Versatility of *p*-sulfonatocalix[5]arene in building up multicomponent bilayers†

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The ability of pyridine *N*-oxide molecules to form host–guest complexes with *p*-sulfonatocalix-[5]-arene was probed and resulted in the formation of europium complexes incorporating 2- or 4-picoline *N*-oxide, and 4,4′-dipyridine *N*,*N*′-dioxide. Relative to lanthanide complexes of *p*-sulfonatocalix[5]arene incorporating pyridine *N*-oxide, the presence of a methyl group on the aromatic ring for the picoline *N*-oxides, or a larger dipyridine dioxide guest dramatically alters the self-assembly, resulting in the formation of three new supramolecular motifs for the calixarene.

Introduction

The *p*-sulfonatocalix[*n*]arenes (where $n = 4, 5, 6, 8$) are a versatile class of molecule that has been studied extensively and that continues to attract attention in the field of supramolecular chemistry.[1] The assembly of *p*-sulfonatocalix[4]-arene ($SO_3[4]$) with various organic or inorganic species has been explored to a significant extent, and is the primary source of structural literature on this family of water soluble calixarenes.[2–4] This is partly due to the truncated cone-shape and amphiphilic nature of the tetramer, both of which result in a propensity to form 'up–down' antiparallel bilayer arrangements in the solid state (Fig. 1).[2,3] These arrangements are capable of hosting guest molecules in the hydrophobic cavities, and $SO_3[4]$ can assemble into various complex structural motifs which include molecular capsules, 'Russian dolls', 2-D or 3-D coordination polymers (that can also incorporate molecular capsules) and 'Ferris wheels'.[2a,b,v] When $SO_3[4]$ is crystallised under particular conditions, the formation of the bi-layer can be drastically circumvented.[4] In certain cases, the host then assembles (with other molecular components) into either nanometre scale dodecahedral arrays (based on the Platonic[4a] {icosahedron} or Archimedean[4b] {cuboctahedron} solids) or helical tubule arrays.[4a]

p-Sulfonatocalix[5]arene ($SO_3[5]$) is similar to $SO_3[4]$ in that it typically adopts a 'bowl' conformation, although the cavity is normally broader due to splaying of some aryl rings within the molecule (Fig. 1).[5] Until recently, there have been few structural studies incorporating $SO_3[5]$, presumably due to the more laborious synthesis of the precursor that was typically isolated in low yields.[6] With the goal of forming new supramolecular architectures with *p*-sulfonatocalix[5]-arene, we have been exploring the associated host–guest chemistry with various lanthanide metals and/or guests/molecules.

When crystallised with charged organic species (under acidic conditions) in the absence of metals, the 'bowl' conformation of $SO_3[5]$ can be dramatically perturbed with significant consequences. With $[2H(1,4\text{-diazabicyclo}[2.2.2]\text{octane})]^{2+}$ as a guest, the conformation of $SO_3[5]$ is a 'pseudo-double cone', and two molecules shroud two guests in a bis-molecular capsule arrangement.[5e] Also, crystallisation with $[2H(1,2\text{-bis}(4,4'\text{-dipyridinium})\text{ethane})]^{2+}$ results in the inversion of one aryl ring within the host and the formation of an unusual supramolecular array.[5g]

In closer relation to the current study, a number of lanthanide complexes of $SO_3[5]$ with pyridine *N*-oxide ligands have been shown to assemble as 'molecular capsule' type arrangements.[5a] In addition, some transition metal complexes of $SO_3[5]$ (formed with *N*,*N*-dimethylacetamide guest molecules)

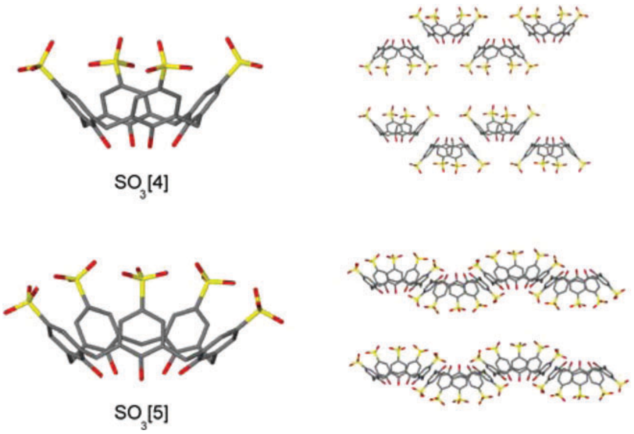

Fig. 1 The 'bowl' conformations and resultant 'up–down' antiparallel bilayer arrangements found for *p*-sulfonatocalix[4 and 5]arene (not to scale).[3,5]

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assembled into what was termed a 'supercavity'.[5b] Our recent studies focused on the formation of $SO_3[5]$ europium complexes with either mono- or diaza-crown ethers as guest species.[5d] In those studies, 1-aza-18-crown-6 was incorporated as a 'Ferris wheel' type arrangement in infinite coordination polymer chains, facilitated by unusual coordination of a sodium ion to the crown ether and a europium aquo ligand. Diaza-18-crown-6, in the doubly protonated form, was also found to reside in the $SO_3[5]$ cavity with homoleptic europium aquo ions residing at the upper rim of the calixarene. Also, di-protonated diaza-15-crown-5 was found to form a similar bi-layer array to the diaza-18-crown-6 analogue.

