Rapid capture of 4,13-diaza-18-crown-6 molecules by p-sulfonatocalix[4]arene in the presence of trivalent lanthanide ions

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4,13-Diaza-18-crown-6 in the presence of aquated trivalent lanthanide ions and p-sulfonatocalix[4]arene results in a 'molecular capsule' type arrangement with two 4− charge calixarenes and two water molecules shrouding the di-protonated crown ether with overall charged balance from two lanthanide ions. Analogous chemistry in the presence of 1-aza-18-crown-6 under the same conditions results in an unusual bi-layer structural motif devoid of the crown ether, the difference in chemistry being in part ascribed to any 'molecular capsule' formed for the mono-aza crown ether taking on an overall 7− charge rather than a 6− charge, requiring fractional lanthanide ions for charge balance.

Introduction

Much work has been performed on the supramolecular chemistry of water soluble calixarenes.[1] They have been shown to be highly versatile as host molecules for hydrophobic guests and also for water molecules which hydrogen bond through OH ··· aromatic-π interactions.[2] They also form a vast range of metal coordination complexes in both solution and the solid state.[1–9] p-Sulfonatocalix[n]arenes have been shown to form large molecular assemblies with highly complex supramolecular architectures in the presence of suitable guest molecules. In particular p-sulfonatocalix[4]arene, which is the most studied in the series, is a versatile supramolecular tecton able to splay in all directions or pinch to form a cavity suitable for both globular and disc like guest molecules respectively.[10–14]

In recent studies we focused on the supramolecular chemistry of p-sulfonatocalix[4]arene in water with disc shaped host molecules such as crown ethers,[1,15] and tetra-protonated cyclam,[16,17] and also amino acids.[18] In addition, we have been able to confine more globular host molecules in the cavity of the calixarenes, notably [2.2.2]cryptand in the di-protonated form, as part of 'molecular capsule' type arrangements, with the calixarenes forming a continuous bi-layer motif.[14] The formation of bi-layer structures, shown in cartoon form in Fig. 1, is common-

Fig. 1 Schematic representation of the bi-layer arrangement of p-sulfonatocalix[4]arene.

place, and often these are based on 'molecular capsules'. More complicated structures are found in systems with 'ferris wheel' type structures, and 'molecular capsules' formed with poly-nuclear metal cations of Al^{3+},[11] Cr^{3+},[10] or Rh^{3+}.[19] In the di-protonated [2.2.2]cryptand example mentioned above we reported the bi-layer stacking with optimum CH ··· π

interactions rather than π-stacking interactions demonstrating different types of assembly of bi-layers.[14]

Furthermore, in a related study, Atwood et al. have shown that p-sulfonatocalix[4]arenes form large molecular assemblies with pyridine N-oxide and trivalent lanthanide ions, either spherical arrays of 12 calixarenes with the cavities directed away from the centre of the cluster, or nano-tubes with the calixarene cavities directed outwards.[1,13]

Related to the inclusion of the aforementioned di-protonated [2.2.2]cryptand chemistry,[14] is the inclusion of the same di-cation into the cavity of oxacalix[3]arene.[20] The present study also deals with inclusion chemistry of a dication, diprotonated 4,13-diaza-18-crown-6, as the disc shaped cyclic analogue of globular bicyclic [2.2.2]cryptand. The results include the rapid formation, and structural authentication, of a 'molecular capsule' type arrangement, 1, within which is encapsulated 4,13-diaza-18-crown-6 in the di-protonated form, similar to that of the cryptand example previously reported. We also report the characterisation of a new structural motif generated in the presence of 1-aza-18-crown-6 as a potential host for molecular capsules but surprisingly is not included, 2, under a range of conditions.

