FULL PAPER

Controlling the Conformation and Interplay of *p*-Sulfonatocalix[6]arene as Lanthanide Crown Ether Complexes

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Abstract: Control over the conformational flexibility of *p*-sulfonatocalix[6]-arene in the solid state is possible in the presence of varied stoichiometric amounts of [18]crown-6 and selected lanthanide(III) chlorides. Complexes **1** and **2** have the calixarene in the elusive "up–up" double cone conformation, whilst complex **3** has the calixarene in the centrosymmetric "up–down" double partial cone conformation, whereby it acts as a divergent receptor. Complex **1** has a double "molecular capsule" arrangement which is composed of two *p*-sulfonatocalix[6]arenes shrouding two [18]crown-6 molecules, also with both coordinated and homoleptic aquated lanthanide ions around the hydrophilic sulfonate rims of the calixarenes. Complex **2** has a "ferris wheel" arrangement with one lanthanide metal centre coordinated to a sulfonate group and another coordinated to the crown ether whilst tethered to a sulfonate group of the calixarene. Complex **3** forms from a solution with large excess of [18]crown-6, and possesses a crown ether molecule in each of the partial cones and has homoleptic aquated lanthanide ions involved in a complicated hydrogen-bonding regime within the extended structure.

Keywords: calixarenes · crown compounds · host–guest systems · self-assembly · supramolecular chemistry

Introduction

For some time, much attention has been focused on the ability to control conformational and structural aspects of supramolecular materials in solution and the solid state.[1–5] A significant proportion of this current research topic can be attributed to the use of various functionalised calixarenes and the related *C*-methylcalix[4]resorcinarene in hydrogen-bonded assemblies whilst in the presence of various other guests or supramolecular tectons.[6–8] In addition, Fujita et al. have synthesised metal–organic nanobowl structures through the self-assembly process, structures that are effective mimics of calix[3]arene.[9]

p-Sulfonatocalix[*n*]arenes are readily accessible versatile compounds for inclusion phenomena and the formation of coordination complexes.[10–17] The ubiquitous *p*-sulfonatocalix[4]arene forms extended bilayer clay-type structures, and depending on the nature of the included species and metal ions present, the bi-layers can be regarded as being built up from "molecular capsules" composed of two calixarenes shrouding a crown ether type molecule, such as [18]crown-6 and 4,13-diaza-[18]crown-6, or two amino acids, as so-called Russian dolls.[11, 18, 19] Other structural motifs include "ferris wheels",[11, 20] hydrogen-bonded polymers, two-dimensional coordination polymers[21] and, most spectacularly, spheroidal-like arrays of twelve calixarenes with the cavities directed away from the centre of the arrays or nanotubes with the calixarenes cavities similarly directed outwards.[22] In contrast, the supramolecular chemistry of *p*-sulfonatocalix[6]arene remains relatively unexplored. Atwood et al. reported the structures of the sulfonic acid and the octasodium salt;[23] more recently Asfari et al. reported the structures of rubidium and caesium complexes.[24] In all these structures, the calixarenes are in the "double partial cone" (*1,2,3-alternate* or *three up*, *three down*) conformation, that is, one partial cone pointing up and the other down. In the only other structurally authenticated compound based on this sulfonated calixarene, the molecule is in a pseudo-"up–up" double cone conformation, whereby one sulfonate group points "downwards" although the calixarene is in the *O*-methylated form that lacks the potentially conformational directing phenolic OH-hydrogen bonding.[25]

Unlike *p*-sulfonatocalix[4,5]arene, controlling the conformation of the larger and more highly charged calix[6]arene analogue presents a formidable challenge, a likely reason for its limited supramolecular chemistry thus far. The "up–up"

