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Supramolecular assemblies of *p*-sulfonatocalix[4]arene with aquated trivalent lanthanide ions

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New structural motifs incorporating trivalent lanthanoid ions and *p*-sulfonatocalix[4]arene, derived from solutions with or without potential host molecules for the calixarene, notably 18-crown-6, 1-aza-18-crown-6, and cryptand[2.2.2], have been authenticated. These include coordination polymers which form bi-layer sheet structures and an unprecedented combined 'ferris wheel' and 'molecular capsule' structure for Ce^{3+} which incorporates two previously reported structural motifs associated with this type of chemistry, respectively for elements to the left and right of cerium in the lanthanide series.

Introduction

Water soluble calix[*n*]arenes have been widely investigated, and are becoming increasingly important in the field of supramolecular chemistry and crystal engineering, showing interesting inclusion properties and a wide range of metal coordination complexes both in solution and in the solid state.[1–9] One such type of calix[*n*]arene is the *p*-sulfonated calixarenes which can form large molecular assemblies with various guest molecules leading to highly complex supramolecular architectures.[10–13]

In recent studies we focussed on the supramolecular chemistry of water soluble sulfonated calix[4]arenes with disc shaped host molecules such as crown ethers,[1,14] and tetra-protonated cyclam,[15,16] and also amino acids and related molecules.[17] The formation of bi-layer structures, shown in cartoon form in Fig. 1, is commonplace, and often these are based on 'molecular capsules', 'ferris wheel' type structures, and 'molecular capsules' formed with polynuclear metal cations of Al^{3+},[11] Cr^{3+},[10] or Rh^{3+}.[18]

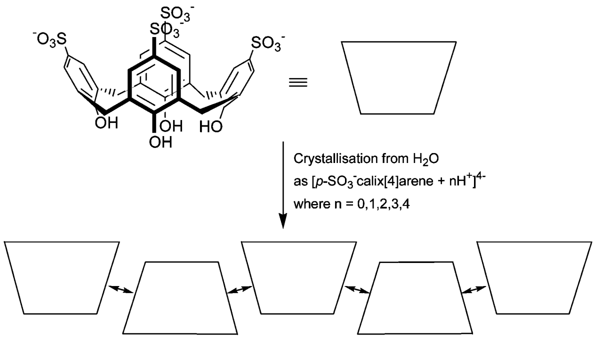

Fig. 1 Schematic representation of the π-stacked (shown by double arrows) bi-layer of *p*-sulfonatocalix[4]arene.

Furthermore, in a related study we have shown that sulfonated calixarenes form large molecular assemblies with pyridine *N*-oxide, resulting in spherical arrays of 12 calixarenes with the cavities directed away from the centre of the cluster, and the formation of nano-tubes with the calixarene cavities directed outwards.[1]

This contribution concerns extending the lanthanoid work on the inclusion of 18-crown-6 into the calixarenes, and ascertaining the influence of related 1-aza-18-crown-6, and also [2.2.2]cryptand on forming supramolecular assemblies of *p*-sulfonatocalix[4]arene. We report the characterisation of two structures comprised of bi-layer arrangements of sulfonato-calix[4]arenes linked by lanthanoid cations in different environments, **1** and **2**, as well as a combined hybrid 'ferris wheel'–'molecular capsule', **3**, where each calixarene has an 18-crown-6 molecule in the cavity. The 'ferris wheel' arrangement has a lanthanoid in the 18-crown-6 which binds to one of the sulfonate groups of a calixarene, previously observed for La^{3+}.[19] The 'molecule capsule' arrangement has a crown ether shrouded by two calixarenes, as a 'Russian Doll' assembly, either with a sodium or lanthanoid in the core of the crown ether, or with the crown ether devoid of metal ions.[14]

Results and discussion

2D hydrogen bonded polymers; $[M(H_2O)_8][p\text{-sulfonatocalix[4]arene} + H^+]$ (M^{3+} = Gd, Tb, Tm) 1

The title compounds were prepared by slow evaporation of an aqueous mixture of MCl_3, [2.2.2]cryptand or 1-aza-18-crown-6, and *p*-sulfonatocalix[4]arene [eqn. (1)]. The resulting supramolecular structure possesses an octa-aqua lanthanoid(III) cation rather than being directly bound to at least one of the sulfonate groups of the calixarene, as is always the case for 'lanthanides', except for Sc^{3+}, but where the ions are associated as dimeric bridging hydroxide species, $[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(H_2O)_5]^{4+}$.[20] Nevertheless, changing the conditions does result in the formation of a coordination polymer now with each scandium of $[(H_2O)_4Sc(\mu\text{-}OH)_2Sc(H_2O)_4]^{4+}$ bound to a single sulfonate group. Overall, the lack of direct sulfonate–metal interplay in the present study is particularly noteworthy. The sulfonated calixarene molecules adopt the commonly observed bi-layer structure which optimises hydrophobic–hydrophobic π-stacking interactions between adjacent macrocycles (Fig. 2).