Results and discussion

Synthesis of (4,13-diaza-18-crown-6 + 2H⁺)⊂[(H₂O)₂-[M(H₂O)ₓ³⁺]₂[p-sulfonatocalix[4]arene]₂] (M³⁺ = Ce, Nd, Eu, Gd; x = 8, 9), 1

The title compounds were prepared by mixing the corresponding lanthanide(III) chloride, 4,13-diaza-18-crown-6, and p-sulfonatocalix[4]arene, eqn. (1). The discovery of rapid formation of the corresponding [2.2.2]cryptand complex prompted similar reactions for the current guest bearing in mind the possibility for di-protonation.[14] Indeed, this was the case with formation of crystals suitable for X-ray diffraction after only 30 minutes. The speed of crystallisation possibly relates to the charge balance achieved on di-protonation of the diaza crown ether requiring two trivalent lanthanide ions to balance the charge, noting the tetra anionic nature of the calixarene which is expected at pH 3.[20] The anaologous cryptand complexes occur only for the early lanthanides with a similar pattern emerging in the present study.

The complex crystallises in the monoclinic space group $P2_1/n$ with the asymmetric unit comprised of one calixarene, half the crown ether, a nona-aqua lanthanoid(III) cation, and one water molecule hydrogen bonded to the crown ether, which is half a 'molecular capsule', Fig. 2 (see below), along with several
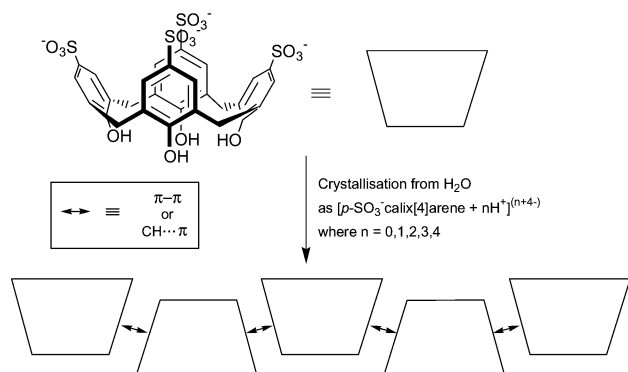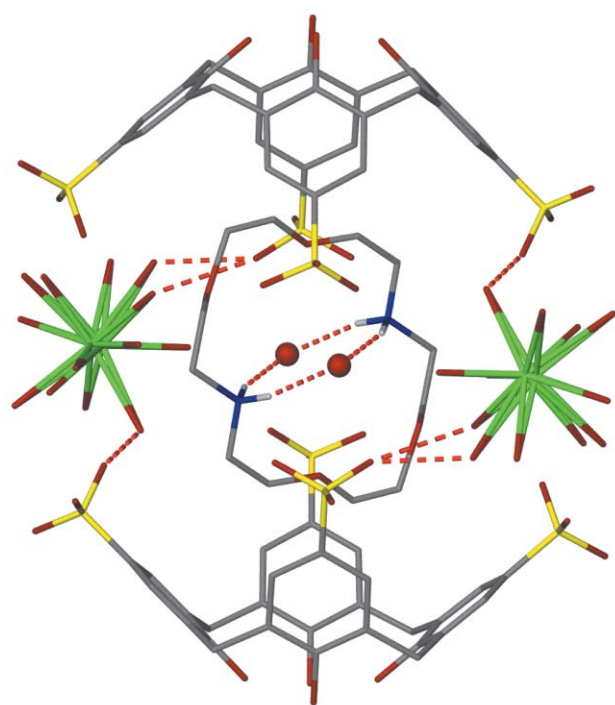
$$MCl_3 \ (M^{3+} = Ce, \ Nd, \ Eu, \ Gd) \ + \ 4,13\text{-diaza-18-crown-6} \ +$$

pH <3, H₂O

30 min

(1)

Fig. 2 Projection of a 'molecular capsule' in (4,13-diaza-18-crown-6 + 2H⁺)⊂[(H₂O)₂[Nd(H₂O)₉³⁺]₂[p-sulfonatocalix[4]arene]₂] showing the disordered aquated lanthanide ions at the rim of the calixarenes (hydrogen atoms [except NH] and solvated water molecules have been omitted for clarity).

disordered water molecules. Interestingly the homoleptic lanthanide ions are not bound directly to any sulfonate groups, but they do form part of the secondary coordination sphere through hydrogen bonding. This is in contrast to analogous complexes of the diprotonated [2.2.2]cryptand where direct sulfonate lanthanide bonding is found as part of a coordination polymer. The poly-aquated lanthanide cation is disordered over two orientations but incorporation of octa-aqua species such as $Gd(H_2O)_8^{3+}$ as counterions to the calixarenes does not alleviate the disorder problem. In contrast, this tactic has proved to be successful in previous studies.[21]