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double cone conformation is of interest in forming "molecular capsules" based on upper-rim-to-upper-rim interplay between two or more calixarenes,[26] and we find that it is accessible, for the first time in the solid state, in the presence of [18]crown-6 and selected lanthanide ions, depending on the ratios of crown ether to the aquated lanthanide ions. Indeed, we have isolated "molecular capsule" (smaller lanthanides), and "ferris wheel" (larger lanthanides) type arrangements, complexes **1** and **2** respectively, Scheme 1. We also find that for the same system (calixarene/crown ether/lanthanide), it is possible to form complexes with the calixarene in the "double partial cone" conformation complex **3**, Scheme 1(excess crown ether), with the calixarene now acting as a divergent receptor towards disc-shaped crown ether molecules. Complexes **1** and **2** have the same 1:1 stoichiometry with respect to crown ether and calixarene, whereas **3** has a 2:1 ratio, their formation depending on the size of the lanthanide ions. The three complexes show a marked difference in the nature of the lanthanides present, 1) homoleptic aquated (**1** and **3**), 2) metal/sulfonate linkages (**1** and **2**) and 3) metal/crown ether complexation (**2**). Interestingly, the parent unsubstituted calix[6]arene forms a complex with C_{60}, with a fullerene in each of the cavities for the "up–up" conformation, noting the maximum diameter of the crown ether is similar to that of the fullerene.[27]