Surprisingly the calixarenes do not self assemble into the typical 'molecular capsule'. This is a special bi-layer arrangement such that bi-layers are linked together through non-covalent interactions with the host molecule in the cavities of

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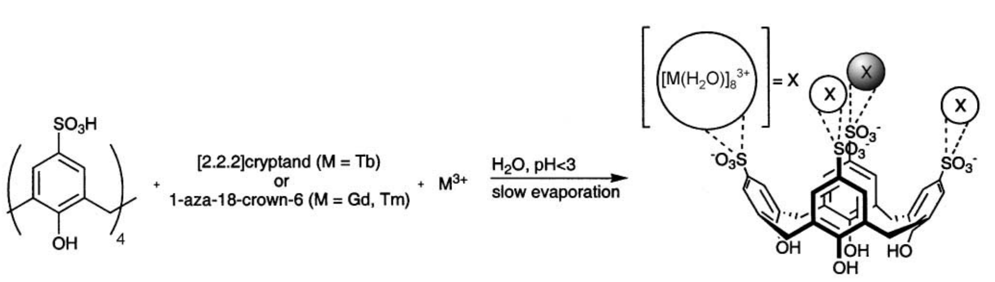

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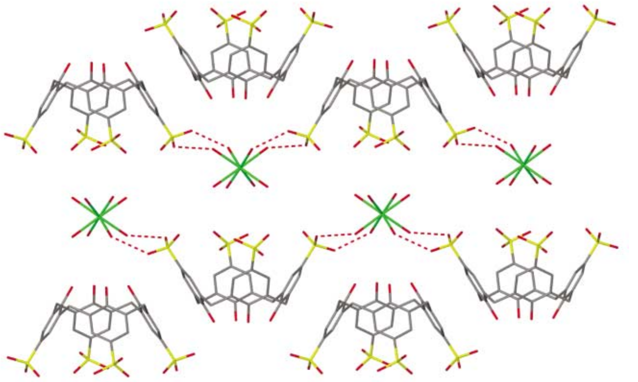


Fig. 2 Crystal packing of $[M(H_2O)_8][p\text{-sulfonatocalix[4]arene} + H^+]$ showing the bi-layer structure of calixarenes and hydrogen bonding of the $M(H_2O)_8{}^{3+}$ cations to two of the four nearest neighbouring calixarene molecules (non-coordinated water molecules and hydrogens omitted for clarity).

two calixarenes, as has been previously reported even in the absence of 18-crown-6 as a guest molecule.[20] In such cases, the bi-layers are arranged with the cavity of one calixarene from one bi-layer directly above the cavity of a calixarene from an adjacent bi-layer. In the present structure, the cavity of one calixarene resides directly above the base of another calixarene, Fig. 2. The bi-layers are separated by the aquated lanthanoid ions, Fig. 2, and also by disordered water molecules.

It is pertinent to mention that one water molecule resides within the cavity of the sulfonated calixarene on a C_4 crystallographic symmetry axis (Fig. 3) showing OH-aromatic π-hydrogen bonding to the water.[7,11] Interestingly this arrangement has also been established for a sulfonated calixarene as part of a complex structure also containing 'molecular capsules', which are not part of bi-layers, and Al^{3+} Keggin ions.[11]

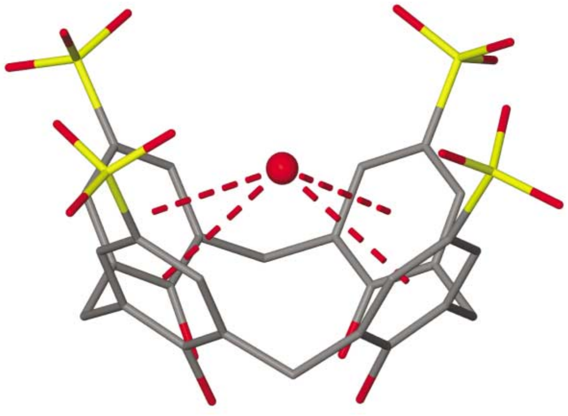


Fig. 3 Projection of the calixarene showing the water molecule (on a C_4 symmetry axis) in the cavity of a sulfonated calixarene; centroid–O distance 3.754 Å.

