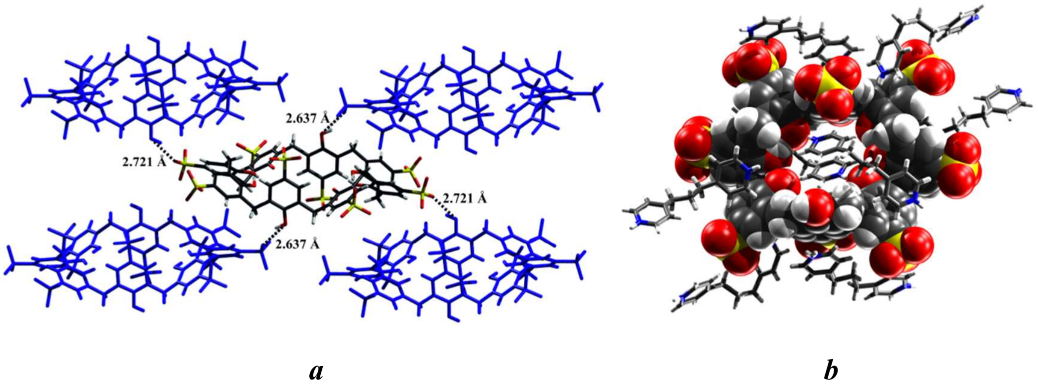

Figure 9. Intermolecular interactions: (a) between **C8S** anions; (b) mutual fitting between the host and guest ions in the organic salt.

Each host molecule interacts with two **BPP** cations forming 1:2 (host:guest) supramolecular assembly. The guest molecules which both display the *anti*-*anti* conformation around the two C−C bonds of central carbon atom in the propylene bridge are retained primarily through N–H···O between nitrogen atom of BPE and oxygen atom of hydroxyl group of the calixarene (2.686 Å in the first assembly and 2.708 Å in the second assembly). Secondly, N–H groups of both **BPP** cations interact with sulphonate groups of **C8S** *via* water molecules (N–H···O_{water}: 2.515 and 2.749 Å, O_{water}–H···O: 2.796 and 2.649 Å for the first and second assembly, respectively). Additionally, this inclusion is stabilized by edge-to-face C–H···π interaction (C···centroid distances 3.290 and 3.281 Å for the first and second assembly, respectively). The two **BPP** cations in the supramolecular assembly interact between each other through the internal gap in the calixarene anion by weak parallel-displaced π–π stacking (distances between planes: 3.607 and 3.352 Å for the first and second assembly, respectively) forming dimers (Figure 8b). The presence of cationic charges on the aryl rings together with geometrical restrictions prevents eclipsed face-to-face π-stacking, leading to the displaced arrangements of pyridinium rings (the plane-to-plane angles are 0°, interplanar distances: 3.607 and 3.352Å, and the closest N···C atom approaches 3.643 and 3.374 Å for the first and second assembly, respectively). Similar host-guest assembly was found in calix[8]arene-pyridine complex.[30]

The supramolecular assemblies further interact with neighbouring **BPP** cations which are in excess in the crystal by van der Waals interactions and it looks like there is mutual fitting between the host and guest ions in the organic salt which is visible in different **BPP** cations conformations depending on their location in the structure (Figure 9b).

As shown in (Figure 10a) the overall structure reveals a layered character of the packing. One layer is formed by **C8S** anions and **BPP** cations which are engaged in supramolecular assembly formation; the second layer consists of the remaining **BPP** cations (Figure 10b.).The majority of water molecules is located between the two layers and play the determinant role in the layer cohesion.

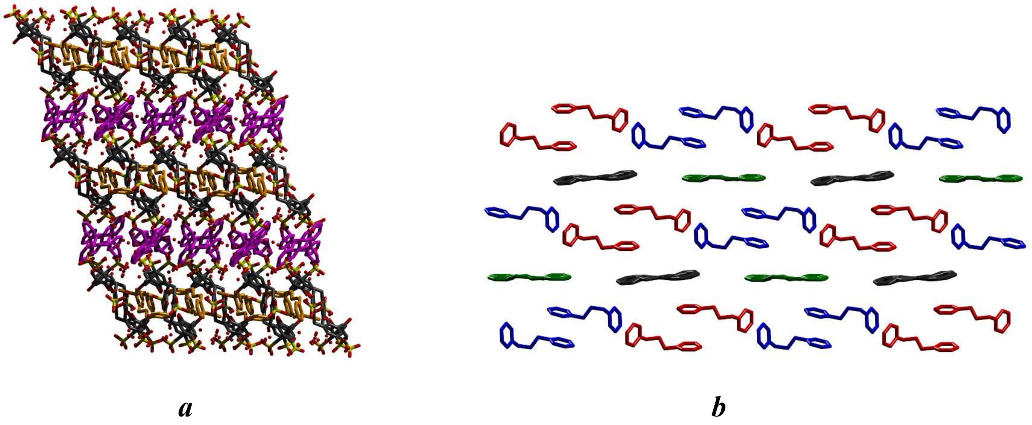

Figure 10. Packing diagram in the complex **2**; (a) layer-type packing: **BPP** cations in supramolecular assemblies are marked in orange, the rest of **BPP** cations are marked in violet, water molecules are displayed as red balls, view along [001] direction; (b) **BPP** cations forming the second layer – symmetry independent molecules are indicated with different colours, water molecules are omitted for clarity.