Results and Discussion

Within the extended structure of **1** (M = Tb), the calixarenes assemble into bilayers with each layer composed of π-stacked calixarenes, aligned in opposite directions, and clearly this optimises overall hydrophobic–hydrophobic and hydrophilic–hydrophilic interactions (Figure 1); closest aromatic ring centroid–centroid distance 3.956 Å. With two terbium centres/calixarene, charge neutrality dictates the calixarene is in the hexa-anion form. For each centrosymmetric "molecular capsule", two terbium cations are attached to one sulfonate group from different calixarenes and seven water molecules, one of which is disordered over two positions. Each of these coordinated cations also hydrogen bonds to one sulfonate group of the attached calixarene (TbO···OS distance of 2.860 Å) and, in addition, hydrogen bond to sulfonate groups of both neighbouring calixarenes arranged in the nearest "molecular capsule" (TbO···OS distances ranging from 2.904 to 3.045 Å). The other two metal centres are attached exclusively to eight water molecules; there are also secondary coordination sphere hydrogen-bonding interactions to the oxygen centres of the crown ethers (TbO···O distances of 2.819 and 2.867 Å) and to sulfonate groups of two neighbouring calixarene moieties, through two and one of the ligated
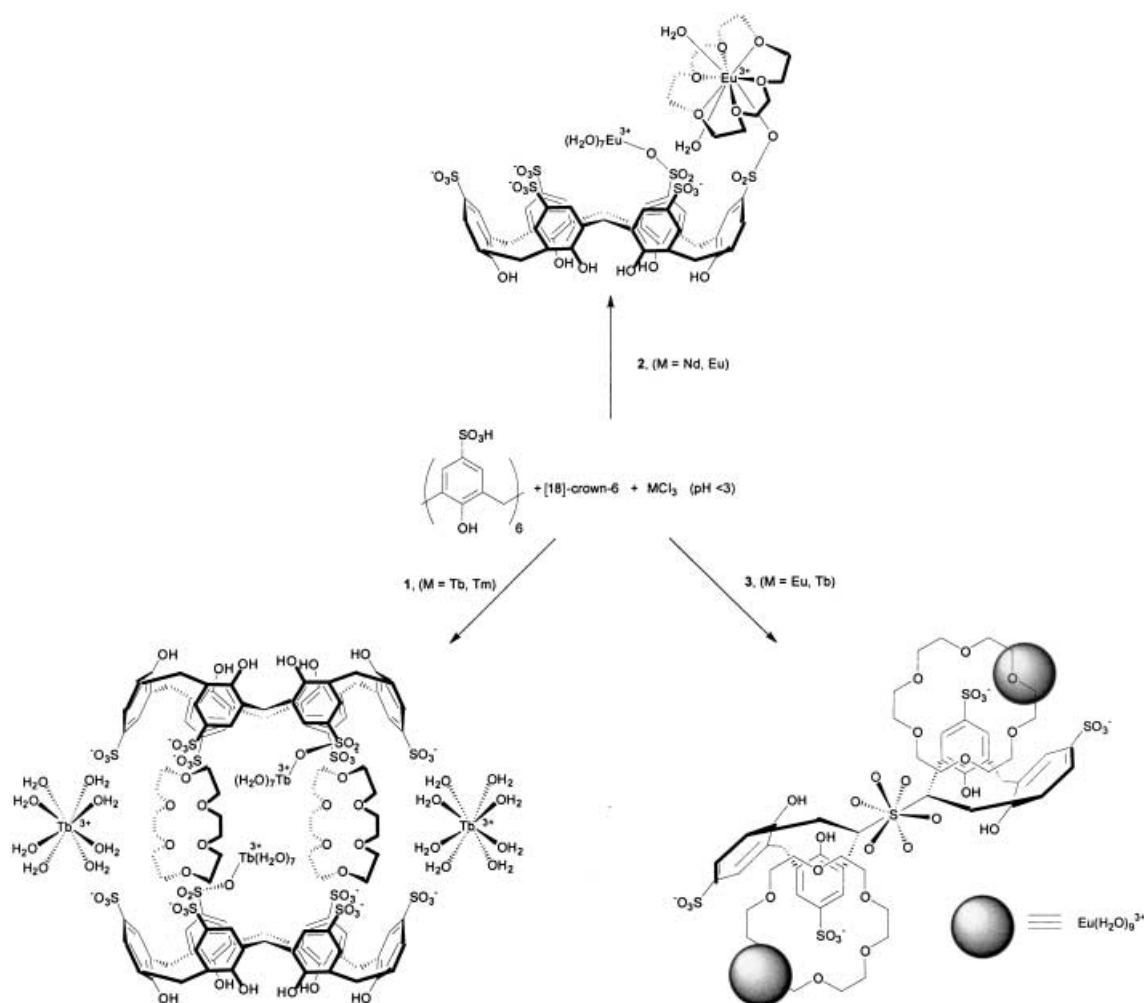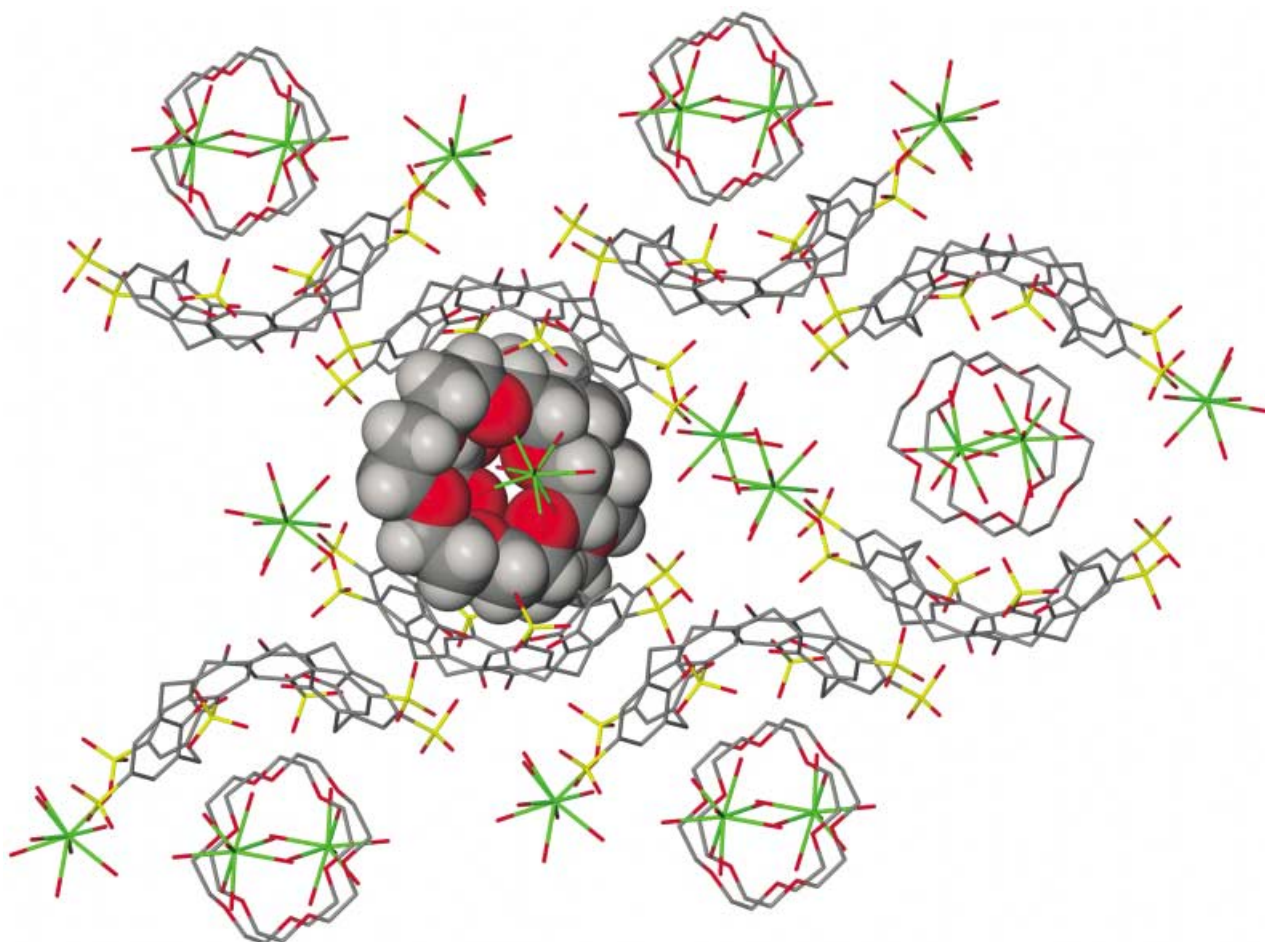