A striking feature of this structure is the infinite hydrogen bond network between $M(H_2O)_8{}^{3+}$ cations and four nearest neighbour calixarene molecules (Fig. 4) thereby connecting layers of calixarenes (TbO–OS 2.751 and 2.731 Å). This network type structure is mirrored by Ce–O–S bonding in the cerium bi-layer sheet structure discussed below.

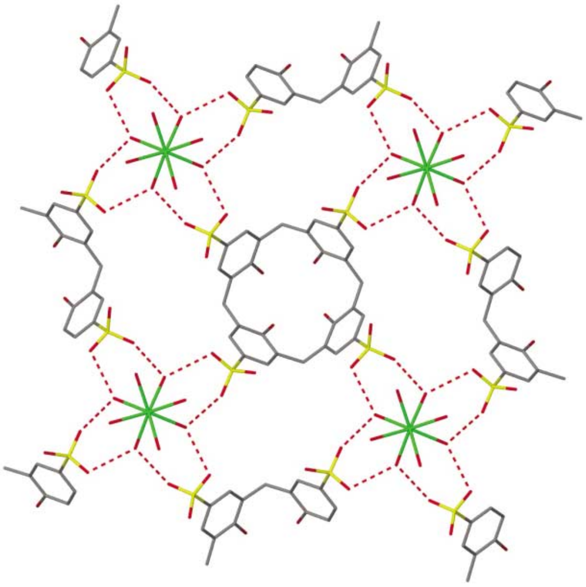
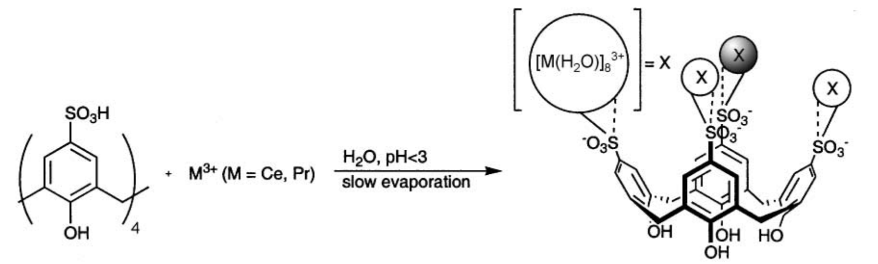


Fig. 4 Hydrogen bonding network of calixarene molecules and $Tb(H_2O)_8{}^{3+}$ cations; each aquo-metal cation experiences eight hydrogen bond interactions between four nearest calixarenes (other calixarenes of the bi-layer and disordered, non-coordinating water molecules have been omitted for clarity).

[2.2.2]Cryptand has been shown to act as a guest in supramolecular chemistry with C-methylresorcin[4]arene[21] and cyclotriveratrylene.[22] In these instances, the cryptand resides in the bowl of the resorcinarene and CTV host molecules. In the present case however, attempts to incorporate the [2.2.2]cryptand into materials with *p*-sulfonatocalix[4]arene have thus far been unsuccessful. This may perhaps be attributed to both the size and nature of the cryptand in conjunction with the large bulky sulfonate functionality at the upper rim of the calixarenes.

Within the structure, four aqua ligands of the metal cation are hydrogen bonded to sulfonate groups pointing towards the upper rims of the calixarenes whilst the remaining four ligated water molecules point into the hydrophilic layer separating hydrophobic layers (Fig. 2), Tb–OH_2 2.382(10) and 2.364(6) Å. It should be noted that there are no MO–OS hydrogen bond interactions between the four aqua ligands pointing into the hydrophilic layer and the sulfonate groups of the layer directly above and below them.

When analogous chemistry is performed in an attempt to incorporate 1-aza-18-crown-6 in place of the cryptand (or 18-crown-6), the same solid state structure results for gadolinium and thulium in which the lanthanoid metal cation is not coordinated to the sulfonate groups of the calixarenes. As was stated earlier, the presence of 18-crown-6 generates a 'molecular capsule' type structure and the presence of other potential guests described here results only in the hydrogen bonded polymer. It was anticipated that the host molecule would form the 'Russian-doll' structure due to its similarity in size to



(2)

18-crown-6, and also that it is related to cyclam which also forms ‘molecular capsules’, at least with polyaquated transition metal ions. The fact that this is not observed suggests there is a delicate balance between inclusion/exclusion of the host. This most likely is a result of crystal packing since sulfonated calixarenes readily form inclusion complexes in aqueous media. As is seen commonly for this type of structure, several disordered water molecules (equivalent to four water molecules) are present in the asymmetric unit, residing near the hydrophilic bases and rims of the calixarenes.

