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Metal sulfonatocalix[4,5]arene complexes: bi-layers, capsules, spheres, tubular arrays and beyond

Jerry L. Atwood [a], Leonard J. Barbour [a],
Michaele J. Hardie [b], Colin L. Raston [b,*]

[a] *Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA*
[b] *School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK*

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Contents

Abstract

The main focus of this review is the self-assembly in aqueous solutions of bowl-shaped sodium *p*-sulfonatocalix[4,5]arenes with main group, transition metal and lanthanoid species,

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* Corresponding author.
E-mail address: c.l.raston@chem.leeds.ac.uk (C.L. Raston).

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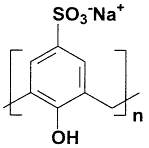
and with various organic molecules as additional supramolecular building components, for example 18-crown-6, and other macrocycles, pyridine *N*-oxide, amino-acids, and more. The versatility of building up new materials based on these components is demonstrated by the formation of a diverse range of complex inclusion structures assembled through π-stacking, hydrogen bonding and coordination interactions. There are up–down arrangements of calix[4]arenes in hydrophobic–hydrophobic bi-layer structures with the positively charged species and included molecules between the layers. A variant of this is prevalent in structures incorporating 18-crown-6 which, in essence, are built up of globular superanions or ionic capsules, for example $\{Na^+ \subset (\text{18-crown-6})(H_2O)_n\} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}^{7-}$, $n = 0$ or 2. These can crystallize, often selectively, polynuclear hydrolytic M(III) cations $[M_2(OH)_2(H_2O)_8]^{4+}$, $[M_3(OH)_4(H_2O)_{10}]^{5+}$, $[M_4(OH)_6(H_2O)_{12}]^{6+}$, M = Cr or Rh, or $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, depending on the pH and other synthetic parameters. Lanthanide(III) ions form a range of complexes at specific pH in the presence of the calixarene and crown ether, including complexes containing the capsule $[\{\text{18-crown-6}\} \subset \{(M(H_2O)_7^{3+})_{1.33}(p\text{-sulfonatocalix[4]arene}^{4-})\}_2]$, for the smaller lanthanides, or the Ferris-wheel type structure $[\{La^{3+} \subset (\text{18-crown-6})(OH_2)_3\} \cap \{(p\text{-sulfonatocalix[4]arene}^{4-} + 2H^+)\}]^+$, for the larger lanthanide. In the presence of pyridine *N*-oxide, at pH 4 where the calixarenes take on 5 − charge, an up–up arrangement of sulfonated calixarenes results, either assembled in icosahedral spheres, or infinite chiral, helical nano-tubes.

Keywords: Sodium *p*-sulfonatocalix[4,5]arenes; Supramolecular building components

1. Overview

Large, highly charged ions are important in the formation of micelle-like species and other nano-structures in solution, in developing enzyme models, and in crystal engineering for building up complex assemblies in the solid state. One such class of highly charged species consists of the water-soluble sodium *p*-sulfonatocalix[4,5]arenes. Most studies have concentrated on the calix[4]arene since it is readily available and usually adopts a cone or bowl-shaped conformation. Thus there is no compromise arising from any pre-organization energy required for the binding of hydrophilic moieties within the calixarene cavity. While the same can be said for sulfonated calix[5]arene, non-cone conformations are lower in energy for the higher oligomers. The hydrophobic pockets of the calix[4,5]arenes are capped with anionic sulfonate groups on the upper rim while the lower rim contains phenolic groups. The former can be protonated in strongly acidic media whereas one of the latter is deprotonated at ca. pH 4.0 with two of the remaining groups following suit successively in basic media. It should be noted that many of the studies involving *p*-sulfonatocalix[4]arene have been carried out using the pentaanion.



Early work on sulfonated calix[4,5]arenes established the formation of clay-like bilayer structures which show remarkable inclusion properties encompassing ionic guests and molecules [1–14] including water in the hydrophobic cavity associated with H_2O···aromatic–π hydrogen bonding [4], and incorporating metal ions. More recent advances relate to two independent lines of endeavor, both involving coordination chemistry. One of these, which originates from the Raston research group, focuses on the ability of two *p*-sulfonatocalix[4]arenes to align face-to-face across the upper rim, thus sharing a common hydrophobic molecule such as a crown ether, with the ensuing ionic capsules or superanions forming parts of bi-layer structures or variants thereof [15–21]. The second major endeavor, which stems from the Atwood research group, demonstrates the remarkable ability to control the assembly of *p*-sulfonatocalix[4]arene into nano-scale spheres and tubules with the cavities of the calixarene entities now directed away from the center of the sphere or the axis of the tube [22]. It is noteworthy that the generation of molecular capsules and spheres has received considerable attention in recent years, particularly with regard to the use of non-covalent self-assembly principles to build up such supermolecules. These include hydrogen-bonded interactions between bowl-shaped calixarenes other than sulfonated analogues, as well as related resorcinarene supramolecular synthons or building blocks [23–28].

This review is a comprehensive survey and critical treatise of the literature dealing with coordination chemistry of sulfonatocalix[4,5]arenes, and is divided according to the class of structures, namely bi-layers and capsules (noting that in some cases the distinction between the two is nebulous) and nano-scale spheres and tubules, and others. Our interest in sulfonated calixarenes relates mainly to their inclusion phenomena, separation science, and gaining access to novel nano-structures, relying on a combination of supramolecular interactions, notably coordination, hydrogen bonding, electrostatic and van der Waals, where there is size, shape and electronic complementarity between the molecular components [22]. It should also be noted that sulfonated calixarenes have attracted interest with respect to the binding of guest species in solution [29,30].

2. Bi-layers and capsules

2.1. Calix[4]arenes

2.1.1. Bi-layers

Essentially, *p*-sulfonatocalix[4]arene is shaped like a truncated cone with hydrophilic upper and lower rims separated by a hydrophobic mid-region. Usually the solid-state packing arrangements of structures involving this molecule are overwhelmingly dominated by these strongly structure-directing topological and electronic characteristics. Water-solubility is an important property of the compound and crystals grown in aqueous media tend to produce structures in which the hydrophobic aromatic regions associate with one another, leaving the hydrophilic ends exposed. This arrangement results in a high degree of solvation at the upper and lower rims of the molecules. Indeed, early work by Atwood and co-workers [2,3] showed that the preferred packing motif consists of an up–down arrangement to form bi-layers as shown in Fig. 1. These bi-layers are reminiscent of clays with broad hydrophilic and hydrophobic regions. The hydrophilic layer consists of sodium cations and a vast array of hydrogen-bonded water molecules and sulfonate head groups of the calixarenes.

In the presence of water alone, the sodium salt of [*p*-sulfonatocalix[4]arene]$^{4+}$ crystallizes with a water molecule deeply imbedded within the calixarene cavity. This observation constituted the first X-ray diffraction evidence for aromatic π hydrogen bonding to water [4]. The water in the cavity can be displaced by an appropriately sized hydrophobic part of an organic molecule as evidenced by the inclusion of neutral (e.g. acetone [2]), anionic (e.g methyl sulfate [3]) and cationic (e.g. pyridinium [5,6], morpholinium [6] and NMe_4^+ [7,8]) species. It was also shown [9] that varying the alkali metal cation from Na to Cs does not alter the bi-layer structure, but that the degree of hydration decreases accordingly (i.e. the following stoichiometries are obtained: Na_5(*p*-sulfonatocalix[4]arene] · $12H_2O$, K_5[*p*-sulfonatocalix[4]arene] · $8H_2O$, Rb_5[*p*-sulfonatocalix[4]arene] · $5H_2O$, Cs_5[*p*-sulfonatocalix[4]arene] · $4H_2O$). Substitution of the alkali metal cation with organic cationic species such as in the structures of [adeninium]$_4$[*p*-sulfonatocalix[4]arene] · $14H_2O$ [10] and $[NMe_4]_5$[*p*-sulfonatocalix[4]arene] $4H_2O$ [8] still results in the formation of the bi-layer structure. The latter structure reveals that one cation is embedded in the calixarene cavity with the remainder of the NMe_4 cations situated in the hydrophilic region, Fig. 2. However, in the former structure, the cavity contains a water molecule and all of the adeninium cations are situated in the hydrophilic layer.

Complexation of organic molecules by the calixarene cavity was further extended to include the second-sphere coordination of the transition metal complex $[Ni^{II}(Py)(H_2O)_5]_2(Na)_2$[*p*-sulfonatocalix[4]arene] · $3.5H_2O$ [11]. The structure contains two unique pentaaquopyridinenickel(II) ions. The pyridine ligand of one is

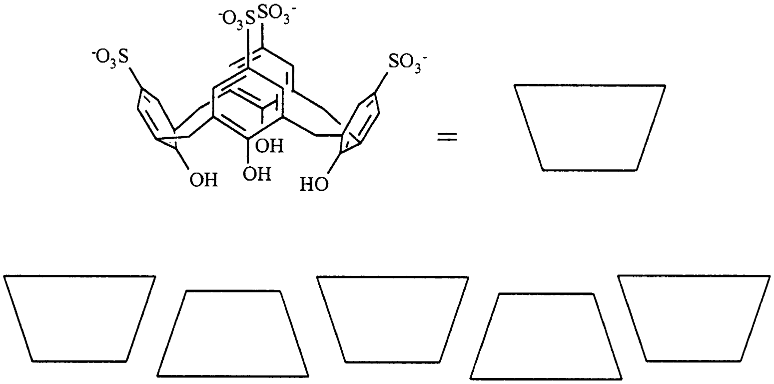


Fig. 1. Diagrammatic representation of the hydrophilic–hydrophobic bi-layer structure often adopted by *p*-sulfonatocalix[4]arenes.

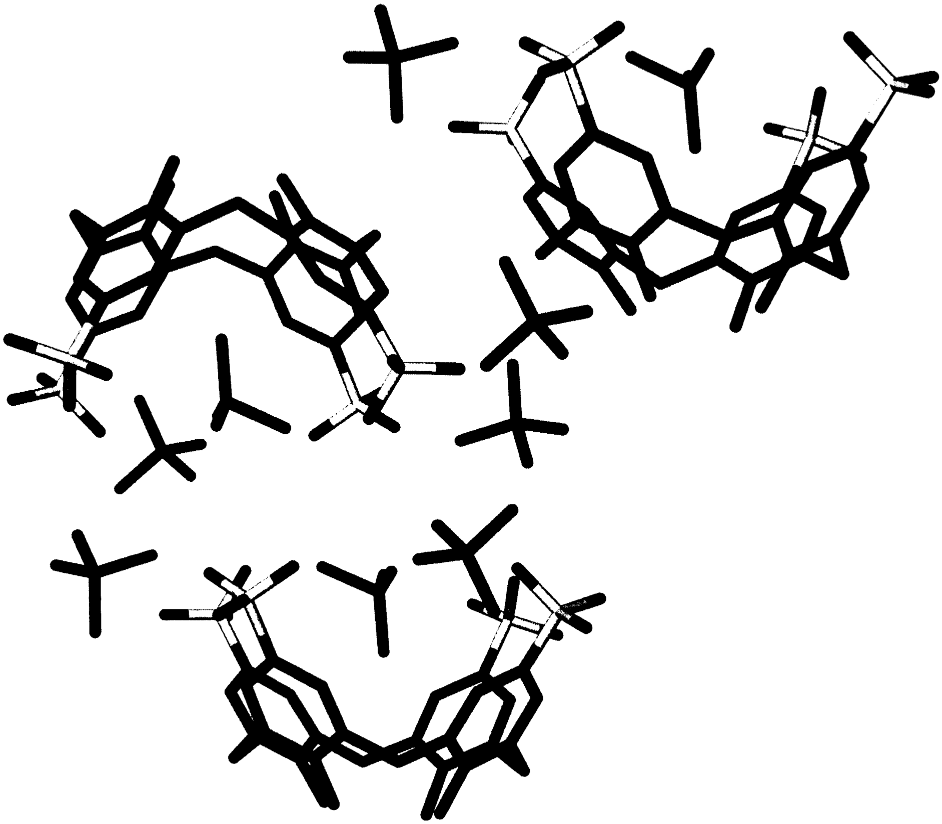


Fig. 2. Partial packing diagram from the crystal structure of $[NMe_4]_5$[*p*-sulfonatocalix[4]arene] · $4H_2O$. Solvent water and hydrogens omitted for clarity.