The 'molecular capsules' reside over a centre of inversion, and these are arranged into a π-stacked bi-layer arrangement with aryl-centroid · · · centroid distances of 3.393 Å, Fig. 3. A
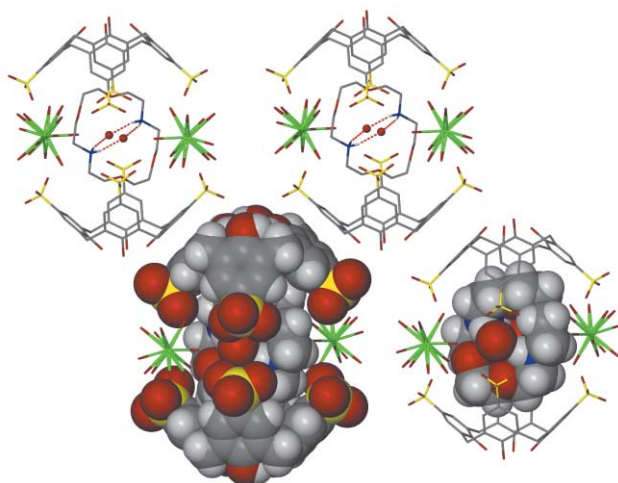

Fig. 3 The bi-layer arrangement found in (4,13-diaza-18-crown-6 + 2H⁺)⊂[(H₂O)₂[Nd(H₂O)₉³⁺]₂[p-sulfonatocalix[4]arene]₂]. One 'molecular capsule' is space filling whilst in another only the crown ether and associated water molecules are space filling (some hydrogen atoms and solvated water molecules have been omitted for clarity).

noteworthy feature of this 'molecular capsule' type arrangement is the presence of a water molecule on either side of the di-protonated diaza-crown ether guest molecule. The crown ether/water molecule hydrogen bonded assembly is reminiscent of the classical 'Russian doll' arrangement of a sodium ion in the centre of 18-crown-6 with two *trans* ligated water molecules, collectively shrouded by two *p*-sulfonated calix[4]arenes.[15] The water molecules hydrogen bond to the di-protonated nitrogen atoms of the crown ether with N · · · O distances, 2.866 and 2.935 Å (corresponding O · · · HN distances of 2.016 and 2.072 Å respectively). These distances are unexceptional relative to examples previously reported.[22]
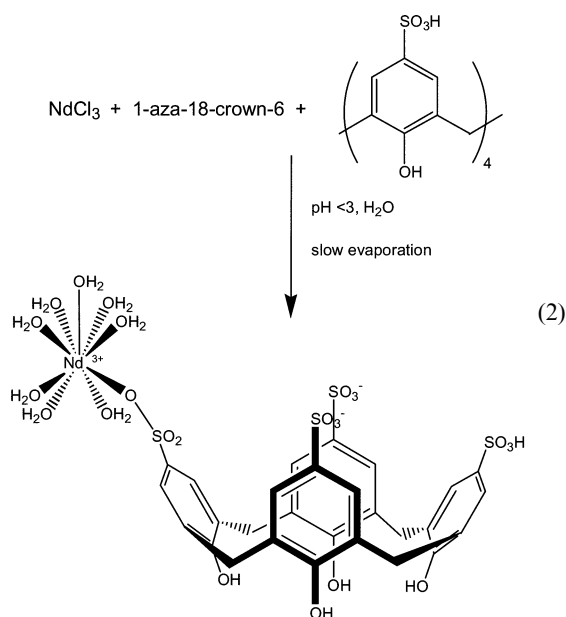
There is extensive hydrogen bonding from the disordered ligated water molecules of the neodymium ions to sulfonate groups of the two calixarenes in the nearest 'molecular capsule' with nearest potentially hydrogen bonding MO · · · OS distances ranging from 2.586 to 2.960 Å. Other ligated water molecules also hydrogen bond to sulfonate groups of calixarenes from neighbouring 'molecular capsules' with similar MO · · · OS distances ranging from 2.749 to 2.969 Å. Two of the ligated water molecules which have a partial occupancy of 0.5 hydrogen bond to an oxygen atom of the crown ether molecule with MO · · · O distances of 2.715 and 2.773 Å. Several of the aforementioned hydrogen bonds have been omitted for clarity in all diagrams.