It is noteworthy that the above structures resulted from incorporation of lanthanide metals which lie from the middle to right hand side of the lanthanide series. When several analogous experiments were performed using trivalent samarium and europium, no crystals suitable for X-ray diffraction studies were obtained. Although europium lies directly to the left of gadolinium, there appears to be a point at which the above structure dominates perhaps due to the specific size of the cation in question.

2D *p*-sulfonatocalix[4]arene coordination polymers; $M(H_2O)_5$-(*p*-sulfonatocalix[4]arene + H^+) (M^{3+} = Ce, Pr), 2

A two dimensional *p*-sulfonatocalix[4]arene coordination polymer, $M(H_2O)_5$(*p*-sulfonatocalix[4]arene + H^+), is formed using the larger rare earth ions, Ce^{3+} and Pr^{3+}. The title compound forms in the absence of any potential guest molecule merely from the corresponding metal trifluoromethanesulfonate nonahydrates and *p*-sulfonatocalix[4]arene [eqn. (2)]. In contrast to the previous compounds, this structure exhibits Ce–O–S linkages rather than $CeOH_2$–OS hydrogen bonding. Nevertheless, analysis of the crystal packing reveals the bi-layer array as described earlier (Figs. 1 and 5). As for the above structures, the calixarenes and lanthanoids reside on crystallographic C_4 symmetry axes. Within the structure, each metal is nine-coordinate, and binds to an oxygen atom of four sulfonate groups belonging to four different calixarenes [Ce–OSO_2 2.441(4) Å]. This coordination environment and associated bond lengths are typical for structures involving Ce^{3+}.[23,24] The Ce–OSO_2 bonds are oriented at 79.08(9)° with respect to each other, and all the calixarenes for a particular Ce^{3+} have all their cups facing in the same direction, creating a plane of pockets. In addition to this each Ce^{3+} is bound to four water molecules, which are oriented in the same direction as the sulfonate groups on the calixarenes [Ce–OH_2 2.535(4) Å]. One water molecule is in a cavity defined by the benzene moieties of four calixarenes within the sheet [Ce–OH_2 2.66(1) Å]. The latter water molecules are within hydrogen-bonding distance of the sulfonato groups belonging to several calixarenes within this sheet (CeO–OS 2.906 Å) (Fig. 6). The possibility that it is actually a tetravalent ceric ion can be ruled out on the basis that crystals obtained from similar solutions containing Pr^{3+} possessed unit cells indicative of analogous structures, consistent with the fact that praesodymium is not stable as a tetracation in aqueous solution.[25]

A marked difference between the present and previous structures is the presence of hydrogen bonding between the aqua ligands of cerous ions in any layer and the sulfonate and phenolic groups of the calixarenes sitting above and below respectively (Fig. 5). In the previous structure, the hydrophilic layer is wide enough to separate the layers, presumably preventing hydrogen bonding analogous to that occurring here.

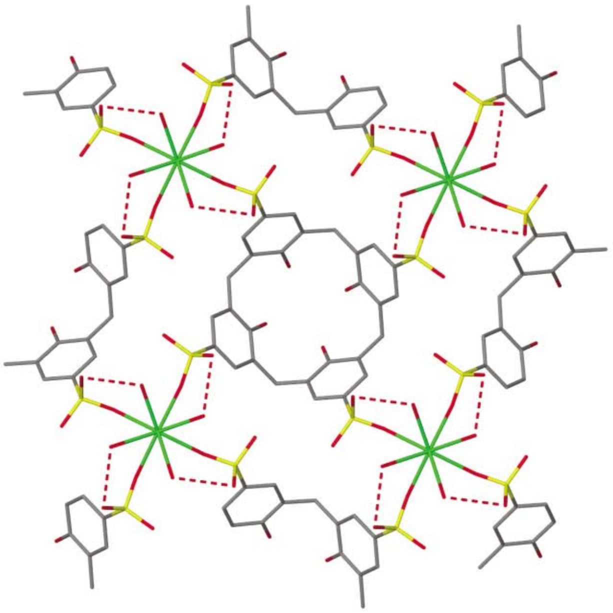


Fig. 5 Cross-section of the two dimensional coordination polymer in the $Ce(H_2O)_5$(*p*-sulfonatocalix[4]arene + H^+) structure showing the bi-layer packing and hydrogen bonding interactions.