Scheme 1.

Figure 1. Extended structure of **1**, showing the "molecular capsule" and bilayer packing, along with terbium cations in both coordinated and un-coordinated environments (several disordered water molecules residing around the hydrophilic regions of the structure have been omitted for clarity in all diagrams).

water molecules (TbO⋯OS distances ranging from 2.666 to 2.786 Å). We have recently reported examples of un-coordinated octa-aqua trivalent lanthanide cations (M = Gd, Tb, Tm) interacting with *p*-sulfonatocalix[4]arene to form 2D hydrogen-bonded polymers.[21] Ignoring any hydrogen bonding associated with disordered water molecules, the above hydrogen-bonding regime is similar to that in the analogous *p*-sulfonatocalix[4]arene structure.

The "pinched" structure of the "up–up" conformation optimises hydrogen-bonding interactions between the six phenolic OH groups, and effectively has two pseudo "calix[3]arene" cavities, which have complimentarity of fit with the crown ether molecules (Figure 1).

For the "ferris wheel" in the structure of **2** (M = Eu), the lanthanide crown ether complex, in which the metal is bound to all of the oxygen centres, is tethered to a sulfonate group of the calixarene, mimicking a similar type of structural motif seen for *p*-sulfonatocalix[4]arene.[11, 20] Two water molecules are attached to the same metal centre, one on the opposite side of the crown ether plane as the Eu−OS linkage, with one hydrogen bond to an adjacent sulfonate group (EuO⋯OS distance 2.854 Å). In addition, each "supermolecule" has a hepta-aqua-europium centre attached to a sulfonate group, Eu−OS = 2.417(5) Å (Figure 2).

Hydrophobic–hydrophobic interplay of adjacent calixarenes in **2** is through π-stacking in helical arrays (aryl-centroid separations of 3.882 Å, Figure 3); note that the space group
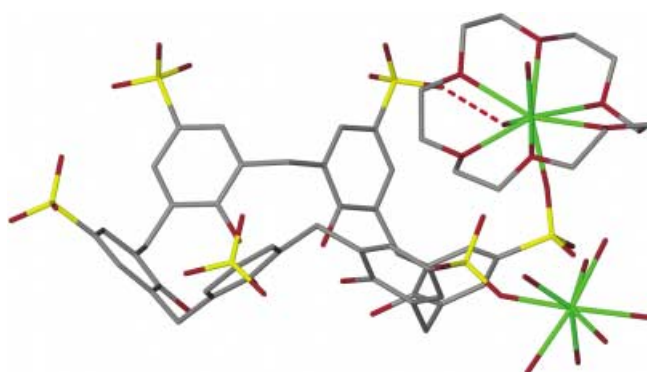

Figure 2. Projection of the "ferris wheel" arrangement in **2** (hydrogen atoms and solvent water molecules omitted for clarity).