complexed by the calixarene cavity, Fig. 3, while the other inserts its pyridine ring into the hydrophobic layer. In the structure of $[Cu(Py)_2(H_2O)_3](Na)_3$[*p*-sulfonatocalix[4]arene] · $13H_2O$ [5], we see a dimeric association of second-sphere coordination complexes. The copper(II) ion is strongly coordinated to a square planar array of two pyridine nitrogen atoms and two water oxygen atoms. The remaining two axial sites of a strongly Jahn–Teller distorted octahedral arrangement are filled by the oxygen atoms of a water molecule and a sulfonate group. The latter weak interaction is seen to bind the copper complex to the exterior of one calixarene, while one of the pyridine ligands is inserted into a calixarene cavity across the hydrophilic layer. The remaining pyridine ligand is intercalated into a hydrophobic calixarene layer and the dimer is thus held together by two weak Cu···O(sulfonate) bonds and two hydrophobic interactions. An analogous dimeric arrangement is observed in the structure of Na_4(pyridinium)[*p*-sulfonatocalix[4]arene] · $8H_2O$ [5] where the pyridinium cation is inserted into a calixarene cavity with its NH group directed into the hydrophilic layer. An N–H···O hydrogen-bonded interaction across the hydrophilic layer links the pyridinium to a sulfonate group of a calixarene in an adjacent layer. The dimer is situated on a crystallographic inversion center and is held together by a combination of two hydrogen bonds and two hydrophobic interactions. The presence of the sulfonate groups at the upper rim of the calixarene cavity presents several interesting possibilities for the binding of metal complexes: (1) intercalation of the metal-containing species into the hydrophilic layer with no direct metal–sulfonate oxygen bond; (2) interaction between the metal ion and the sulfonate groups of one calixarene unit; (3) interaction between the metal ion and the sulfonate groups of more than one calixarene. These three possibilities are illustrated by the structures of $[Cr(OH_2)_6]$ [Na] [*p*-sulfonatocalix[4]arene] (acetone) $\cdot$ $10H_2O$, $[Yb(OH_2)_7]$[Na][*p*-sulfonatocalix[4]arene] $\cdot$ $9H_2O$ and $\{[Cu(OH_2)_4][Na][p\text{-sulfonatocalix[4]arene}] \cdot 7.5H_2O\}_2$, respectively [12].

We have seen that the interaction of *p*-sulfonatocalix[4]arene with metal complexes encompasses the utilization of a hydrophobic pocket, double-recognition of a substrate as well as binding of catalytically active metals at the upper rim. This has led to these complexes being described as enzyme mimics and this has further been demonstrated by the structures of $(H_3O^+)[La(ONC_5H_5)_2(H_2O)_6(p\text{-sulfonatocalix[4]arene})]^- \cdot 6.5H_2O$ and $Na_2[Zn(H_2O)_4(ONC_5H_5)_2]$[*p*-sulfonatocalix[4]arene] $\cdot$

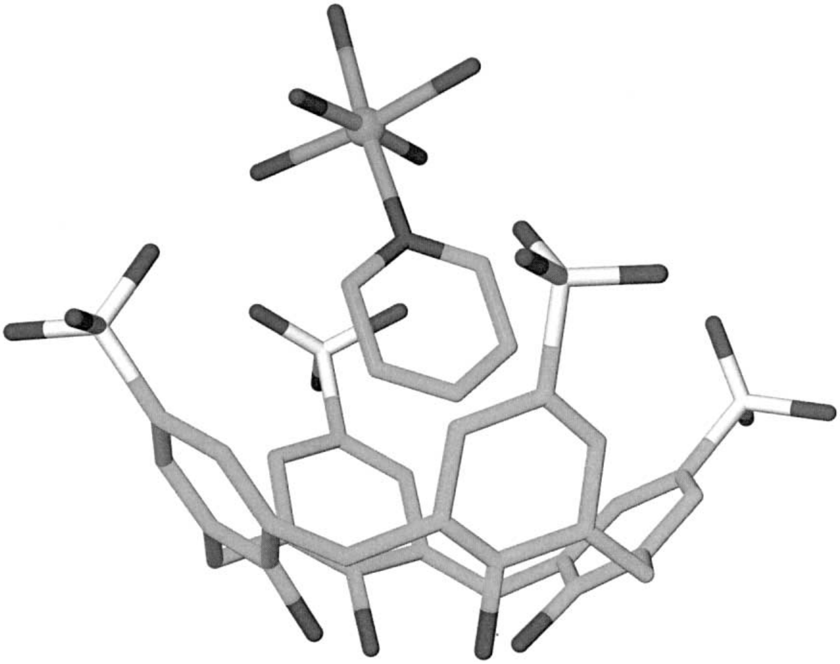


Fig. 3. Second-sphere coordination of Ni(II) in the complex $[Ni^{II}(Py)(H_2O)_5]_2(Na)_2$[*p*-sulfonatocalix[4]arene] $\cdot$ $3.5H_2O$.

$8.5H_2O$. In the structure of $[(H_2O)_5Ni(Py)]_2(Na)[p$-sulfonatocalix[4]arene$] \cdot 3.5H_2O$, [13] there are two environments for the nickel-containing cations. One is positioned within the hydrophilic layer with the pyridine ligand intercalated into the hydrophobic layer. The second cation is also positioned within the hydrophilic layer, but the pyridine ligand is inserted into the hydrophobic cavity of the calixarene. The calixarene thus functions as a second-sphere ligand for the nickel atom. The structure of $[(H_2O)_4Cu(Py)_2](H_3O)[p$-sulfonatocalix[4]arene $\cdot 10H_2O$ is similar with the exception that there is only one copper-containing cation per calixarene unit. One pyridine ligand is inserted into the calixarene cavity while the other is intercalated into the hydrophobic layer. In this structure the copper complexes appear as pillars that hold the calixarene bi-layers apart.

Second-sphere coordination holds promise as an organizational principle upon which larger supramolecular assemblies may be constructed, and other examples include the Russian doll structures discussed below [15,16,19] and a metal-cryptate-cavitand assembly [24] as well as second-sphere cyclodextrin complexes [32].

However, this concept can be extended to yield third and higher-sphere coordination. Third-sphere coordination is exemplified by the structure of $Na[Eu_3(p$-sulfonatocalix[4]arene$)_2(OH_2)_{18}(ONC_5H_5)_3] \cdot 14H_2O$ [14], where the first coordination sphere of one of the three europium atoms consists of seven water molecules, the oxygen atom of a pyridine *N*-oxide molecule, and a sulfonate oxygen atom from one of the two independent calixarene. The second-sphere coordination consists of the second calix[4]arene which is bound to the coordinated pyridine *N*-oxide via hydrophobic interactions, and a second pyridine *N*-oxide which is hydrogen bonded to a coordinated water molecule. The third-sphere coordination consists of the binding of the second-sphere coordinated pyridine *N*-oxide to the cavity of the first-sphere coordinated calixarene.

A skewed calixarene dimer is found in the complexes $[M(H_2O)_7Na(H_2O)_4(p$-sulfonato-calix[4]arene$)](\text{solvent})_n$ ($M = Y$, Eu) [31], that encapsulates solvent water molecules. Two aquated sodiums bridge between two calix[4]arenes via sulfonate groups, and a terminal aquated rare earth ion is bound to another sulfonate group on each calix[4]arene, and forms multiple hydrogen-bonding interactions to sulfonate groups on its opposite calix[4]arene. Packing of these dimers within the crystal structure also shows the up–down bi-layer arrangement of calix[4]arenes and is similar to that seen in a Yb analogue [12].

2.1.2. Capsules involving polynuclear metal(III) ions

Many of the capsules encountered in our work are essentially inclusion complexes of inclusion complexes and are reminiscent of Russian Matryoslika dolls, and are unusual examples of second-sphere supramolecular complexation.

Thus far we have restricted our studies to identifying complexes precipitating from solution, which usually occurs over a narrow pH regime, mainly at $\text{pH} < 3.5$ which yields the tetra-anionic calix[4]arene or its various protonated forms. At higher pH, deprotonation of the lower rim phenolic OH groups occurs, and this can lead to nano-structures in the presence of lanthanides [22]. The synthons for the formation of capsules are depicted in Fig. 4; there are many variables to be

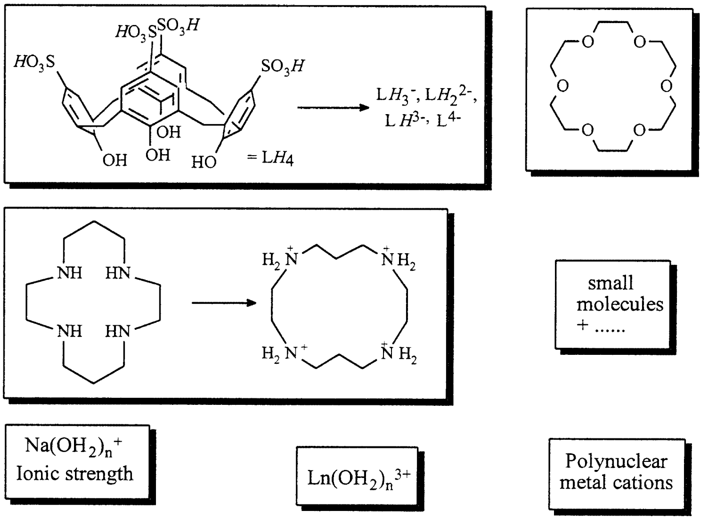
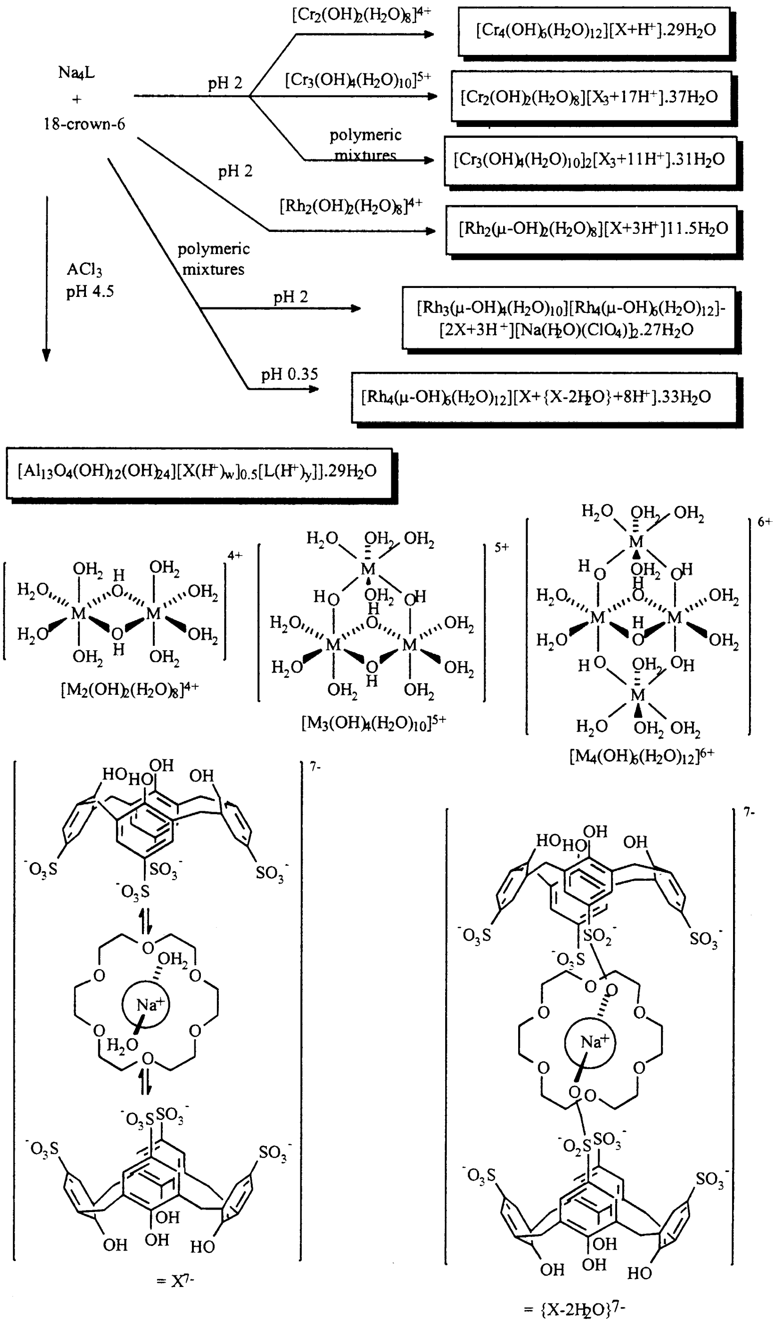