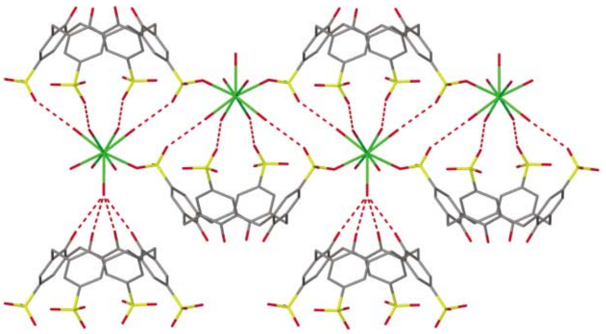
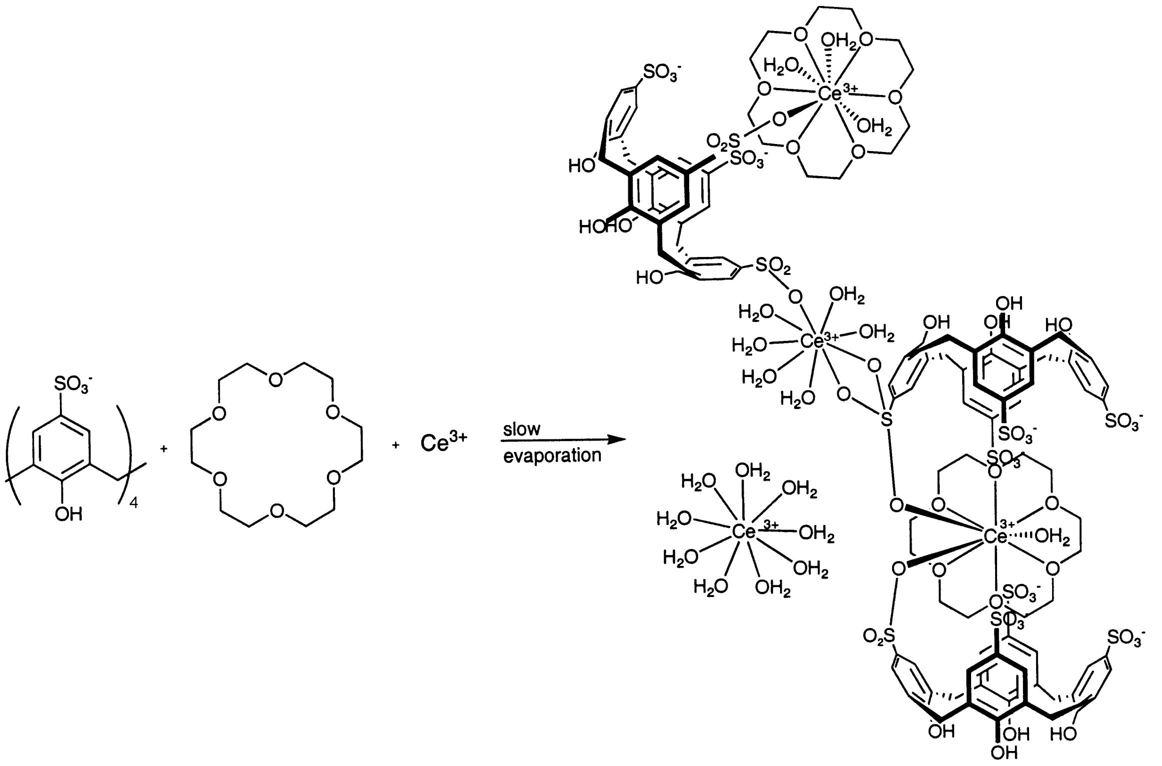


Fig. 6 Projection of the two dimensional coordination polymer in $Ce(H_2O)_5$(*p*-sulfonatocalix[4]arene + H^+) showing the direct Ce–O–S bonding as well as hydrogen bond interactions between four of the five free aqua ligands and the nearest sulfonate groups.