$P2_12_12_1$ is chiral. This contrasts with the bilayer arrangement in **1**. The extended structure also has extensive hydrogen bonding associated with a large number of water molecules in the unit cell and with host–guest interplay between the above
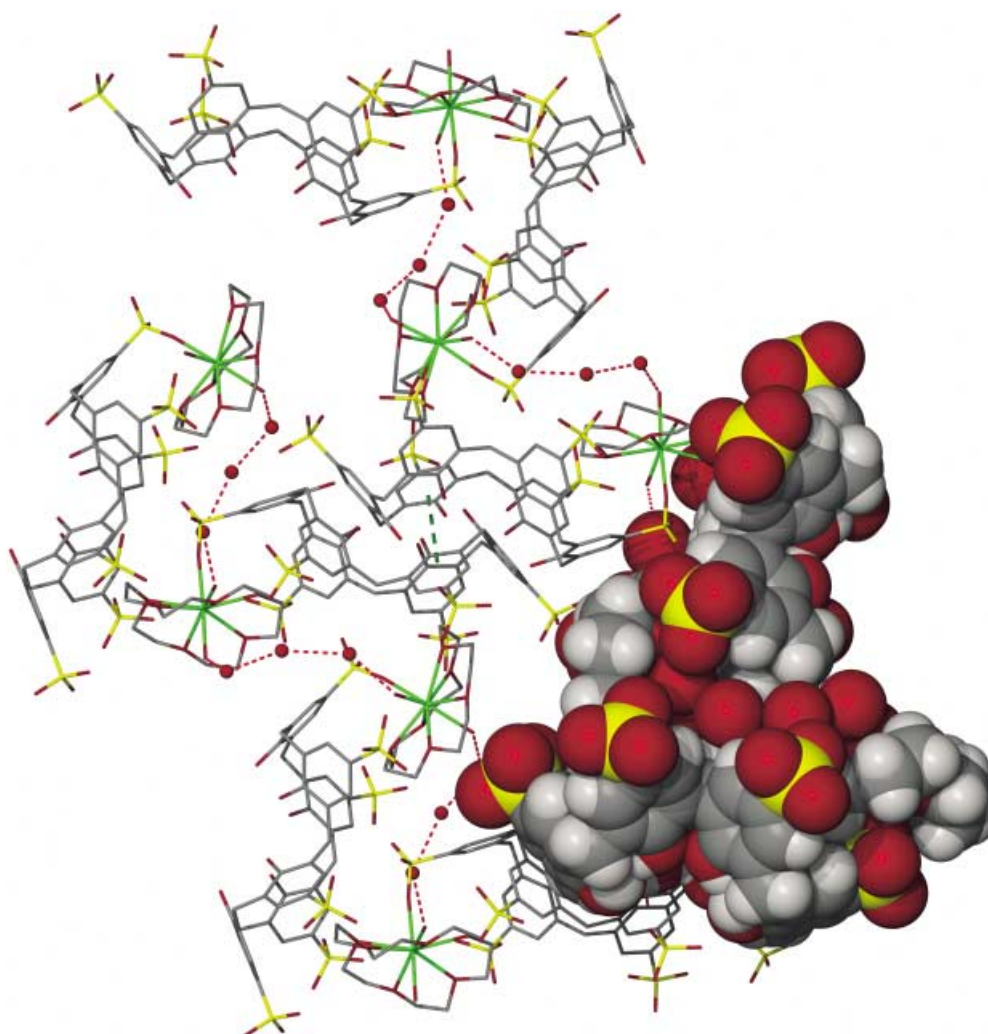
Figure 3. Extended structure of **2** (coordinated europium hepta-aqua cations, hydrogen atoms, and other solvated water molecules omitted for clarity).

"supermolecules". The latter is part of a herring bone type arrangement, whereby the crown ether of one "supermolecule" resides in the otherwise unoccupied cavity of another supermolecule (Figure 3). Three of the solvent water molecules form a hydrogen-bonded chain between "supermolecules" (EuO ··· O and O ··· O distances ranging from 2.676 to 2.884 Å). As in the previous structure, the lanthanide content requires the calixarenes to take on a 6 − charge. Interestingly the "ferris wheel" arrangement in the calix[4]arene analogue acts as a "supercation" with a chloride counterion.[20]

Complex **3**, has a "double partial cone" conformation, which possibly results from excess [18]crown-6 disrupting the hydrogen-bonding regime at the base of the calixarene for the "up – up" conformation. The asymmetric unit is composed of two half *p*-sulfonatocalix[6]arene molecules, two [18]crown-6 molecules, two nona-aqua trivalent europium cations (one of which has a ligated water molecule disordered over two sites) and several solvent water molecules. The extended structure is highly complex, and as for **1** and **2**, the calixarenes take on a 6 − charge. The structure in complex **3** has two distinct "supermolecules" (**3A** and **3B**) based on each calixarene, which are shown in Figure 4, and differ mainly in the hydrogen bonding of the nona-aqua cations.