Fig. 4. Supramolecular synthons used in building up superanion capsules.

considered including the degree of protonation of the calixarenes, the nature of core species within the capsules such as crown ether or cyclam, the polynuclear counterions and other large cations, lanthanide ions, ionic strength, and more.

Solutions containing sodium *p*-sulfonatocalix[4]arene and 18-crown-6 and various polynuclear metal(III) aqua cations are effective in crystallizing, in some cases with selectivity, such metal(III) cations of Cr^{3+}, Rh^{3+}, Sc^{3+} (see Section 2.1.3) and Al^{3+}, as salts of the capsules/superanions. In the case of Cr^{3+}, solutions of non-labile polynuclear Cr^{3+} aqua ions are formed on the base hydrolysis of $[Cr(H_2O)_6]^{3+}$ followed by immediate quenching with perchloric acid [33], and contain $[Cr_2(OH)_2(H_2O)_8]^{4+}$, $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$, $[Cr_4(OH)_6(H_2O)_{12}]^{6+}$ and higher oligomeric cations, which are stable towards the formation of higher polynuclear species provided the pH of the solution is about 3 [33,34]. Aqueous solutions of sodium *p*-sulfonatocalix[4]arene and 18-crown-6 at ca. pH 2 with solutions of purified dinuclear and trinuclear Cr^{3+} species (perchlorate salts) afford the superanion complexes $[Cr_2(OH)_2(H_2O)_8]$ $[X_3 + 17H^+]$ and $[Cr_3(OH)_4(H_2O)_{10}]_2[X_3 + 11H^+]$, $X^{7-} = \{Na^+ \subset (18\text{-crown-6})(OH_2)_2\} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})2\}^{7-}$, Scheme 1 [15]. Using a mixture of the polynuclear cations results in the crystallization of the complex $[Cr_4(OH)_6(H_2O)_{12}][X + H^+]$ where the tetranuclear Cr^{3+} cation has been selectively retrieved from solution [15]. Prior to this finding, the only structurally authenticated polynuclear Cr^{3+} species was the dinuclear cation, $[Cr_2(OH)_2(H_2O)_8]^{4+}$, as was the case for the analogous non-labile, dinuclear Rh^{3+} (see below) [35] and mixed Cr^{3+} and Rh^{3+} species [36]. The ratio of cations to anions in the solid for the di-, tri-and tetranuclear Cr^{3+} complexes are 2:3, 1:2 and 1:1, respectively, and this is maintained even when varying the ratio of calixarene:crown ether and calixarene:polynuclear cations,


Na_4L + 18-crown-6
pH 2
$[Cr_2(OH)_2(H_2O)_8]^{4+}$
$[Cr_4(OH)_6(H_2O)_{12}][X+H^+].29H_2O$
$[Cr_3(OH)_4(H_2O)_{10}]^{5+}$
$[Cr_2(OH)_2(H_2O)_8][X_3+17H^+].37H_2O$
polymeric mixtures
$[Cr_3(OH)_4(H_2O)_{10}]_2[X_3+11H^+].31H_2O$
pH 2
$[Rh_2(OH)_2(H_2O)_8]^{4+}$
$[Rh_2(\mu-OH)_2(H_2O)_8][X+3H^+]11.5H_2O$
polymeric mixtures
pH 2
$[Rh_3(\mu-OH)_4(H_2O)_{10}][Rh_4(\mu-OH)_6(H_2O)_{12}]-[2X+3H^+][Na(H_2O)(ClO_4)]_2.27H_2O$
pH 0.35
$[Rh_4(\mu-OH)_6(H_2O)_{12}][X+\{X-2H_2O\}+8H^+].33H_2O$
ACl_3 pH 4.5
$[Al_{13}O_4(OH)_{12}(OH)_{24}][X(H^+)_w]_{0.5}[L(H^+)_y]].29H_2O$
$[M_2(OH)_2(H_2O)_8]^{4+}$
$[M_3(OH)_4(H_2O)_{10}]^{5+}$
$[M_4(OH)_6(H_2O)_{12}]^{6+}$
= X^{7-}
= $\{X-2H_2O\}^{7-}$

Scheme 1.

despite the different charge and size of the cations and the different degree of protonation of the superanion, X^{7-}, required to balance charge. This highlights a remarkable property of the superanion, which is further evident below, namely its ability to accommodate different charged species by varying the degree of protonation of the sulfonate groups.

The superanions, $X^{7-}+nH^{+}$, are globular structures with axial symmetry, approximately D_{2h}, comprised of a central sodium ion bound by a crown ether and two *trans*-water molecules, which fits snugly into two calixarenes, Fig. 5. The capsules are held together by a number of interactions, most notably hydrogen bonding between the coordinated water ligands and the sulfonate groups of the calixarenes. They have alternating hydrophilic and hydrophobic character in the direction of the principle axis, and this Jovian arrangement relates to how the anions pack in the solid state which appears to be driven by π-stacking between aromatic rings of adjacent superanions. In the complex $[Cr_4(OH)_6(H_2O)_{12}][X+H^{+}]$, the cyclic Cr^{3+} tetranuclear cation sits at the periphery of the hydrophilic sulfonate equator of the superanion (Fig. 5), as would be expected on electrostatic considerations, with each cation forming hydrogen bonding interactions with two superanions. The incorporation of crown ether in the cavities of the calixarenes in $[Cr_4(OH)_6(H_2O)_{12}][X+H^{+}]$ also yields an up–down bi-layer arrangement [15] (Fig. 1) in which there is slippage relative to displacement between layers allowing formation of the capsule assembly. The trinuclear and dinuclear Cr^{3+}-containing complexes (which are essentially isostructural), form a more irregular highly distorted bi-layer arrangement.

In the case of Rh^{3+}, the Russian doll superanion approach to crystallizing large cations yields new polynuclear metal(III) aqua cations, notably, $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]^{5+}$ and $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$ [19], as well as crystallizing the previously reported dinuclear cation, $[Rh_2(\mu\text{-}OH)_2(H_2O)g]^{4+}$ [35,37]. Solutions of pure dinuclear rhodium(III) cation $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ with crown ether and sulfonated calixarene at low pH give a 1:1 ratio of the rhodium(III) cation to capsule, with composition $[Rh_2(\mu\text{-}OH)_2(H_2O)_8][X+3H^{+}]\cdot 11.5H_2O$, Scheme 1 [19]. The 1:1 ratio of cation to capsule is surprisingly different from that of the Cr^{3+} crown-ether analogue, but the same as that of the cyclam-containing capsule, despite the smaller charge of the core moiety in this case. Three of the total of eight sulfonate groups of the superanion capsule are required to be protonated to achieve overall charge balance. The overall structure takes on the familiar up–down bi-layer arrangement of calixarenes, Fig. 1 [19]. Surprisingly the structure of $Rh_2(\mu\text{-}OH)_2(H_2O)_8][X+3H^{+}]\cdot 11.5H_2O$, is not isostructural with, or extensively disordered as in, the chromium(III) analogue [15], where the cations are disordered over several sites. These differences may relate to the larger size of the cation in the present case and/or different polarization effects.

Complex mixtures of polynuclear Rh^{3+} aqua ions in perchloric acid, formed by treating aqueous Rh^{3+} solutions with sodium hydroxide at pH 13 then acidifying with perchloric acid, contain mononuclear, dinuclear, trinuclear and higher oligomer cations [35,38]. Remarkably on the addition of sodium *p*-sulfonatocalix[4]arene and 18-crown-6 at pH 2, selective retrieval of the tri- and tetranuclear

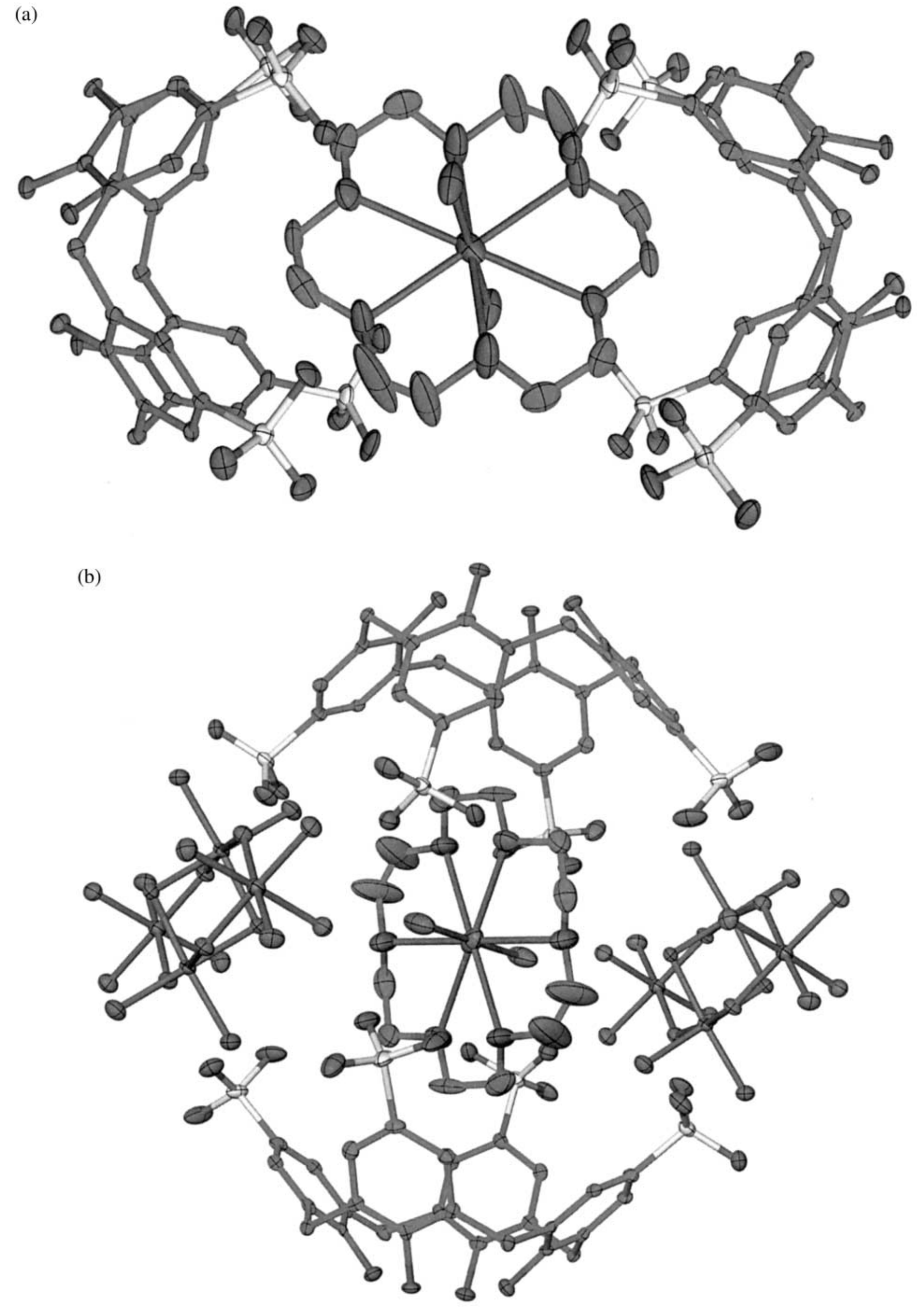


Fig. 5. (a) The superanion capsule $X^{7-} + H$, where $X = \{Na+ \subset (18\text{-crown-6})(OH_2)_2\} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}$ taken from the X-ray structure of $[Cr_4(OH)_6(H_2O)_{12}][X + H^+]$; (b) the superanion with $[Cr_4(OH)_6(H_2O)_{12}]$ tetramers at its hydrophilic equator. Ellipsoids shown at 50% probability.