The intermolecular interactions between **BPP** cations forming the second layer include π–π stacking interactions and N–H···O hydrogen bonds *via* water molecules. Arrangement of **BPP** cations is shown in Figure 10b. Two symmetrically independent **BPP** cations (marked in blue and red in Figure 10b) and both display the *gauche-anti* conformation around the two C–C bonds of central carbon atom in the propylene bridge. They both form centrosymmetric dimers by parallel-displaced π–π stacking of one of the pyridyl ring (centroid···centroid distance: 3.634 and 3.949 Å for dimers blue and red, respectively). The two dimers interact one with other also by weak π–π interactions (centroid···centroid distance: 4.002 Å, nearest C···C distance: 3.415 Å). These two symmetry independent molecules form infinite ribbons along [-101] direction. Between the ribbons there are two other symmetry independent **BPP** cations marked as grey and green in Figure 10b. Both of them are located at the crystallographic centre of symmetry and are planar (one is slightly disordered). They interact by weak π–π stacking with those **BPP** cations which are forming ribbons. Some water molecules is also involved in interactions between **BPP** cations.

In summary the structure of the salt of *para*-sulphonato-calix[8]arene, **C8S**, with 1,2-bis(4-pyridyl)-ethane (**BPE**) can be compared to that of an extremely complex zeolite, and that with 1,3-bis(4-pyridyl)-propane (**BPP**) to the type of organic clay first observed for the sodium salt of *para*-sulphonato-calix[4]arene.[13]

It is preferred that porosity, a physical property, should be proved experimentally rather than simply claimed on the basis of crystallographic data. Sorption experiments were performed in the case of the **C8S-BPE** salt and they have shown that indeed in the solid state the complex is capable of taking up organic gas molecules, in this case propane, using the methodology previously used by ourselves to measure alcohol uptake by amphiphilic calix[n]arenes.[18] The results are shown in Figure 11 below, the frequency response is of the order 100Hz and is clearly reproducible over a number of vacuum-gas cycles. The data are very preliminary, the work relating to the sorption of other gases and using different experimental techniques are being continued and will be published separately.

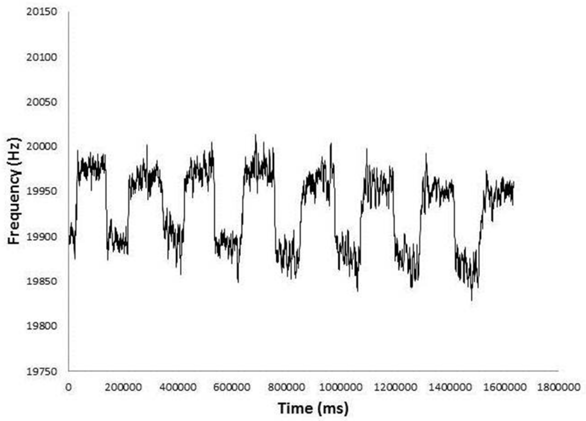

Figure 11. SAW response curve for the **C8S-BPE** salt towards propane.

Conclusions

The structures of the organic salts of *para*-sulphonato-calix[8]arene with 1,2-bis(4-pyridyl)-ethane (**BPE**) and 1,3-bis(4-pyridyl)-propane (**BPP**).have been determined and show very large differences. While the salt with **BPE** shows true porosity that with **BPP** shows no porosity. The structure of the *para*-sulphonato-calix[8]arene with 1,2-bis(4-pyridyl)-ethane salt shows a complex network of interconnecting channels of variable size, one of which contains a cation effectively blocking this channel, the others contain water and solvents and are thus accessible for other guest molecules. Gas take-up has been demonstrated, to show the porous nature of this solid. The effect of a single carbon atom between the **BPE** and **BPP** cations on the complexity of the crystal structure is remarkable. The combination of the ordering of supramolecular assemblies in the **S8C-BPE** complex and porous features of this crystalline material provides the Supramolecular Organic Framework, (SOF) a concept of which was proposed by Neil R. Champness and Martin Schröder.[31] Work is currently underway to study other complexes of *para*-sulphonato-calix[8]arene with rigid and flexible organic cations and to open up the way to novel SOFs.

Acknowledgements

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Molecular graphics and analyses were performed with the UCSF Chimera package.[32] Chimera is developed by the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco (supported by NIGMS P41-GM103311).

Notes and references

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Crystal growth

Suitable crystals for X-ray diffraction were grown by slow diffusion. A solution of the **BPP** or **BPE** in ethanol and methanol at 4 equiv. was layered onto 1 mL of aqueous solution containing 100 mg of *para*-sulphonatocalix[8]arene, **C8S**. Finally a layer of methanol was added above the ethanol. The crystallization experiments were carried out at 20 °C in sealed tubes. Complex **1** is $\mathbf{C8S}^{8-}\cdot 2.5\mathbf{BPE}^{2+}\cdot 3H_3O^+\cdot 5.6H_2O\cdot C_2H_5OH\cdot CH_3OH$. Complex **2** is $\mathbf{C8S}^{10-}\cdot 5\mathbf{BPP}^{2+}\cdot 29H_2O$.