"Supermolecule" **3A** has the cations residing close to an [18]crown-6 molecule, with one ligated water molecule pointing directly towards the centre of the crown ether and hydrogen bonding to two of the crown ether oxygen centres, EuO ··· O distances 2.716 and 2.964 Å, Figure 4 (top). Another ligated water molecule hydrogen bonds to one of the crown ether oxygen centres, EuO ··· O distance 2.901 Å. The same crown ether is noticeably distorted due to hydrogen bonding of two oxygen donor atoms of the [18]crown-6 to a water molecule situated on the opposite side of the crown ether to the lanthanide cation species (O ··· O distances 2.758 and 2.903 Å). The same water molecule hydrogen bonds to one phenolic group of the calixarene (O ··· OPh distance 2.645 Å). Supermolecule **3B** (Figure 4, bottom) has the crown ether now interacting with two water molecules, each of which reside on either side of the crown ether. Both of these hydrogen bond to two oxygen centres of the [18]crown-6- (O ··· O distances 2.746 to 3.071 Å). One of the water molecules also hydrogen bonds to one of the phenolic groups of the other partial cone (O ··· OPh distance 2.575 Å), whilst the second water molecule hydrogen bonds to a ligated water molecule of the trivalent lanthanide metal cation (O ··· OEu distance 2.693 Å).

Figure 5. Cartoon showing hydrogen bonding and π-stacking interactions in complex **3**.
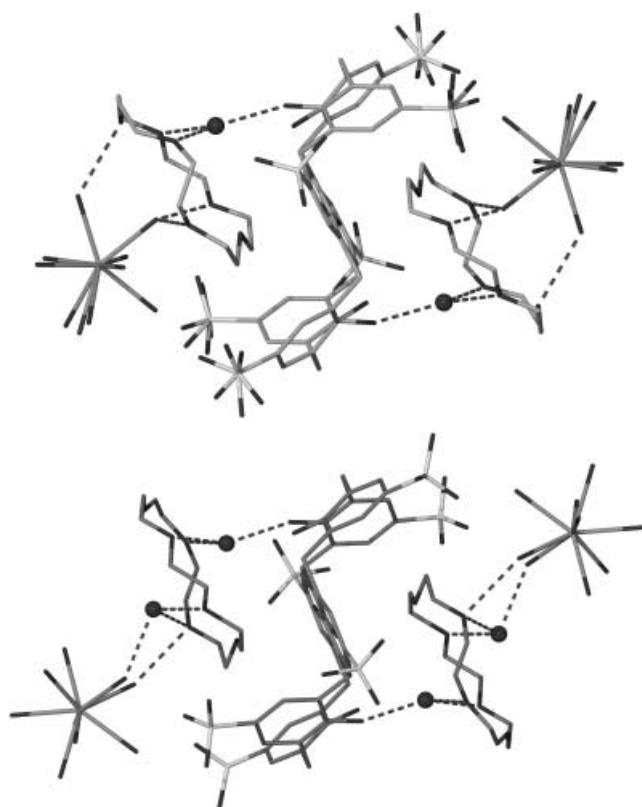

Figure 4. Projections of **3**: "supermolecule" **3A** (top; two of the three sulfonate groups of in the asymmetric unit are disordered equally over two sites) and **3B** (bottom).

The two "supermolecules" independently alternate, forming columns within one plane of the extended structure. These columns are assembled through hydrogen bonding between ligated water molecules of the lanthanide species and sulfonate groups from the nearest identical building unit (EuO···OS distances 2.744 and 2.758 Å for **A** and **B**, respectively). In addition, intercolumn hydrogen bonding is also evident (EuO···OS distances 2.758 (**A**) and 2.917 Å (**B**)). As the structure is extended further, a simple gridlike packing of these columns becomes apparent, shown in cartoon form, as projected along the *a* axis (Figure 5). The nearest dissimilar "supermolecules" also hydrogen bond to each other in a similar manner (Figure 6; EuO···OS distance 2.627 Å). π-Stacking occurs in the extended structure between one phenyl ring of nearest dissimilar supermolecules with aryl centroid–centroid separations of 3.616 Å (Figure 6, dashed green line).
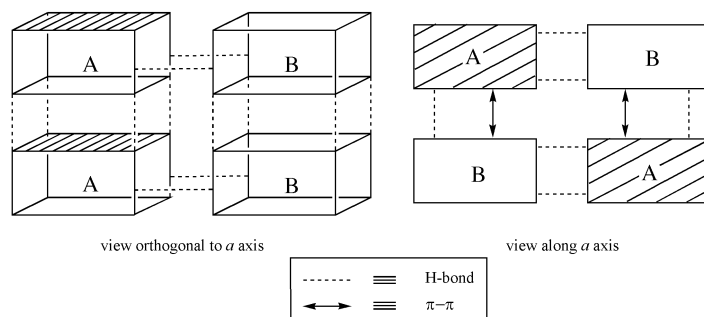
Conclusion