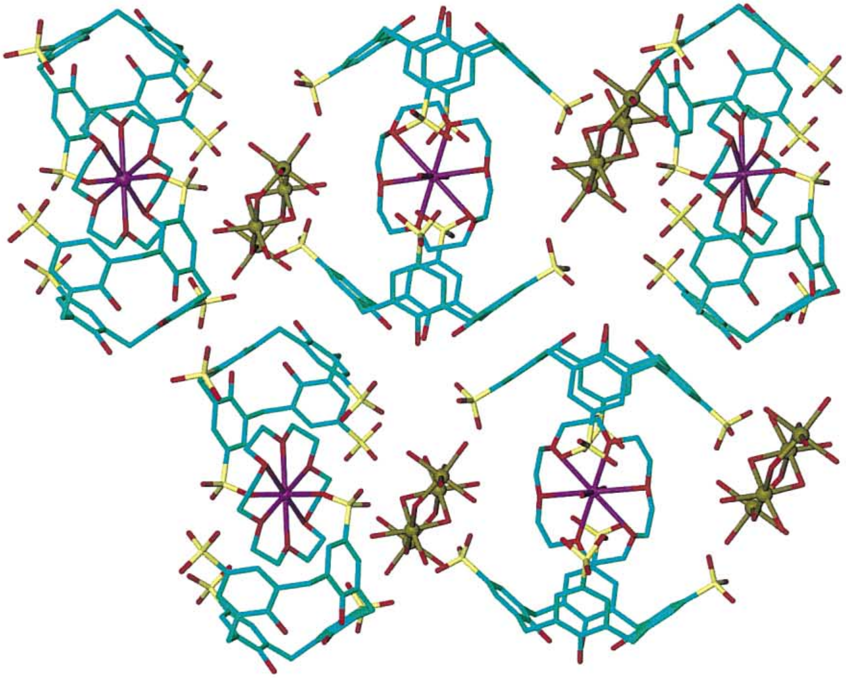


Fig. 6

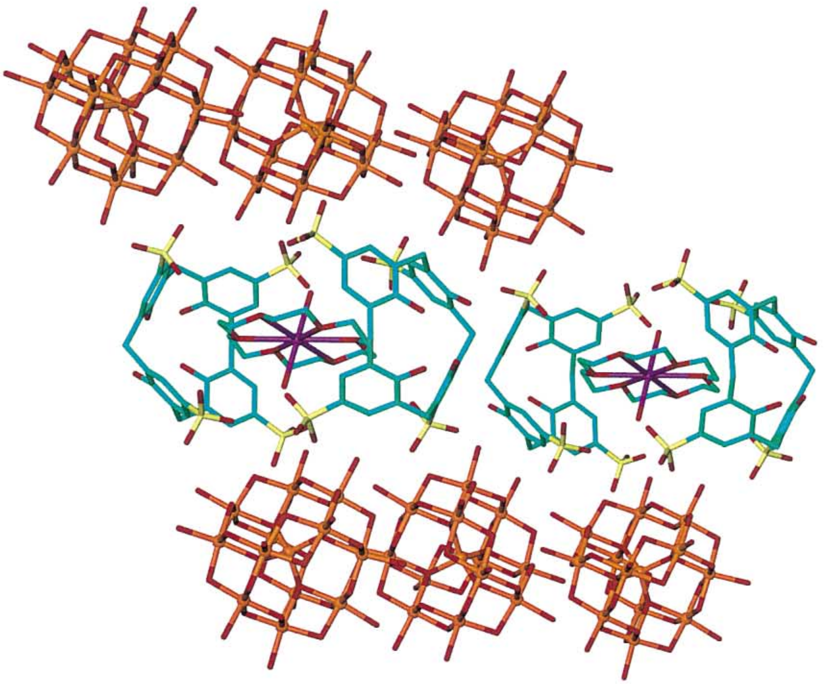


Fig. 7

Rh^{3+} species in a single 1:1 co-crystallized phase results, $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}][Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][2X+3H^+][Na(H_2O)(ClO_4)]_2\cdot 27H_2O$ [19]. The tri- and tetranuclear Rh^{3+} cations both have a cyclic structure with μ-hydroxide and terminal water ligands, Scheme 1. This complex has an additional coordination of a *exo*-capsule Na^+ by the calixarenes, but despite this, the overall arrangement of superanions is in the up–down bi-layer motif. The ability to co-crystallize two large polynuclear aqua cations, $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]^{5+}$ and $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$, in the same solid is without precedent. Moreover, of these two cations, only the trinuclear instance has been studied with its existence in solution postulated on the basis of NMR experiments [37], and there is considerable uncertainty as to the nature of higher nuclearity species. At pH 0.35 an otherwise identical reaction mixture leads to the selective retrieval of the tetranuclear Rh^{3+} cation in the complex $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X+\{X-2H_2O\}+8H^+]\cdot 33H_2O$. The richness of the chemistry in this area now manifests itself in the presence of two types of capsule which further reflects the versatility of the parent superanion X^{7-} which is present in the structure along with its dehydrated form where the two sodium-bound water molecules have been replaced by O-centers of calixarene sulfonate groups, Scheme 1. This structure assumes a distorted up–down bi-layer arrangement, Fig. 6, presumably because of the less-symmetrical shape of the superanion devoid of the *trans*-water molecules around the central sodium ion [19]. The Na–OS distance of 2.319(9) Å requires that one sulfonate group from each of the calixarene subunits is pulled in towards the Na^+ perturbing the usual head-to-head arrangement of calixarenes, leaving the superanion open on each side, Fig. 6.

Despite a static disorder of trinuclear species $[Rh_3(\mu\text{-}OH)_4(H_2O)_{10}]^{5+}$ over an inversion center, the atom connectivity is well defined [19], and the μ-OH bridged cyclic structure is isostructural with that of the Cr^{3+} analogue [15], but this is at odds with the assigned linear structure based on ^{103}Rh-NMR studies. However, the NMR data showing two resonances in a 1:2 ratio is consistent with the triangular structure [38]. The conformation of the tetranuclear $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}]^{6+}$ cation is the same in both structures [19], and iso structural with the Cr^{3+} analogue (above) [15]. Interestingly the structure of the superanion X^{7-} in the mixed Rh^{3+} cation complex is slightly different to that of other systems [15,16], with the central Na^+ coordinating to only five of the six crown-ether oxygen atoms at Na–O distances from 2.55(1) to 2.740(9) Å as well as two *trans* water molecules [19].

The higher ratio of capsules to cations in $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X+\{X-2H_2O\}+8H^+]\cdot 33H_2O$ relative to that of the above structures is consistent with

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Fig. 6. Crystal packing of $[Rh_4(\mu\text{-}OH)_6(H_2O)_{12}][X+\{X-2H_2O\}+8H^+]\cdot 33H_2O$ (waters and hydrogens omitted). The two types of superanion X^{7-} and the dehydrated $\{X-2H_2O\}^{7-}$ are shown and it is evident that the SO–Na–OS bonding of $\{X-2H_2O\}^{7-}$ skews the structure from the usual head-to-head arrangement of calixarenes. Only one position of several disordered sulfonate groups are shown for clarity.

Fig. 7. Packing of the superanions and cationic Keggin ions in $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]\{X+H)_w\}_{0.5}\{(p\text{-}$sulfonatocalix[4]arene$^{4-})(H^+)_y\}(H_2O)_{29}$; calixarenes not involved in capsule formation, water molecules and hydrogens are not shown for clarity.

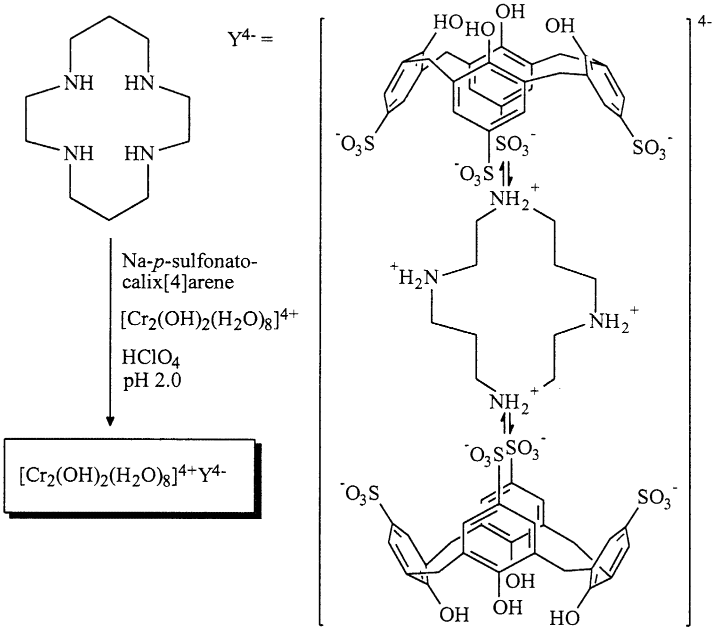
complex formation from a more acidic solution, pH 0.35. Each tetranuclear cation forms hydrogen-bonding interactions to the sulfonate groups of four superanions. The nature of the species present in solution for Rh^{3+} polynuclear species interacting with crown ether and sulfonated calixarene is yet to be realized, and indeed has proved a difficult task for all such systems to date.

The polynuclear cations may initially be acting as a clamp for the two calixarenes of each superanion in building up the supramolecular array, and in this context we note that the Cr^{3+} polynuclear cations can be irreversibly leached out of the crystalline hydrated complexes of the di- and trinuclear cations on treatment with aqueous $HClO_4$, leaving a white crystalline powder. The same conditions for the complex of the tetranuclear species results in dissolution and solvation of the complex [15]. Mononuclear $[Cr(H_2O)_6]^{3+}$ forms a complex with the superanion at a lower pH of 1, presumably with a higher degree of protonation of the superanion capsule [39]. At higher pH, the lower charge on the mononuclear cation (3+ cf 4+, 5+ and 6+ for polynuclear species) is likely to be insufficient to compensate for the electrostatic repulsion between the calixarenes within the superanions.