Single-crystal X-ray diffraction

The X-ray data were collected at 100(2) K on a Nonius KappaAPEXII diffractometer. The data were corrected for Lorentz and polarisation effects but not for absorption. Structures were solved by direct methods and refined using SHELXL-97.[33] Hydrogen atoms were included in geometric positions and refined as 'riding' atoms with isotropic thermal parameters based upon the corresponding bonding carbon atom ($U_{\mathrm{iso}} = 1.5U_{\mathrm{eq}}$ for hydroxyl groups and $U_{\mathrm{iso}} = 1.2U_{\mathrm{eq}}$ for the rest). Hydrogen atoms of hydroxyl groups were refined in geometric positions for which the calculated sum of the electron density is the highest (rotating group refinement). Where possible (only in complex **2**) hydrogen atoms of water molecules were located on Fourier difference maps and refined with positional parameters. Some of the calix[8]arene sulphonate groups and guest molecules were found to be disordered over two positions and were refined with split atom model. Because of the poorly diffracting crystals and the presence of the disorder of some groups and molecules, the structures had refined to relatively high *R* and w*R* values as well as the low θ_{max} values and relatively poor data/parameter ratios are observed. Due to the same reason, it was not possible to establish, without any doubts, hydrogen positions from electron density maps for hydroxyl groups and water molecules and it was not possible to decide which groups were protonated or deprotonated. Therefore we had to make a few assumptions. To balance the charges of anions and cations a complete deprotonation of the **C8S** was assumed. For such an assumption in complex **1** to balance the charge it was necessary that 1.5 water molecules in asymmetric unit are protonated and they are in form of hydronium cations. In complex **2** to balance the charge deprotonation of two hydroxyl groups was necessary to be assumed. It must be noted that in complex **1** other model of protonation/deprotonation could be possible but this will not influence the overall structure and the conclusions drawn.

Crystal data for 1. $C_{56}H_{40}O_{32}S_8{}^{-8}\cdot 2.5C_{12}N_2H_{14}{}^{+2}\cdot C_2H_5OH\cdot CH_3OH\cdot 5.6H_2O\cdot 3H_3O^+$, $M_r = 2182.90$, colourless, 0.50 × 0.45 × 0.43, orthorhombic, space group *Fddd*, $a = 26.6699(5)$, $b = 37.3628(9)$, $c = 54.356(1)$ Å, $V = 54164(2)$ Å^3, $T = 100(2)$ K, $Z = 4$, $\mu(\mathrm{Mo}K\alpha) = 0.247$ mm^{-1}, $\theta_{\mathrm{max}} = 20.82°$, 7063 independent reflections, 5082 with $I > 2\sigma(I)$. $R = 0.143$, w$R = 0.374$ ($R = 0.180$, w$R = 0.394$ for all data), $GOF = 1.61$.

Crystal data for 2. $C_{56}H_{40}O_{32}S_8{}^{-10}\cdot 5C_{13}N_2H_{16}{}^{+2}\cdot 29H_2O$, $M_r = 3002.86$, colourless, 0.50 × 0.25 × 0.20, triclinic, space group *P*-1, $a = 14.6443(4)$, $b = 19.4468(6)$, $c = 26.594(1)$ Å, $\alpha = 99.790(2)$, $\beta = 90.699(1)$, $\gamma = 107.796(4)°$, $V = 7089.5(4)$ Å^3, $T = 100(2)$ K, $Z = 2$, $\mu(\mathrm{Mo}K\alpha) = 0.247$ mm^{-1}, $\theta_{\mathrm{max}} = 22.46°$, 16723 independent reflections, 18369 with $I > 2\sigma(I)$. $R = 0.109$, w$R = 0.272$ ($R = 0.176$, w$R = 0.311$ for all data), $GOF = 1.00$.

Electronic suplementary information (ESI) available. CCDC reference numbers 970626-970627. For ESI and crystallographic data in CIF.

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Structural characterization of inclusion complexes of *para*-sulphonato-calix[8]arene with 1,2-bis(4-pyridyl)-ethane and 1,3-bis(4-pyridyl)-propane. New ‘double cone’ and ‘up-flat-down’ conformations of *para*-sulphonato-calix[8]arene

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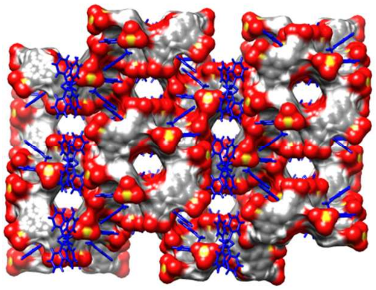
Table of contents entry:



New conformations of *para*-sulphonated-calix[8]arenes are proved in supramolecular complexes with **BPE** and **BPP**. The **S8C-BPE** complex shows true porosity and for this solid the gas take-up has been demonstrated.