The potential for water soluble *p*-sulfonatocalix[6]arene in forming novel structural arrays has been developed, along with control of the conformation of the calixarenes, and this is likely to lead into larger arrays such as spheres and nanorods. Given that the structural motifs are similar to those accessed with the smaller sibling *p*-sulfonatocalix[4]arene, for which the incorporation of amino acids, peptides, and other (bis)-amino functionalised guests is possible,[11, 19, 20, 28] the incorporation of such species in the system involving *p*-sulfonatocalix[6]arene should be possible under varied conditions.

Experimental Section

p-Sulfonatocalix[6]arene was prepared by literature methods, whilst [18]crown-6 and the lanthanide(III) chlorides were purchased from Aldrich and used as supplied.[29]
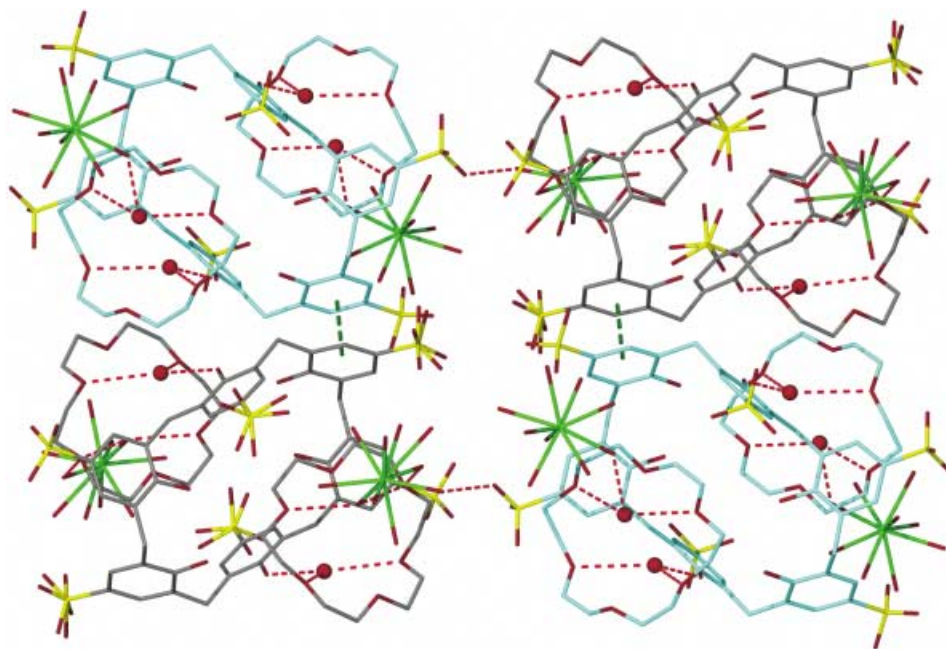

Figure 6. The 2D grid resulting from packing of columns of molecules of **3A** and molecules of **3B** showing hydrogen bonding within the columns and between adjacent dissimilar columns; some of the water molecules bound to the metal centres are disordered equally over two orientations.

[Tb(H₂O)₈]³⁺[([18]crown-6[Tb(H₂O)₇](*p*-sulfonatocalix[6]arene)]³⁻ · 22H₂O (1): *p*-Sulfonatocalix[6]arene (8 mg, 7 µmol), [18]crown-6 (8 mg, 30 µmol), and anhydrous terbium(III)chloride (10 mg, 38 µmol) were dissolved in distilled water (2 cm⁻³); small prismatic colourless crystals formed on slow evaporation.

[M(H₂O)₇]³⁺[{M ⊂ ([18]crown-6)(H₂O)₂} ∩ (*p*-sulfonatocalix[6]arene)]³⁻ · 17H₂O (2: M³⁺ = Nd, Eu): *p*-Sulfonatocalix[6]arene (10 mg, 8.9 µmol), [18]crown-6 (8 mg, 30 µmol) and anhydrous europium(III)chloride (10 mg, 39 µmol) were dissolved in distilled water (2 cm⁻³). On standing over three days, large purple/brown prismatic crystals formed.