In extending this work to larger cations, the labile main group Keggin ion, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, was targeted, and it can be selectively precipitated in the presence of the crown ether and sulfonated calixarene [16]. This ion has been the subject of numerous ^{27}Al-NMR studies [40] and a preliminary X-ray structure determination of the sulfate or selenate salts [41]. It crystallizes within the complex $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]\{Na(18\text{-crown-}6)(OH_2)_2(p\text{-sulfonatocalix[4]arene})2(H^+)_W\}^{x-}_{0.5}$ $\{(p\text{-sulfonatocalix[4]arene}^{4-})(H^+)_y\}^{x-}\}(H_2O)_{29}$, from aqueous solutions of $AlC1_3$ treated with NaOH to pH 4.5 where there are significant quantities of $[Al(H_2O)_6]^{3+}$ and $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and minor amounts of higher oligomers, the quantities of which vary with time [40], then the addition of the crown ether and sodium salt of the sulfonated calix[4]arene, Scheme 1 [16].

The crystal structure of this complex features three distinct elements; the cationic Keggin ion $[Al_{13}O_4(OH)_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, a water-bearing calixarene and an superanion capsule $\{X(H^+)_w\}^{X-}$, along with numerous water molecules, Fig. 7. One sulfonate group of each of the calixarenes of the ionic capsule or one sulfonate group of the other calixarene is required to be protonated to achieve overall charge balance. The superanion capsule is similar to those found in the Cr^{3+} and one of the Rh^{3+} complexes, with a bi-capped hexagonal central sodium ion core bound by 18-crown-6 and two *trans*-water molecules. The superanions run in chains and the overall arrangement is distinctly different to the above structures, with no resemblance of the up–down bi-layer structure because of the incorporation of an additional calixarene in the lattice.

The Al(III) Keggin ion is a Al_{13} cluster made up of discrete aluminum–oxygen groups where twelve AlO_6 octahedra are joined together by means of common edges and the central tetrahedron of oxygen atoms contains the four-coordinate aluminum atom, AlO_4. The Keggin ions run in hydrogen-bonded chains perpendicular to the hydrogen bonded chains of superanions with hydrogen bonded inter-Keggin contacts (O···O 2.70–2.85 Å). The Keggin ion to superanion ratio is 2:1, with the Keggin ions positioned at both the periphery of the hydrophilic sulfonate



Scheme 2.

equator of the globular superanion, and at the outer edges of the sulfonates, thus overcoming electrostatic repulsion between the calixarenes. The presence of both the superanion and a calixarene in the solid-state structure implies that a delicately balanced equilibrium between the superanion and water-containing calixarene may exist in solution, as shown in Scheme 1.

The additional calix[4]arene that is not part of a capsule has water in the cavity with the closest interactions consistent with O–H···π hydrogen bonding, with closest contacts to distal aromatic rings within the calix[4]arene. This embedded water molecule forms additional hydrogen bonded interactions with two other water molecules. The calixarene water complex species is similar to that reported in Na_4(calix[4]arene sulfonate)·$13.5H_2O$ [4] with aromatic π hydrogen bonding to a water molecule in the cavity which also hydrogen bonds to two additional water molecules.

The tetra-protonated form of cyclam (= 1,4,8,11-tetra-azacyclotetradecane), $[H_4(\text{cyclam})]^{4+}$, Fig. 4, adopts an *exodentate* conformation [42] which, like 18-crown-6, has complementarity of size and curvature with that of the cavity of *p*-sulfonatocalix[4]arene, along with hydrogen bonding possibilities. At pH 2 these components assemble with the dinuclear Cr^{3+} aqua ion, crystallizing as $[Cr_2(OH)_2(H_2O)_8]^{4+}[H_4(\text{cyclam})]^{4+} \subset \{(p\text{-sulfonatocalix[4]arene}^{4-})_2\}]^{4-}$ as the hexahydrate, Scheme 2 [20]. The new ionic capsule has a central tetra-protonated cyclam shrouded by two *p*-sulfonatocalix[4]arenes associated through numerous hydrogen-bonding interactions as well as electrostatics, Fig. 8. The extra charge on the core relative to the superanions containing a crown ether, with or without a metal ion (see below) reduces the need for protonation of the sulfonate groups to overcome the electrostatic repulsion between the calixarenes. Indeed the 4 + charge on the Cr^{3+} counter cation balances that of the capsule assembly without any protonation. Thus the ratio of *exo*-capsule cations to capsules is 1:1 which contrasts with 2:3 for the crown ether analogue (see above). Nevertheless the dinuclear Rh^{3+} cation forms a 1:1 complex with the X^{7-} (see below) [19].

The cyclam-containing capsule is not as symmetrical as those containing the crown ether, Fig. 8 [20]. with the two calixarene bowls offset relative to one another, which maximizes hydrogen-bonding interactions between the components. The overall lattice has the up–down bi-layer structure. The dinuclear chromium cations are well defined and fully ordered, unlike those in the above crown ether capsule example, and are located at the hydrophilic equator of the superanions. We note that the same tetra-protonated form of cyclam has been used as a template in crystal engineering studies, as has the *endodentate* di-protonated form, which forms polymeric arrays with a variety of anions [42,43].

2.1.3. Other capsule-based metal systems

Mono-nuclear lanthanide complexes based on capsules shrouding 18-crown-6, now without sodium in the core, have been developed for lanthanides or rare earths using a combinatorial approach, Scheme 3 [17,18,44]. These are found for the smaller lanthanides. At the other extreme, 'Ferris-wheel' type structures are formed with just one calixarene associated with each crown ether (see below), or a combination of both structural types, depending on the relative sizes of the lanthanides. The chemistry is also distinctly different in that the lanthanides are directly bound via oxygen coordination to one or two sulfonate groups of the calixarenes. The new type of capsule is found in the complexes, $[\{18\text{-crown-6}\} \subset \{(M(H_2O)_7^{3+})_{1..33}(p\text{-sulfonatocalix[4]arene}^{4-})\}_2]$, $M = Y^{3+}$, Eu^{3+} [17]. These complexes crystallize from an aqueous solution of sodium *p*-sulfonatocalix[4]arene, 18-crown-6, yttrium(III) or europium(III) chloride, and hydrochloric acid as the tetrahydrate at a pH between 1.0 and 4.0, with no solid complex formation outside of this pH regime.

In these structures the rare earth cations coordinate to the 1,3-sulfonate groups of the calixarene with two calixarene subunits encapsulating an 18-crown-6 molecule. Surprisingly the 18-crown-6 is devoid of Na^+, unlike in several of the above capsules, and also devoid of Y^{3+} or Eu^{3+}, but it is noteworthy that these smaller lanthanide ions are not well suited to interact with this crown ether [45]. There are two types of lanthanide metal center, Fig. 9 [17]. Both coordinate to seven water molecules and one sulfonato group of the calixarene and are involved

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Fig. 8. Capsule assembly from the crystal structure of $[Cr_2(OH)_2(H_2O)_8][H_4(\text{cyclam})] \subset \{(p\text{-sulfonatocalix[4]arene})_2\}] \cdot 6H_2O$. Cyclam molecule shown in green.

Fig. 9. Capsule formation in the complex $[\{18\text{-crown-6}\} \subset \{(Y(H_2O)_7)_{1.33}(p\text{-sulfonatocalix[4]arene})\}_2]$. There are two types of $[Y(H_2O)_7]^{3+}$ moiety, one is positioned towards the center of the capsule, the other, with the other Y center disordered with a 1/3 occupancy and points away from the capsule core. Eu^{3+} forms an isostructural complex.

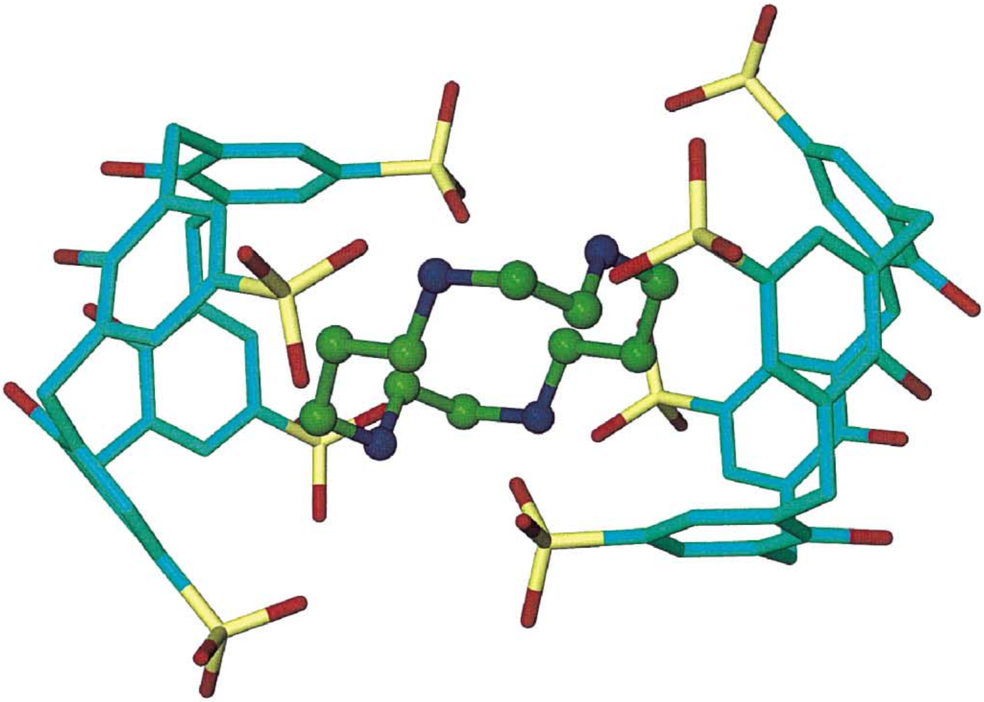


Fig. 8

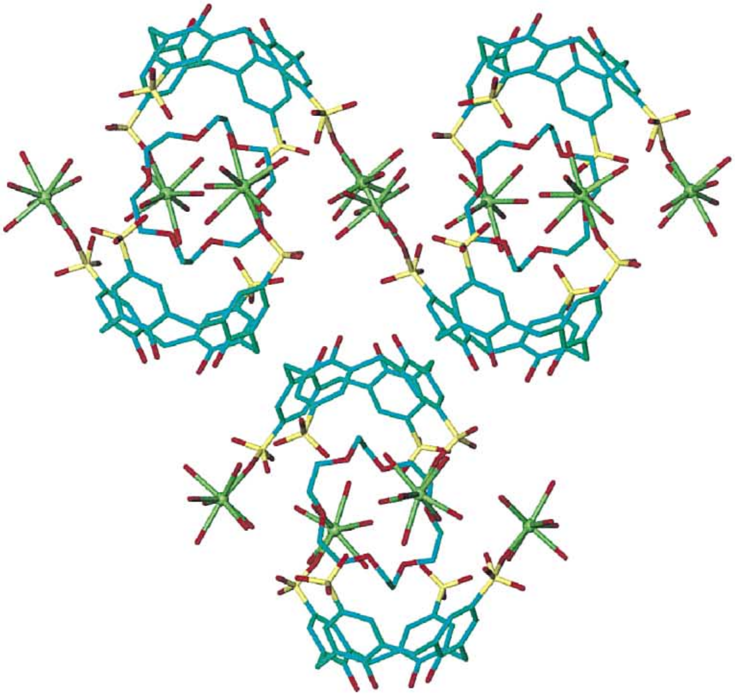
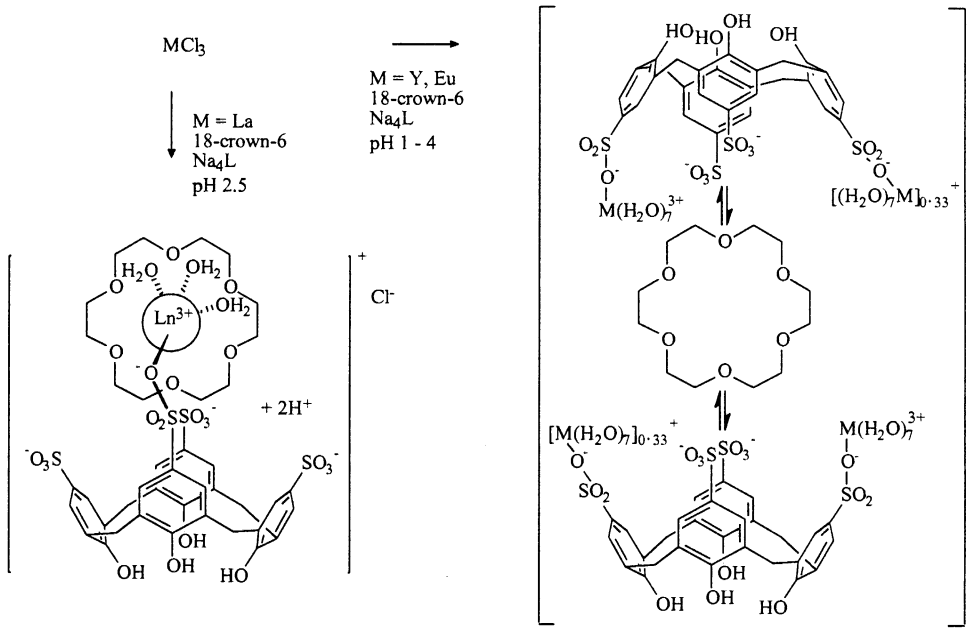