As is common in these types of complexes, two solvated water molecules in the asymmetric unit reside near the hydrophilic rim of the calixarenes which form a hydrophilic layer in the extended structure. Electron density located within the cavity has been modelled as a disordered water molecule, demonstrating the recurrence of aromatic π hydrogen bonding as seen previously. That free water molecules also hydrogen bond to sulfonate groups and metal-aqua ligands, is not unusual given the organic clay like structure.[26] In order to satisfy charge balance, as with the previous case, each calixarene must possess one protonated sulfonate group which is acceptable given the pH of the reaction solution.



(3)

'Ferris wheel'–'molecular capsule' hybrid structure; [(Ce(H_2O)$_3$⊂18-crown-6∩*p*-sulfonatocalix[4]arene)Ce(H_2O)$_6$(Ce(H_2O)⊂18-crown-6⊂*p*-sulfonatocalix[4]arene)]Ce(H_2O)$_9$·23.5H_2O, 3

Ce^{3+} has a radius intermediate with that of La^{3+} and the trivalent lanthanide ions which form molecular capsules (Pr^{3+}–Lu^{3+}). When solutions of aquated Ce^{3+} ions are in contact with solutions of aquated sodium *p*-sulfonatocalix[4]arene and 18-crown-6, an assembly of the title compound forms [eqn. (3)]. It is a hybrid of the two general structural types associated with La^{3+} and the smaller rare earths consisting of a 'ferris wheel' fused with a capsule motif. This structure is a second example of a previously unreported non-coordinating mononuclear lanthanoid cation which interacts with sulfonated calixarenes as described earlier.

The asymmetric unit consists of three *p*-sulfonatocalix[4]arenes, two crown ethers, four Ce^{3+} ions, and solvated water molecules. The four Ce^{3+} ions are each in very different coordination environments, as illustrated in Fig. 7.

Ce1 resides in the centre of an 18-crown-6 molecule. It is coordinated to all six oxygens of the crown ether [Ce–O 2.651(10) to 2.731(9) Å], as well as three water molecules [Ce–O 2.458(10), 2.522(10), 2.505(10) Å]. The crown is in turn cupped in the bowl of a calixarene, allowing Ce1 to bind to a single sulfonate group [Ce–OSO_2 2.432(10) Å]. The second cerium ion, Ce2, also lies at the centre of an 18-crown-6 molecule. However, in this instance, the crown ether is encapsulated by two calixarene molecules. Ce2 binds to six crown ether oxygens [Ce–O range from 2.560(2) to 2.720(2) Å], one water molecule [Ce–OH_2 2.447(10) Å], and one disordered sulfonate group from each calixarene.

Hydrogen bonding occurs between the metal-bound water molecule and sulfonato groups from both calixarenes (O–O distances are 2.764 and 2.723 Å). The capsule structure is consistent with the complimentarity of curvature of the crown ether and the bowl of the calixarene, which optimises van der Waals and hydrophobic interactions between these tectons.

The two structural moieties described are linked by Ce3 which coordinates to a sulfonate group on the 'ferris wheel' [Ce–O 2.426(8) Å], as well as a sulfonate group on the upper calixarene of the capsule [*via* two O-linkages Ce–O 2.581(9) and 2.738(9) Å]. It also ligates six water molecules [distances range from 2.474(9) to 2.592(12) Å], one of which is within hydrogen bonding distance of a sulfonato group of the 'ferris wheel' motif (the O–O distance is 3.007 Å). Finally, Ce4 is positioned near the sulfonate group of the 'ferris wheel'. It is bound by nine water molecules [2.352(3) to 2.674(17) Å], four of which hydrogen bond with sulfonato groups on the capsule (O–O distances range from 2.604 to 2.967 Å). This fully aquated ion

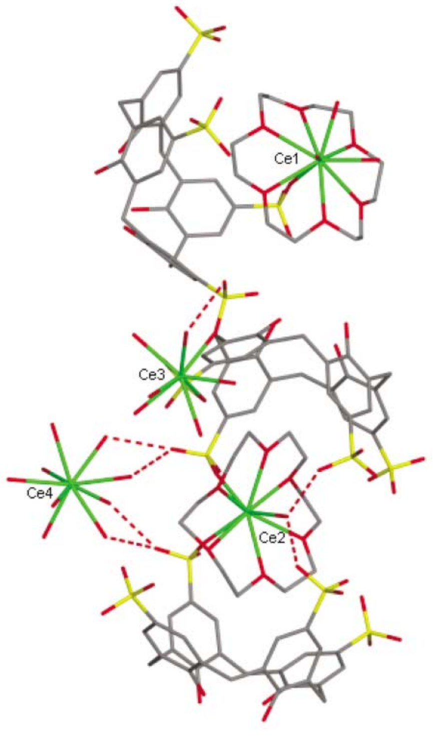


Fig. 7 Projection of [(Ce(H_2O)$_3$⊂18-crown-6∩*p*-sulfonatocalix[4]arene)Ce(H_2O)$_6$(Ce(H_2O)⊂18-crown-6⊂*p*-sulfonatocalix[4]arene)]Ce(H_2O)$_9$·23.5H_2O showing hydrogen bonding arising from metal-coordinated water molecules and the four different coordination environments of Ce^{3+}.

serves to balance the charge of the attenuated capsule and is another example of non-sulfonate coordinating aqua species.