[M(H₂O)₉]₂³⁺[([18]crown-6) ∩ (*p*-sulfonatocalix[6]arene)₀.₅]₂³⁻ · 24H₂O (3: M³⁺ = Eu, Tb): *p*-Sulfonatocalix[6]arene (10 mg, 8.9 µmol), [18]crown-6 (20 mg, 75 µmol) and anhydrous europium(III) chloride (8 mg, 31 µmol) were dissolved in distilled water (2 cm⁻³). On standing over three days, large colourless prismatic crystals formed.

X-ray crystallography: X-ray data for all compounds was collected on an Enraf–Nonius KappaCCD diffractometer details of which are given in Table 1. CCDC-202193–202195 contain the supplementary crystallograph-

Table 1. X-ray crystallographic data for compounds **1–3**.

Complex	1	2	3
formula	$C_{54}H_{140}O_{32}S_6Tb_2$	$C_{54}H_{106}O_{56}S_6Eu_2$	$C_{66}H_{152}O_{76}S_6\,Eu_2$
M_r	1811.86	2147.67	2658.16
crystal size [mm]	$0.10 \times 0.12 \times 0.16$	$0.13 \times 0.14 \times 0.18$	$0.09 \times 0.13 \times 0.16$
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$
T [K]	150(2)	150(2)	150(2)
a [Å]	22.026(4)	17.1494(2)	14.6331(3)
b [Å]	18.798(4)	17.9560(2)	21.2138(4)
c [Å]	24.923(5)	26.9000(3)	21.5897(4)
α [°]			110.254(10)
β [°]	104.75(3)		103.205(10)
γ [°]			105.409(10)
V [Å³]	9979.0(3)	8283.3(16)	5668.4(19)
Z	4	4	2
ρ_{calcd} [Mg m⁻³]	1.206	1.722	1.317
θ range [°]	1.37 to 26.00	1.64 to 26.00	1.52 to 25.00
reflns collected	145103	58373	69386
independent reflns (R_{int})	19587 (0.1116)	16184 (0.0691)	19411 (0.1093)
parameters	1217	1063	1322
final $R1$ [$I > 2\sigma(I)$]	0.1102	0.0476	0.1505
S	1.196	1.039	1.123
$wR2$ (all data)	0.2623	0.1263	0.3639
min/max residual electron density [e Å³]	3.63/ − 2.50	2.81/ − 1.14	4.70/ − 1.94

ic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk). Some solvent water molecules in compounds **1** and **3** were refined isotropically. Residual electron density in compounds **1** and **2** is associated with disordered metal cations. Residual electron density in compound **3** is associated with a disordered metal cation, mainly two peaks of 4.70 and 4.08 which reside around 1.3 Å either side of a Eu metal centre.

Isostructural complexes

Complex 1: For the isostructural thulium complex, the unit cell parameters were $a = 18.8349(3)$, $b = 21.7860(4)$, $c = 25.2678(5)$ Å, $\alpha = 89.9998(18)$ $\beta = 77.6929(20)$ $\gamma = 90.1601(9)$°.

Complex 2: For neodymium, structural elucidation showed a high degree of disorder surrounding the sulfonate groups of the calixarene as well as the poly-aqua neodymium species. $C_{54}H_{80}O_{50}S_6Nd_2$, $M_r = 2010.02$, orthorhom-

bic, $a = 17.515(4)$, $b = 18.248(4)$, $c = 27.042(5)$ Å, $V = 8643(3)$ Å³, $\mu = 1.545$ mm⁻¹, $T = 150$ K, space group $P2_12_12_1$ (no. 19), $Z = 4$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), GoF = 2.026, $R_1 = 0.1444$, 94714 reflections measured, 15094 unique ($R_{int} = 0.1503$), which were used in all calculations. The final $\omega R(F^2)$ was 0.3383 (all data).

Complex 3: For the isostructural terbium complex, the unit cell parameters were $a = 14.6462(4)$, $b = 21.3919(7)$, $c = 21.7261(6)$ Å, $\alpha = 111.423(9)$ $\beta = 104.375(9)$ $\gamma = 103.305(11)$°.

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