Fig.9

in RSO–Y–HOH···OSR hydrogen bonding leading to the dimerization of calixarene sub-units in two distinct modes. One of these modes involves a head-to-head dimerization of the calixarenes to form a capsule. The other mode forms an S-type motif and involves the partially occupied $M(H_2O)_7$ disordered over two adjacent sites with 1/3 occupancy each. The crown ether core molecule is involved in hydrogen bonding and presumably this results in a significant distortion from its usual 'crown' shape due to *exo*-crown ether cavity hydrogen bonding.

A similar type of capsule is seen with the smallest of the rare earths, Sc^{3+}, in the complex $\{(p\text{-sulfonatocalix[4]arene})(18\text{-crown-}6)_{0.5}[Sc_2(OH)_2(H_2O)_8]_{0.5}[Sc(H_2O)_4]\}\cdot 8H_2O$ [21]. The capsule consists of a central unmetallated crown ether surrounded by two calix[4]arenes and there are two modes of Sc^{3+} coordination to the calix[4]arenes, both of which involve coordinate bridges to another calix[4]arene. An aquated Sc^{3+} binds to a calix[4]arene phenolic oxygen and sulfonate group of an adjacent calix[4]arene in a *cis* arrangement, while a dimeric $[Sc_2(OH)_2(H_2O)_8]^{4+}$ is also bound between two calix[4]arenes, this time solely via sulfonate groups, Fig. 10 [21]. This creates 2D coordination networks between the calix[4]arenes and Sc cations, and adjacent networks pack together such that capsules are formed around the 18-crown-6 guest molecules.

In the absence of crown ether, Ln^{3+} (Ln = Yb, Eu) can form complexes with *p*-sulfonatocalix[4]arene with the metal center also bound to one sulfonato group. Some of these form slipped capsules with water or other solvent molecules in the cavities of the calixarenes [12,31], but for others, different structural types are formed [12], including nanotubes and vesicles in the presence of pyridine *N*-oxide [22].



Scheme 3.

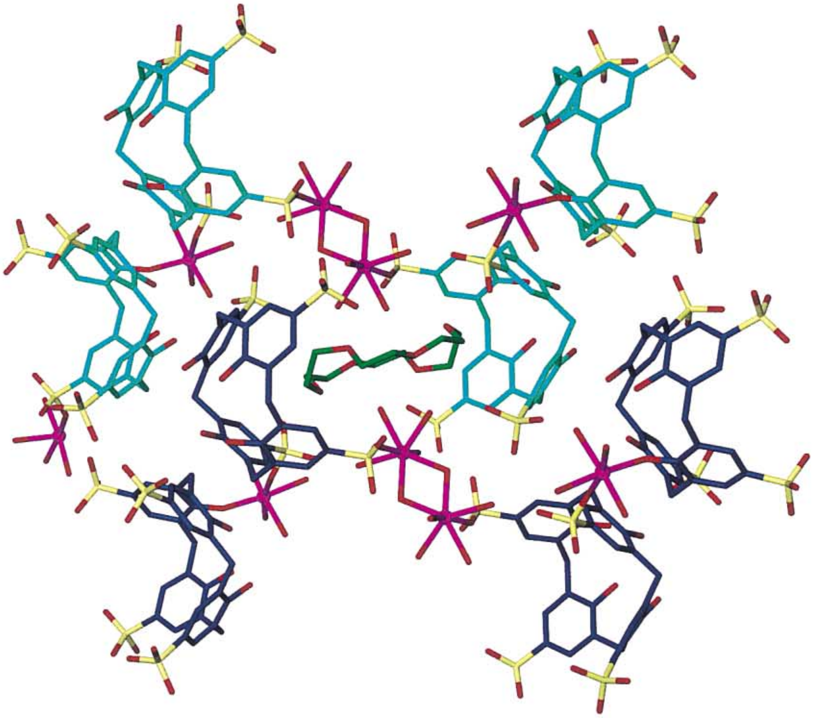


Fig. 10

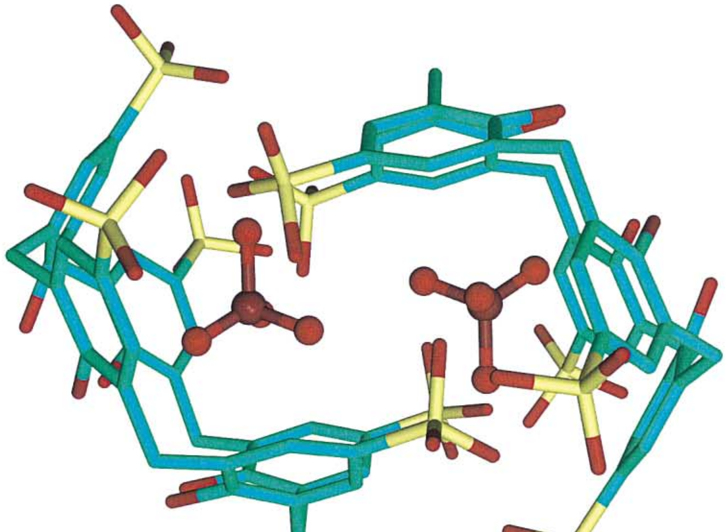


Fig. 11

Fig. 10. Capsule formation in the complex {*p*-sulfonatocalix[4]arene)(18-crown-6)$_{0.5}$[Sc$_2$(OH)$_2$(H$_2$O)$_8$]$_{0.5}$-[Sc(H$_2$O)$_4$]} · 8H$_2$O. The Sc(III) ions and *p*-sulfonatocalix[4]arenes form a 2D coordination polymer and the polymers (two of which are shown here in light and dark blue, respectively) pack together around 18-crown-6 to give a capsule motif.

Fig. 11. The flattened capsule structure of $[(H_2SO_4)_2\} \subset \{(\text{calix[5]arenesulfonic acid})_2]$.

2.2. Calix[5]arenes

2.2.1. Bi-layer structures

Structural studies show that *p*-sulfonatocalix[5]arene adopts the cone conformation with all of the phenolic oxygen atoms in an approximate plane while the overall packing mode resembles that observed for the bi-layer structures of the cyclic tetramer. Potentiometric determination of the pK_a values for the phenolic moieties demonstrates that the molecule possesses three ionizable phenolic protons pK_a values 10.96, 7.63 and 4.31) [1]. Crystallization of the sodium salt of *p*-sulfonatocalix[5]arene at pH 2 yields the solvate $Na_{10}[p\text{-sulfonatocalix[5]arene}]_2 \cdot 33.5H_2O$ in which all the phenolic protons are present [46]. However, crystallization at pH 7 results in the formation of $Na_7[p\text{-sulfonatocalix[5]arene}] \cdot 18H_2O$ with two deprotonated phenolic groups [1]. Despite the necessary differences in the hydrogen bonding pattern at the lower rim, the penta- and hexaanions are remarkably similar in conformation. Furthermore, both structures reveal a single water molecule within the calixarene cavity. In contrast to the structure of $Na_4[p\text{-sulfonatocalix[4]arene}] \cdot 13.5H_2O$ [4], the cavity-contained water molecules do not engage in OH···aromatic–π hydrogen bonding but rather form long hydrogen bonds to the phenolic oxygen atoms of the calixarene.

Crystals grown from an aqueous mixture of $Na_5[p\text{-sulfonatocalix[5]arene}]$, *N*,*N*-dimethylacetamide (= DMA) and $Co(NO_3)_2 \cdot 6H_2O$ yielded the structure of $Na_8[Co(H_2O)_4(p\text{-suifonatocalix[5]arene})_2] \cdot 2CH_3C(O)N(CH_3)_2 \cdot 37H_2O$ in which the conformation of the calixarene is significantly more 'upright' than in the structures of the hydrated sodium salts described above [46]. Two calixarene molecules coordinate to Co via sulfonate oxygen atoms to form a face-to-face capsule type dimer hinged on one side by an octahedral '$Co(H_2O)_4^{2+}$' moiety. The cavity of each calixarene is occupied by a DMA guest molecule with the *N*-methyl group penetrating most deeply into the cavity. The DMA guest does not act as a ligand to the cobalt center but serves to bridge two Na^+ ions. The sodium and cobalt ions, as well as a large quantity of enclathrated water, form part of an extensive hydrophilic layer which separates the calixarene bi-layers.

Structural studies have also been carried out on complexes of *p*-sulfonatocalix[5]arene with hydrated metal salts of La(III), Eu(III), Gd(III), Th(III) and Yb(III) and pyridine or pyridine *N*-oxide [1]. In the structure of $Na_2[La(H_2O)_9][p\text{-sulfonatocalix[5]arene}] \cdot ONC_5H_5 \cdot 10H_2O$, the La(III) center is not coordinated to the macrocycle and exists simply as a $La(H_2O)_9^{3+}$ counterion. The calixarene serves as a second-sphere ligand to the $La(H_2O)_9^{3+}$ ion with a large number of hydrogen-bonded contacts formed between the lanthanum aqua ligands and the calixarene sulfonato oxygen atoms. A pyridine *N*-oxide molecule is situated in the calixarene cavity and interacts with sodium ions and water molecules in the lattice, but is not coordinated to the La^{3+} center.

Under identical experimental conditions, crystallization with $Gd(NO_3)_3 \cdot H_2O$ yields $Na_7[Gd(H_2O)_6[p\text{-sulfonatocalix[5]arene})_2] \cdot 2(ONC_5H_5) \cdot 34H_2O$ in the solid state. Note that in this complex the metal ion:calixarene ratio is 1:2 rather than 1:1 as observed for the La analogue. The Gd center adopts an approximately dodecahedral eight-coordinate geometry comprising six water molecules and the sulfonate oxygen atom from two symmetry-related calixarene ligands, thus forming a 'hinge' structure similar to that observed for $Na_8[Co(H_2O)_4(p\text{-sulfonatocalix[5]arene})_2] \cdot 2CH_3C(O)N(CH_3)_2 \cdot 37H_2O$. However, in the Gd case, the calixarene units are not arranged in a face-to-face fashion, but are rotated by 180° relative to one another about the calixarene–Gd–calixarene axis. Despite the similarity in ionic radius, substitution of europium for gadolinium results in a somewhat different structure for $Na[Eu(H_2O)_9]_2[Eu(ONC_5H_5)(H_2O)_5(p\text{-sulfonatocalix[5]arene})_2] \cdot ONC_5H_5 \cdot 17.5H_2O$. In this case, one of the two crystallographically unique pyridine *N*-oxide molecules which occupy the calixarene cavities also forms part of the primary coordination sphere of the bridging Eu(III) ion while the second coordinates only to sodium. Two $[Eu(H_2O)_9]^{3+}$ counterions are situated in the hydrophilic layer of the structure in a manner similar to that of the lanthanum complex.