The asymmetric unit assumes four different orientations in the extended structure, allowing a radical departure from the bi-layer packing mode (Fig. 8).

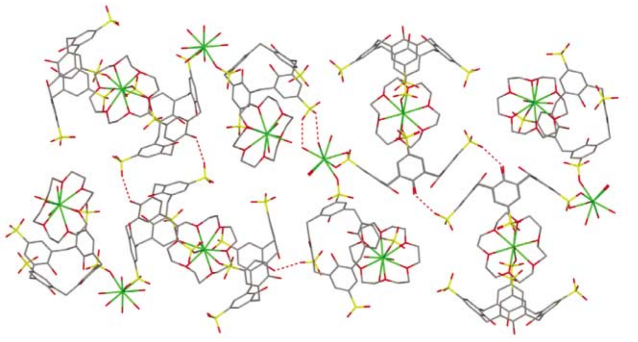


Fig. 8 Cross section of the continuous structure from Fig. 7 showing the four different orientations of the attenuated capsule in the extended structure; Ce4 has been omitted for clarity.

The arrangement is stabilised by extensive hydrogen bonding between phenolic and sulfonate groups (O–O distance 2.764 Å), as well as sulfonate groups and metal-bound waters of adjacent units (O–O distances are 2.714 and 2.919 Å).

Within infinite seams, the water molecules attached to the fully aquated Ce4 hydrogen bond to the sulfonate groups of 'ferris wheels' (O–O 2.872 Å), (Fig. 9). Numerous uncoordinated water molecules also reside around the hydrophilic regions of the structure, and add to the complexity and stability of the hydrogen bonded network.

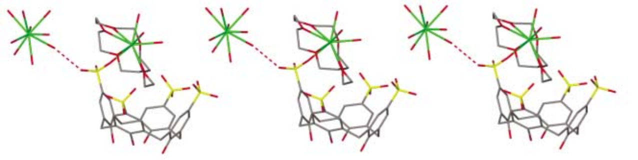


Fig. 9 In the extended structure of [(Ce(H_2O)$_3$⊂18-crown-6∩*p*-sulfonatocalix[4]arene)Ce(H_2O)$_6$(Ce(H_2O)⊂18-crown-6⊂*p*-sulfonatocalix[4]arene)]Ce(H_2O)$_9$·23.5H_2O, metal-coordinated water molecules hydrogen bond to sulfonate groups within the 'ferris wheel' moieties.

Experimental

1-Aza-18-crown-6[27] and sulfonated calixarenes[28] were synthesised by literature methods whilst 18-crown-6 and [2.2.2]-cryptand were purchased from Aldrich and used as supplied. X-Ray data for the hydrogen bonded coordination polymers and direct coordination polymers were collected on an Enraf-Nonius KappaCCD diffractometer. The remaining structures were obtained from data collected on a Bruker SMART CCD diffractometer.

2D hydrogen bonded polymers; [M(H_2O)$_8$][*p*-sulfonatocalix[4]-arene + H^+] (M^{3+} = Gd, Tb, Tm), 1

Terbium(III) chloride (10 mg, 37.7 µmol), *p*-sulfonatocalix[4]arene (10 mg, 13.4 µmol) and [2.2.2]cryptand (8 mg, 21.3 µmol) were dissolved in distilled water (1 cm^3). On slow evaporation over 1 week, colourless rectangular plates which were suitable for X-ray diffraction studies formed, yield = 7 mg (42%).

Crystal data. $C_{28}H_{68}O_{40}S_4Tb_1$, M = 1332.01, tetragonal, a = 13.4475(4), c = 15.0257(4) Å, U = 2717.18(14) Å^3, μ = 1.560 mm^{-1}, T = 150 K, space group $P4/n$ (no. 85), Z = 2, Mo-Kα radiation (λ = 0.71073 Å), Final GOF = 1.296, R_1 = 0.0753, 9583 reflections measured, 2671 unique (R_{int} = 0.0389) which were used in all calculations. The final $\omega R(F^2)$ was 0.1887 (all data).