It is pertinent to mention the splaying effect of the calixarene in the present structure, a common feature for 18-crown-6 also acting as a guest molecule. In the present structure, the dihedral angles of the calixarene are 109.0 and 129.6°. These are similar to those seen before for these disc like hosts with two of the phenyl rings splaying apart to pinch around the crown ether. This is different to the [2.2.2]cryptand structure within which the calixarene splays in all directions to accommodate the globular like di-protonated cryptand with dihedral angles of 130.1°. The splaying effect observed here and indeed in earlier studies could be the deciding factor in formation of 'molecular capsules' rather than coordination polymer structural motifs observed for the di-protonated cryptand.

It is apparent that by systematically investigating cryptand inclusion for the system reported previously, we have predicted and programmed rapid self assembly of these 'molecular capsules' to generate a new supramolecular structural motif.

Synthesis of a bi-layer arrangement in the presence of mono-aza-crown ether; [(Nd(H$_2$O)$_8$$^{3+}$)(*p*-sulfonatocalix[4]arene + H$^+$)], 2

The title compound was formed by slow evaporation of a solution containing *p*-sulfonatocalix[4]arene, 1-aza-18-crown-6 and the corresponding lanthanide(III) chloride. Early attempts to incorporate the aza-crown ether using the later lanthanides was unsuccessful and generated a hydrogen bonded polymer consisting of only the poly-aqua lanthanide species and the calixarene host molecule existing in the bi-layer structure.[23] The present structure shows the early lanthanide metal cation now bound to a sulfonate group, but nevertheless still with the complete absence of a guest crown ether molecule [eqn. (2)].

$$\text{NdCl}_3 \ + \ 1\text{-aza-18-crown-6} \ + \ \text{(calixarene)} \quad \xrightarrow[\text{slow evaporation}]{\text{pH} <3, \text{H}_2\text{O}} \quad \text{(product)} \tag{2}$$

This exclusion of the potential aza-crown ether guest possibly relates to the charge disparity for any 'molecular capsule' formed, effectively 7− for the protonated mono aza-crown ether, which would require fractional lanthanide counter ions. However, it is not unreasonable for one sulfonate group to be protonated for any 'molecular capsules' given the pH of the solution, resulting in a capsule charge of 6+, and protonation of the 'molecular capsule' is found in 18-crown-6 complexes of polynuclear metal complexes of Cr^{3+} and Rh^{3+}.[10,19]

The complex crystallises in the centrosymmetric triclinic space group with the asymmetric unit of one calixarene and attached aquated lanthanide ion and water molecules of crystallisation. The calixarenes are arranged in a skewed bi-layer arrangement which exhibits both π-stacking and CH · · · π interactions in the bi-layer arrangement (nearest C · · · C and CH · · · aryl centroid respective distances of 3.515 and 3.499 Å). The calixarenes are splayed in a similar fashion to **1**, with dihedral angles of 141.5 and 109.1° which is common for host–guest interactions of disc shaped crown ethers. Each of the octa-aqua neodymium cations reside above the base of a neighbouring 'down' calixarene fragment in the bi-layer with one of the ligated water molecules hydrogen bonding to two of the hydroxyl groups at the base (MO · · · O distances of 2.847 and 2.925 Å). The same ligated water molecule hydrogen bonds to a sulfonate group of a neighbouring 'up' calixarene fragment in the bi-layer with an MO · · · OS distance of 2.680 Å. Another of the ligated water molecules hydrogen bonds to a sulfonate group of another two neighbouring 'up' calixarene fragments with MO · · · OS distances of 2.721 and 2.814 Å, Fig. 4.

Within the extended bi-layer structure, significant hydrogen bonding occurs between ligated water molecules of the neodymium octa-aqua species, which reside out of the bi-layer and sulfonate groups of the next nearest bi-layer arrangement, Fig. 5 (relative MO · · · OS distances range from 2.686 to 2.793 Å).