In the case of $Na_8[Tb_4(NOC_5H_5)_4(H_2O)_{18}(p\text{-sulfonatocalix[5]arene})_4] \cdot 52H_2O$, the gross structure was determined in spite of weak diffraction due to poor crystal quality. Each host molecule consists of four calixarene ligands together with four bridging Tb(III) ions which link the structure together. Of the two crystallographically unique Th ions, one is situated on the exterior of the 'supercomplex' and bridges two calixarenes in a manner similar to that in the structures derived from Gd and Eu. This Tb(III) ion is furthermore ligated by two pyridine *N*-oxide moieties, each of which occupies one of the calixarene cavities. This arrangement results in simultaneous first and second-sphere coordination of the Tb ion. The remaining pair of Tb ions are situated at the center of the tetrameric array and engage in a unique triply bridging mode with each metal ion simultaneously binding via the sulfonate oxygen atoms to three calixarene ligands. The latter two Th ions are not coordinated to any pyridine *N*-oxide molecules. In contrast to the previously described structures involving lanthanide ions, the structure of $Na_2[Yb(ONC_5H_5)(H_2O)_6(p\text{-sulfonatocalix[5]arene})] \cdot 13H_2O$ involves the first-sphere coordination of the eight-coordinateYb(III) ion to a single calixarene ligand, once again via one of the sulfonato oxygen atoms. A single calixarene is thus capped by a $Yb(H_2O)_6(ONC_5H_5)^{3+}$ moiety instead of assuming a bridging coordination mode of the metal ion between two calixarene units. All the structures involving *p*-sulfonatocalix[5]arene described above reveal that in spite of different local environments about the calixarene headgroups, the overall packing mode of the bi-layer structure is maintained. This is a tribute to the principles of self-assembly in that, even when presented with a wide range of metal ions, the same basic crystal packing arrangement is sufficiently robust to accommodate these varying requirements.

2.2.2. Capsules

We plan to develop analogous superanion capsule chemistry for sulfonated calix[5]arene which also favors a cone conformation, and the ensuing capsules will have considerably greater internal volumes for binding larger molecules. Interestingly we have found that a molecular capsule comprised of two calix[5]arenesulfonic acid molecules encapsulating two sulfuric acid molecules as a hitherto unknown hydrogen-bonded dimer, crystallizes from sulfuric acid [47]. The supermolecule here is $[(H_2SO_4)_2\} \subset \{(\text{calix[5]arenesulfonic acid})_2]$, Fig. 11 [47]. The structure is notably different from that of the corresponding Na^+ salt where the calixarenes do not form molecular capsules [1,47]. This is in direct contrast to the only other structurally authenticated calixarenesulfonic acid, {calix[6]arenesulfonic acid} $\cdot 23H_2O$, which is isostructural with its corresponding Na^+ salt, and has the calix[6]arene in a double partial cone conformation effectively excluding the possibility of capsule formation [48]. It is likely that the larger calix[5]arene has greater flexibility, being able to form a flattened, slipped structure, or an expanded structure able to encapsulate larger molecules, beyond the crown ether in the above calix[4]arene studies [15,16,19]. This may include C_{60} noting that two linked calix[5]arenes can encapsulate the fullerene [49], and there is therefore the possibility of water solubilization of the fullerene at least at low pH to overcome any electrostatic repulsion between ionized calixarenesulfonic acid molecules in the capsule.

3. Spheres and tubular structures

In almost all of the reported structures involving *p*-sulfonatocalix[4]arene, the truncated cone-shaped molecules have assembled in an up–down fashion to form bi-layers, thus resulting in planar, two-dimensional architectures. As a natural extension of this work, it is easy to envision that an up–up arrangement would necessarily lead to curved structures. Atwood and co-workers have recently shown that such an arrangement is indeed possible [22] using a design strategy involving a three-component system consisting of Na_5[*p*-sulfonatocalix[4]arene], pyridine *N*-oxide and $La(NO_3)_3 \cdot 6H_2O$. An aqueous combination of these components in a ratio of 2:2:1, respectively, readily yields crystals suitable for X-ray diffraction studies. As observed in the bi-layer structures, the hydrophobic regions of the calixarenes are aligned, but in this case they are assembled in an up–up radially symmetric fashion along the surface of a sphere, where they constitute an organic shell around an aqueous polar core, Fig. 12. This spherical assembly measures ~ 28 Å across and has a volume of $\sim 11\,000$ Å^3. The polar outer-shell surface of the sphere consists of the sulfonate head groups of 12 calixarenes and bears a total charge of -48. Similarly, a polar inner-shell surface of the nano-sphere comprises 48 phenolic hydroxyl groups, 12 of which are deprotonated. The interior of the sphere consists of two $Na(H_2O)_6$ ions surrounded by an additional 24 water molecules. The cavities of the calixarenes are situated just below the polar surface of the sphere and constitute a series of hydrophobic pockets. Twelve pyridine *N*-oxide molecules penetrate the polar surface of the sphere and are bound within the hydrophobic pockets via π-stacking interactions. Their oxygen atoms extend outwards and coordinate to La^{3+} ions above the sphere surface. The hydrophilic interstitial regions between the spheres contain, in addition to La^{3+} ions, and intricate array of water molecules and hydrated Na^+ ions. The core of each sphere has a diameter

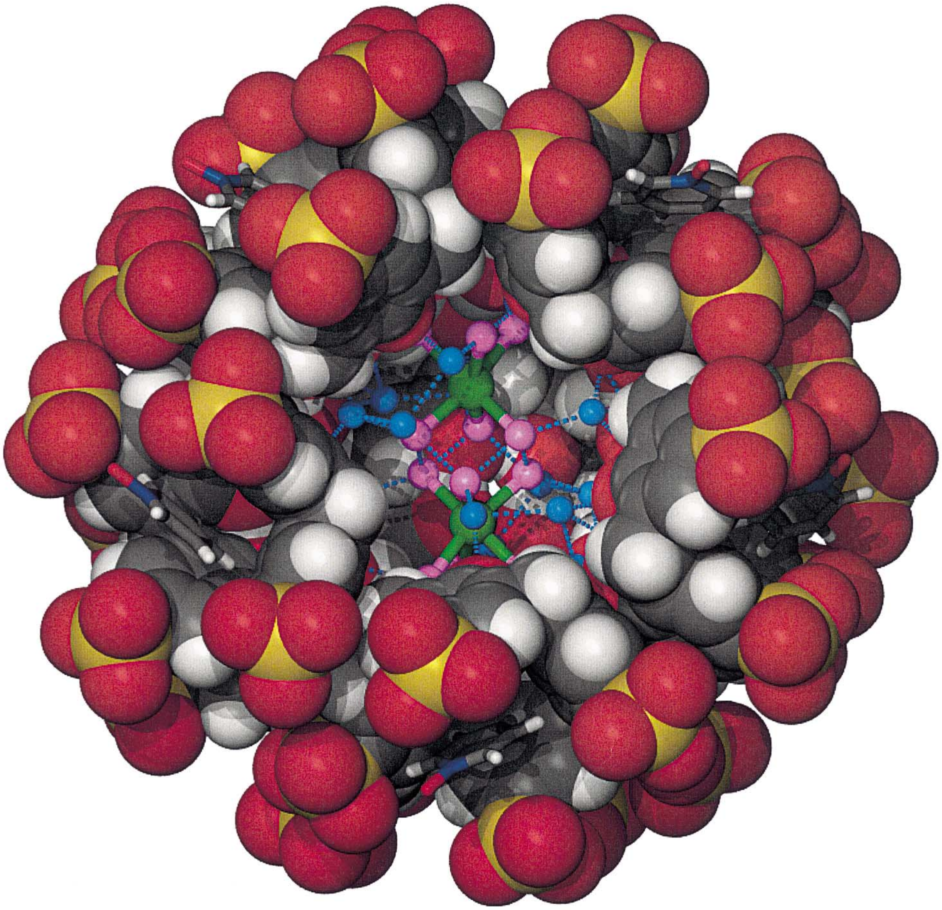


Fig. 12. Spherical structure formed by the up–up assembly of 12*p*-sulfonatocalix[4]arene molecules and pyridine *N*-oxide. Two $[Na(H_2O)_6]^+$ ions and 24 water molecules inhabit the interior of the sphere.

of ~15 Å and a volume of ~1700 $Å^3$. Adjacent spheres are tethered to one another by coordination of sulfonate oxygen atoms to interstitial lanthanum ions. Thus these lanthanum metal centers are both first and second-sphere coordinated to the calixarene molecules.

When the three components are combined in a molar ratio of 2:8:1, crystals are once again obtained quite readily and crystallographic characterization reveals a tubular assembly ~28 Å in diameter. The calixarene molecules are arranged along the surface of a cylinder that is analogous to the spherical assembly in that there is a polar core, a hydrophobic mid-region constituting the tube, and a polar outer shell, Fig. 13. However, the organic shell is no longer composed purely of calixarene molecules, but contains pyridine *N*-oxide molecules intercalated between the aromatic rings of adjacent macrocycles. It is noteworthy that the calixarene and pyridine *N*-oxide molecules form a chiral helical assembly along the length of the tube. The helix consists of a single strand of alternating calixarene and pyridine *N*-oxide molecules and there are 4.5 such units per turn. Both the hydrophilic core and the hydrophilic interstices between the tubules contain complex arrays of sodium, lanthanum and water molecules. In a manner similar to that in the spherical assembly, adjacent tubules are linked via first and second-sphere coordination to La^{3+}.

4. Other structural types

For the larger lanthanides, a perched structure akin to a Ferris-wheel are formed, $[\{La^{3+} \subset (18\text{-crown-6})(OH_2)_3\} \cap \{p\text{-sulfonatocalix[4]arene}^{4-} + 2H^+)\}]^+$, over a narrow pH regime 2.5–3.0 as a chloride salt, Scheme 3 [18]. The lanthanum is ten-coordinate with the crown ether, the calixarene (via one sulfonate group) and three water molecules acting as ligands. The three water molecules are *trans* to the sulfonate group, Fig. 14 [18]. A similar structure results from a solution prepared using lanthanum tris-trifluoromethanesulfonate nonahydrate rather than a chloride, at pH 2.5 [18].