CCDC reference number 188552.

Gadolinium chloride (10 mg, 37.9 µmol), *p*-sulfonatocalix[4]arene (10 mg, 13.4 µmol), and 1-aza-18-crown-6 (5 mg, 18.9 µmol) were dissolved in distilled water (1 cm^3). Once left overnight, colourless plates which were suitable for X-ray diffraction studies had formed.

For Gd^{3+}, unit cell measurements were a = 13.4031(4), c = 15.0593(6) Å, T = 150 K, so it was assumed to be isostructural with the Tb^{3+} structure described earlier which was formed in the presence of [2.2.2]cryptand.

For Tm^{3+}, preparation method was identical to that of the Gd^{3+} analogue and the unit cell measurements were a = 13.3321(6), b = 13.3669(6), c = 14.8787(8) Å, T = 150 K. Therefore, it was assumed to be isostructural with both the Gd^{3+} and Tb^{3+} structures.

2D *p*-sulfonatocalix[4]arene coordination polymers; M(H_2O)$_5$-(*p*-sulfonatocalix[4]arene + H^+) (M^{3+} = Ce, Pr), 2

Reaction of the rare earth trifluoromethanesulfonate nonahydrates (10 mg, 13.3 µmol), where M^{3+} = Ce and Pr, with sodium *p*-sulfonatocalix[4]arene (8 mg, 9.61 µmol) in water (1 cm^3) produced coloured precipitates (red and green) at pH *ca.* 3. After filtration, the supernatants were left to stand. In the case of the reaction containing Ce^{3+} ions, irregularly-shaped red crystals of Ce(H_2O)$_5$(*p*-sulfonatocalix[4]arene + H^+)·8H_2O formed as the solution concentrated, yield = 5 mg (47%).

Crystal data. $C_{28}H_{47}O_{29}S_4Ce_1$, M = 1116.0, tetragonal, a = 11.8043(6), c = 14.2256(7) Å, U = 1982.22(17) Å^3, μ = 1.465 mm^{-1}, T = 123 K, space group $P4/n$ (no. 85), Z = 2, Mo-Kα radiation (λ = 0.71073 Å), Final GOF = 1.093, R_1 = 0.0586, 15658 reflections measured, 2289 unique (R_{int} = 0.0799) which were used in all calculations. The final $\omega R(F^2)$ was 0.1326 (all data).

CCDC reference number 188553.

For Pr^{3+}, unit cell measurements were a = 11.787(6), b = 11.789(6), c = 14.328(7) Å, so it was assumed to be isostructural with the Ce^{3+} analogue.

'Ferris wheel'–'molecular capsule' hybrid structure; [(Ce(H_2O)$_3$⊂-18-crown-6∩*p*-sulfonatocalix[4]arene)Ce(H_2O)$_6$(Ce(H_2O)⊂18-crown-6⊂*p*-sulfonatocalix[4]arene)]Ce(H_2O)$_9$·23.5H_2O, 3

Sodium *p*-sulfonatocalix[4]arene (8 mg, 9.61 µmol) and 18-corwn-6 (8 mg, 30.3 µmol) were dissolved in water and cerium trifluoromethanesulfonate (10 mg, 13.3 µmol) was added. A red precipitate formed at pH *ca.* 3 which was filtered off and the resulting supernatant was allowed to slowly evaporate over several months at room temperature after which time, irregularly shaped red–brown coloured crystals of the title compound grew, yield = 5 mg (13%).

Crystal data. $C_{108}H_{191}O_{102.5}S_{12}Ce_4$, M = 4074.7, monoclinic, a = 17.1712(13), b = 34.7223(26) c = 27.4122(21) Å, β = 99.2100(10), U = 16133(2) Å^3, μ = 1.375 mm^{-1}, T = 173 K, space group $P2_1/c$ (no. 14), Z = 4, Mo-Kα radiation (λ = 0.71073 Å), Final GOF = 1.057, R_1 = 0.1033, 98470 reflections measured, 35526 unique (R_{int} = 0.0957) which were used in all calculations. The final $\omega R(F^2)$ was 0.2843 (all data). Due to complexity within the structural solution, several of the atoms were refined isotropically.

CCDC reference number 188554.

See http://www.rsc.org/suppdata/dt/b2/b206129e/ for crystallographic data in CIF or other electronic format.

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