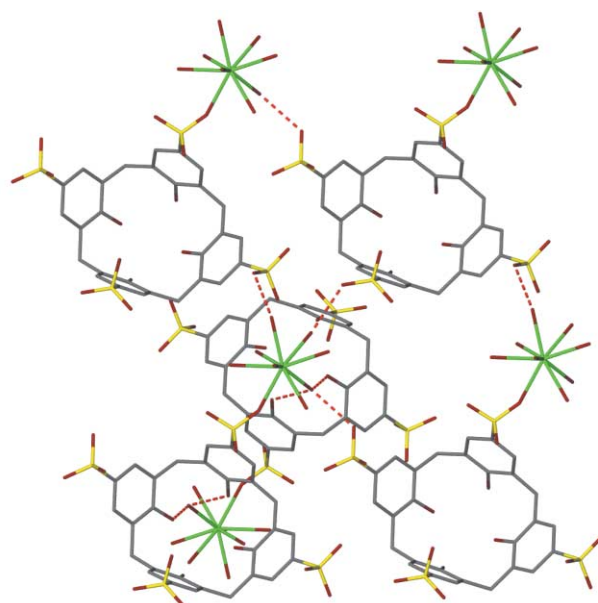**Fig. 4** Diagram of [(Nd(H$_2$O)$_8$$^{3+}$)(*p*-sulfonatocalix[4]arene + H$^+$)] showing the H-bonding between the sulfonate bound poly-aqua neodymium species and neighbouring calixarene anions within the bi-layers.

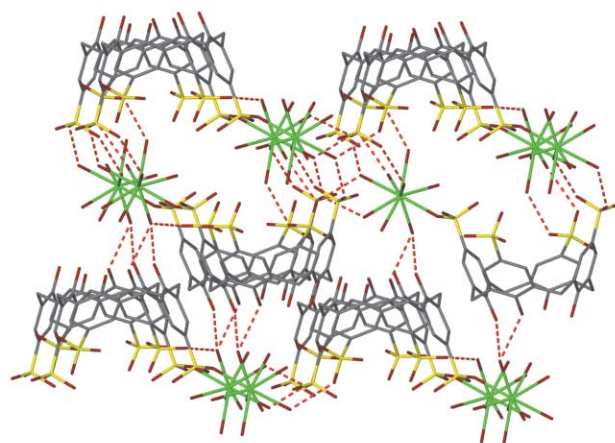**Fig. 5** Extended bi-layer structure in [(Nd(H$_2$O)$_8$$^{3+}$)(*p*-sulfonato-calix[4]arene + H$^+$)] showing the H-bonding between adjacent bi-layers and the resulting channel like structure.

This results in a channel like structure in one direction between bi-layers within which disordered water molecules reside. Taking into account the disordered water molecules, there is very extensive hydrogen bonding within this tightly packed supramolecular structure.

In conclusion we have discovered a rapid encapsulation of 4,13-diaza-18-crown-6 within a 'molecular capsule' arrangement which merits further investigation into the use of *p*-sulfonatocalix[4]arene in the presence of poly-aquated lanthanide ions as a means of purifying bis-amino functionalised molecules such as diaza-crown ethers and cryptands, amongst other things. We have also shown the exclusion of mono-aza-crown ethers which form two different structural motifs depending on the particular lanthanide metal used with an early lanthanide (Nd) generating a tightly packed bi-layer arrangement, and a hydrogen bonded polymer in the presence of the later lanthanides (Gd, Tb, Tm).[24]

Experimental

1-Aza-18-crown-6[25] and sulfonated calixarenes[26] were synthesised by literature methods whilst 4,13-diaza-18-crown-6 was purchased from Aldrich and used as supplied. X-Ray data

was collected on an Enraf-Nonius KappaCCD diffractometer. All the crystals examined were stable upon exposure to air and did not incur solvent loss as is commonly seen for these types of systems. It should be noted that in both reported structures, the hydroxy H-atoms of the calixarenes are fixed into positions optimising hydrogen bonding interactions at the base of the calixarene.