This ferris wheel assembly has a single positive charge and hence two of the sulfonate groups are protonated. Formation of the capsule X^{7-} and its partially

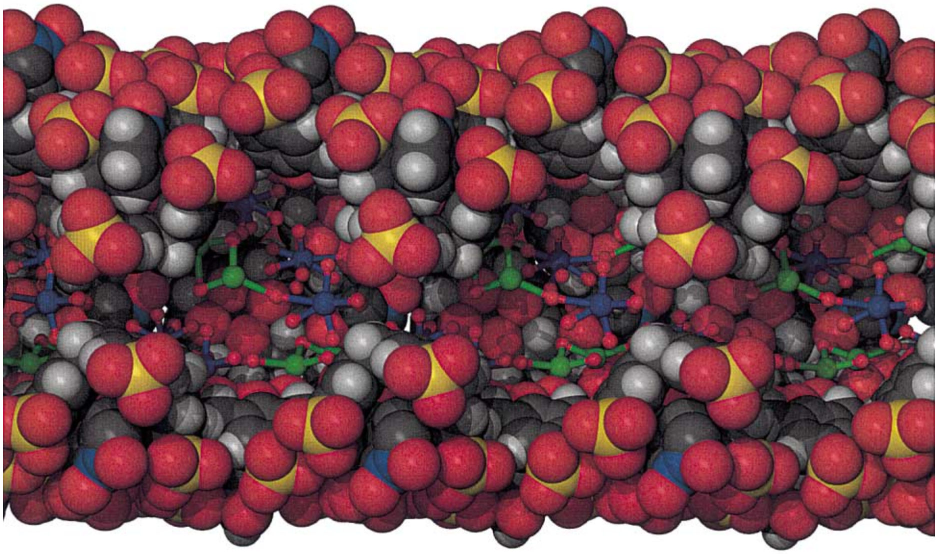
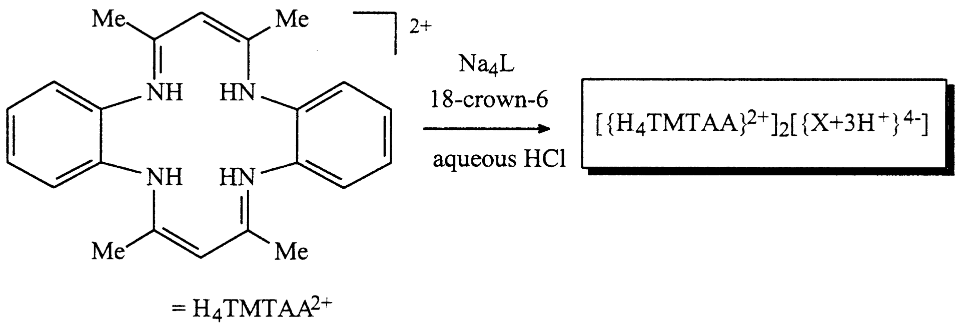


Fig. 13. Tubular assembly of *p*-sulfonatocalix[4]arene and pyridine *N*-oxide from a 2:8:1 molar ratio of *p*-sulfonatocalix[4]arene, pyridine *N*-oxide and $La(NO_3)_3 \cdot 6H_2O$.



Scheme 4.

protonated forms are precluded in this system by: (i) the lanthanum ions effectively competing with sodium to form the central cationic core, demanding a different coordination environment; and/or (ii) the trivalent positive charge of the metal ion being insufficient to overcome the electrostatic repulsion between two calixarenes in any ionic capsule (at least for the pH of the solutions where crystallization occurs). It is noteworthy that this structure, like the Keggin ion structure, does not conform to an up–down hi-layer array of the calixarenes. Interestingly the intermediate-sized lanthanide, Ce, forms a complex comprised of: (a) a capsule which is of a different type again with a cerium in the crown ether and attached to two sulfonate groups, one from each of the calixarenes; (b) a Ferris-wheel type structure; and (c) two other cerium centers. This result suggests that other structures are likely, and may depend on subtle changes in the size of the lanthanide ion, and this has implications for using superanion chemistry to separate the lanthanide cations.

5. Other systems

The concept of preparing superanions with *exo*-cavity organic cations, too large to be incorporated in the capsule, has been realized with the synthesis of $[H_4TMTAA]_2[X+3H^+]$ (where $H_4TMTAA =$ tetrahydro-5,7,12,14-tetramethyl-dibenzo[*b*,*i*] [1,4,6,9]tetraazacyclotetra-decine), Scheme 4, Fig. 15 [50]. Taking the same organic cation, and replacing the crown ether with 2-hydroxybenzimidazol gives a capsule with the same *exo*-cations but with two π-stacked hydroxybenzimidazol cations which are hydrogen bonded to the calixarenes [51]. From here the formations of analogous capsules with biologically important molecules such as histidine and tyrosine is a possibility. In this context we note that Coleman et al. have recently reported the structure of L-lysine with sulfonated calix[4]arene which has an up–down bi-layer structure [29].

6. Future prospects

The self-assembly of sulfonated calixarenes into bi-layers, superanion capsules, and also the ferris wheel cation and spheres and tubular nano-structures for some of the lanthanides lies in the formation of a large number of supramolecular interactions which interplay in concert. The lead compounds authenticated thus far show a remarkably diverse range of structural types possible using simple synthons, using water as a benign solvent, and in some cases using rapid, high through put

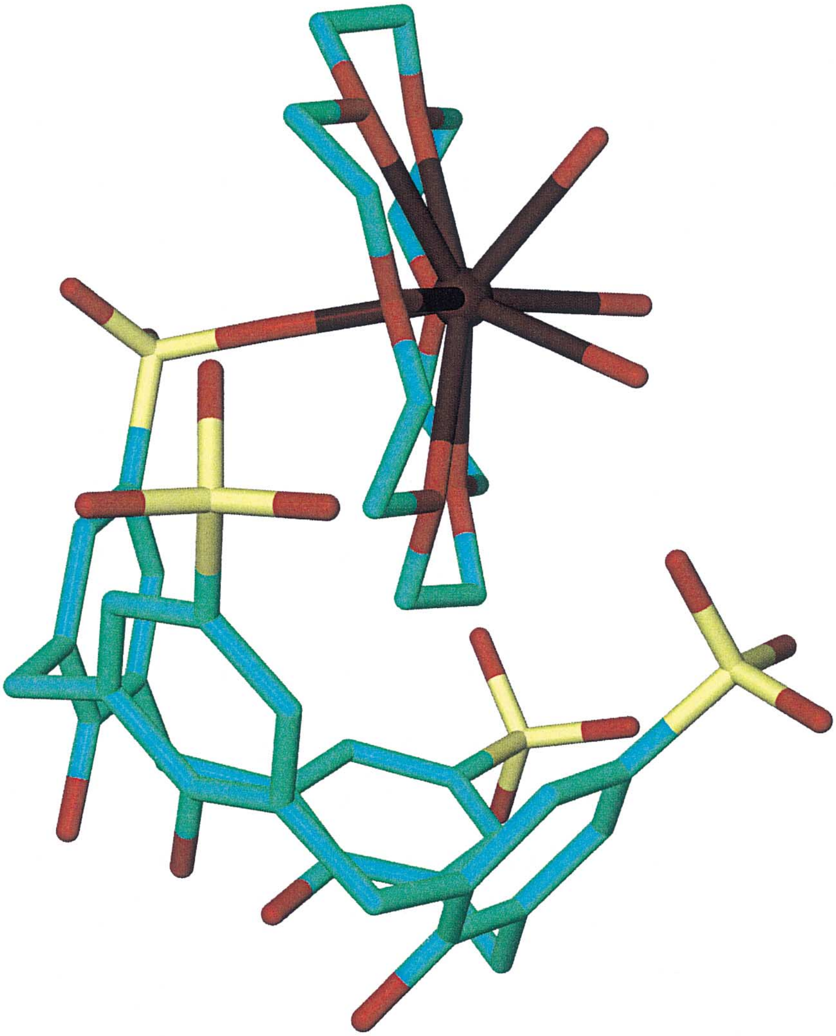


Fig. 14. The ’ferris wheel’ assembly $[\{\mathrm{La} \subset (\text{l8-crown-6})(\mathrm{OH_2})_3\} \cap \{(p\text{-sulfonatocalix[4]arene} + 2\mathrm{H}^+)\}]^+$; hydrated crystals are isolated as the chloride salt.

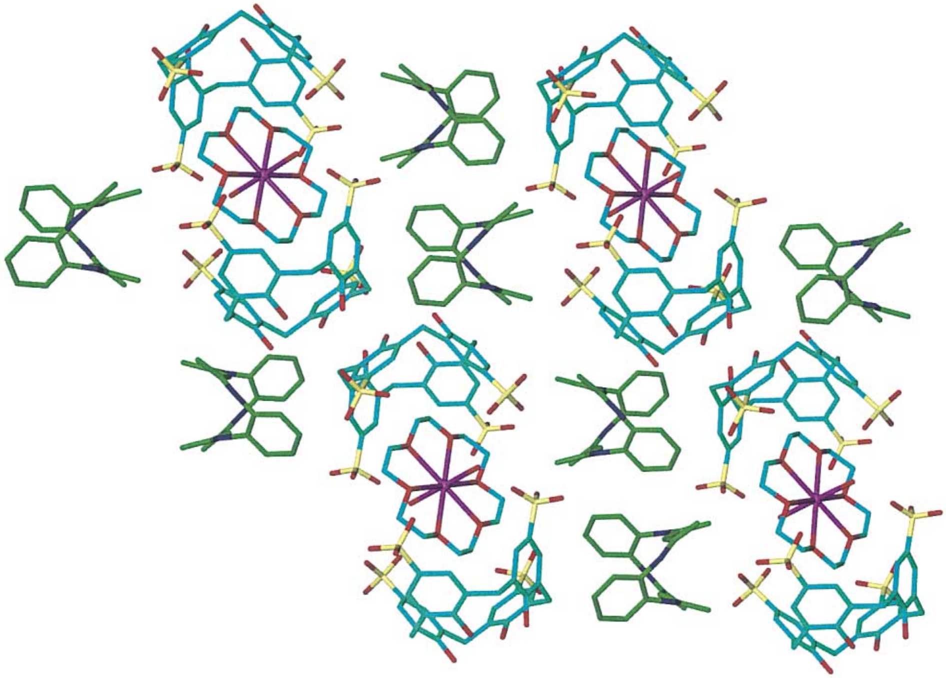


Fig. 15. Superanion capsule with *exo*-cavity organic cation (shown in green). The crystal structure of $[H_4TMTAA]_2[X + 3H^+] \cdot xH_2O$. Solvent water has been omitted for clarity.

reaction optimization techniques. New directions include: (a) the confinement of other cations in the core of the superanion assembly; (b) the binding of organic molecules in the core, which will encompass biologically important molecules; (c) the binding and stabilization of large, highly charged *exo*-capsule cations in general; (d) the formation of ionic capsules based on > 2 calixarenes shrouding large cations, an objective achieved by MacGillivray and Atwood for a neutral resorcinarene [25]; and (e) constructing mesoporous materials and template imprinting associated with leaching of *exo*-cavity components from the supramolecular structures.

The crystallization of polynuclear aqua ions alone has been a challenging problem. The superanion approach is a new general method for the structural characterization of polynuclear metal ions present in aqueous systems. The crystallization process may, however, perturb the structure present in solution, and clearly a challenge is to establish the nexus between species present in solution and the solid state, and the hierarchy of the interacting components prior to crystallization. Understanding the hydrolytic polymerization reactions of metal ions in solution are of fundamental importance and occur widely in biological systems, industrial processes and natural waters. One of the earlier supramolecular methods of crystallizing polynuclear cations involved the use of aromatic sulfonates as counter ions. This relies on the formation of layers of aqua cations and water molecules stabilized in a hydrogen-bonded network by layers of sulfonate anions, and more recently by the inclusion of crown ether molecules in this network [52]. However, this approach has had limited success for some oxo- and hydroxo-bridged binuclear aqua ions including $[M_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ ($M = Cr$, Rh) [52,35], $[CrRh(\mu\text{-}OH)_2(H_2O)g]^{4+}$ [36], and a Mo(IV) trinuclear species [53].

Incorporating crown ether or its metal complexes, or tetra-protonated cyclam in the core of the capsules, allows access to capsules of different charge for particular pH regimes. The ambivalent nature of the capsule X^{7-} versus $\{X - 2H_2O\}^{7-}$ also highlights the complexity in studying these systems, introducing another structural assembly parameter. The lanthanide chemistry is complex and the binding of the metal centers to sulfonate groups also introduces another assembly process, beyond those for the transition metal complexes to date.

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