Synthesis of 'molecular capsules'; (4,13-Diaza-18-crown-6 + 2H$^+$)$\subset$[(H$_2$O)$_2$[M(H$_2$O)$_x$$^{3+}$]$_2$[$p$-sulfonatocalix[4]arene]$_2$] (M^{3+} = Ce, Nd, Eu, Gd; x = 8, 9), 1

The lanthanide(III) chloride (M^{3+} = Ce, Nd, Eu, Gd >10 molar eq.), p-sulfonato-calix[4]arene (10 mg, 13.4 µmol) and 1,4-diaza-18-crown-6 (8 mg, 30 µmol) were dissolved in distilled water (1 cm^3). On standing, large crystals suitable for X-ray diffraction studies formed over 30 minutes.

Crystal data. For Nd^{3+}, colourless crystals formed. C$_{34}$H$_{69}$N$_1$O$_{36.5}$S$_4$Nd$_1$, M = 1348.40, monoclinic, a = 17.345(4), b = 18.729(4), c = 19.462(4) Å, β = 112.31(3)°, U = 5849(2) Å^3, μ = 1.546 mm^{-1}, T = 150 K, space group $P2_1/n$ (no. 14), Z = 4, Mo-Kα radiation (λ = 0.71073 Å), final GOF = 1.050, R_1 = 0.0951, 40525 reflections measured, 10240 unique (R_{int} = 0.0554) which were used in all calculations. The final $\omega R(F^2)$ was 0.2909 (all data). It should be noted that some of the water molecules, solvated and ligated, have been refined isotropically.

CCDC reference number 196888.

For Ce^{3+}, large yellow–orange crystals formed over 30 minutes with unit cell measurements of a = 17.4035(3), b = 18.8261(2), c = 19.5930(2) Å, α = 90.0756(7), β = 67.4716(5), γ = 90.0259(13)°, T = 150 K, and was assumed to be isomorphous with the Nd^{3+} structure described above.

For Eu^{3+}, the preparation method was identical to that above with colourless crystals forming over 30 minutes. The unit cell measurements were a = 17.1943(3), b = 18.6962(4), c = 19.4208(5) Å, α = 90.1112(13), β = 67.7569(15), γ = 90.1442(14)°, T = 150 K and it was therefore assumed to be isomorphous with both the Ce^{3+} and Nd^{3+} structures.

For Gd^{3+}, the preparation method was identical to that above with colourless crystals forming over 30 minutes. The unit cell measurements were a = 17.2262(2), b = 18.7737(2), c = 19.4604(3) Å, α = 90.0184(7), β = 112.1530(17), γ = 90.0037(3)°, T = 150 K and it was therefore assumed to be isomorphous with the above structures.

Synthesis of bi-layer arrangement devoid of mono-aza-crown ether; [(Nd(H$_2$O)$_8$$^{3+}$)($p$-sulfonatocalix[4]arene + H$^+$)], 2

Slow evaporation of a solution containing neodymium(III) chloride (10 mg, 40 µmol), 1-aza-18-crown-6 (10 mg, 30 µmol), and p-sulfonatocalix[4]arene (10 mg, 13.4 µmol) afforded colourless crystals which were suitable for X-ray diffraction studies.

Crystal data. C$_{28}$H$_{55}$O$_{33.5}$S$_4$Nd$_1$, M = 1191.19, triclinic, a = 12.356(3), b = 14.418(3), c = 14.758(3) Å, α = 92.11(3), β = 113.02(3), γ = 98.35(3)°, U = 2381.4(8) Å^3, μ = 1.661 mm^{-1}, T = 150 K, space group $P\bar{1}$ (no. 2), Z = 2, Mo-Kα radiation (λ = 0.71073 Å), final GOF = 1.032, R_1 = 0.0456, 43060 reflections measured, 8319 unique (R_{int} = 0.0841) which were used in all calculations. The final $\omega R(F^2)$ was 0.1272 (all data). It should be mentioned that some of the solvated water molecules were refined isotropically.

CCDC reference number 169886.

See http://www.rsc.org/suppdata/dt/b2/b210840m/ for crystallographic data in CIF or other electronic format.

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