Given the aforementioned studies, we examined the nature of europium $SO_3[5]$ complexes with the picoline *N*-oxides (2-, 3- and 4-derivatives) and 4,4′-bipyridine *N*,*N*-dioxide (DiPyNO) as potential ligands/guests in each case. Herein we report three crystal structures that resulted from the combination of pentasodium *p*-sulfonatocalix[5]arene ($Na_5SO_3[5]$), the potential guest (in excess), and europium(III) nitrate under acidic aqueous conditions. For the picoline *N*-oxides (PicNO), single crystals grew when either 2- or 4-PicNO were employed as guest species. For 2-PicNO, the guest was bound to a europium centre which is also coordinated to an $SO_3[5]$ sulfonate group. For 4-PicNO, the non-coordinating guest was found to reside edge on in the $SO_3[5]$ cavity, and a homoleptic europium aquo cation was found to reside near the 'upper rim'. In addition, a tris-aquo sodium centre was found to link two neighbouring calixarenes whilst spanning the aqueous layer of a resultant bilayer arrangement. When 4,4′-dipyridine *N*,*N*′-dioxide (DiPyNO) was employed, the molecule was found to partially reside in the $SO_3[5]$ cavity, and to form a dimer like arrangement with an neighbouring $SO_3[5]$/DiPyNO moiety, at the same time expanding the bi-layer arrangement of calixarenes. As for the 4-PicNO case, homoleptic europium aquo ions were found to reside near the $SO_3[5]$ upper rims. Further to the above studies, a critical analysis of *p*-sulfonatocalix[5]arene packing in all $SO_3[5]$ structures reported to date is also included.[5] This includes the aforementioned lanthanide/sodium complexes which are distinctly different in being devoid of potentially included organic type molecules, but nevertheless like in the present study, there is a preferred bilayer packing arrangement for $SO_3[5]$ (when in the bowl conformation) in which chains of the host pack efficiently in an alternating manner, a feature that is in contrast to the behaviour of $SO_3[4]$ which can pack in various ways while maintaining the bilayer motif.[2] In addition, it also shows that any pre-organisation of the conformation of the calixarene and interplay with guest/surrounding molecular species is an integral part of the supramolecular arrays.

Results and discussion

Structure of the complex $[(Eu(H_2O)_6(2\text{-picoline-}N\text{-oxide}))(p\text{-sulfonatocalix-}[5]\text{arene})(Na_2(H_2O)_9)]\cdot 2.75H_2O$, 1

Crystals of complex **1** grew upon slow evaporation of an acidic aqueous solution containing a 1:3:1 mixture of $Na_5SO_3[5]$, 2-picoline-*N*-oxide and europium(III) nitrate (pH adjusted to be <1 with 1 M HCl, eqn (1)). Complex **1** crystallises in an orthorhombic cell and the structural solution was performed in the space group $P2_12_12_1$, although the crystals were weakly diffracting and required a synchrotron X-ray source to obtain a meaningful solution. The large asymmetric unit consists of one $SO_3[5]$, a sulfonate bound hexa-aqua europium centre with a 2-PicNO ligand, two poly-aqua sodium centres (one of which is bound to an $SO_3[5]$ sulfonate group), and a total of 2.75 waters of crystallisation that are disordered over eight positions (Fig. 2).

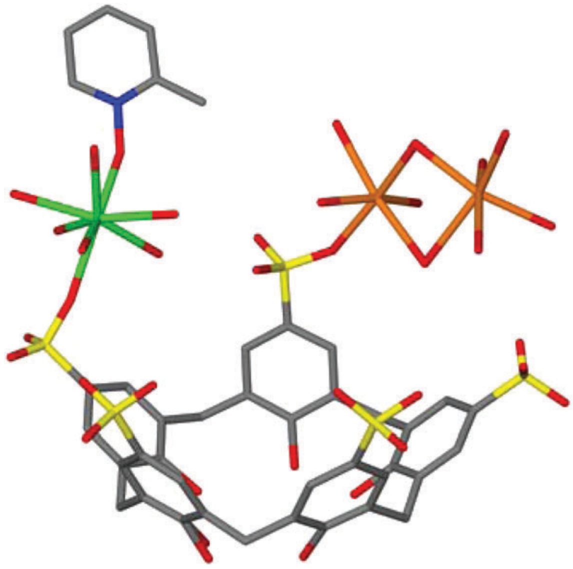
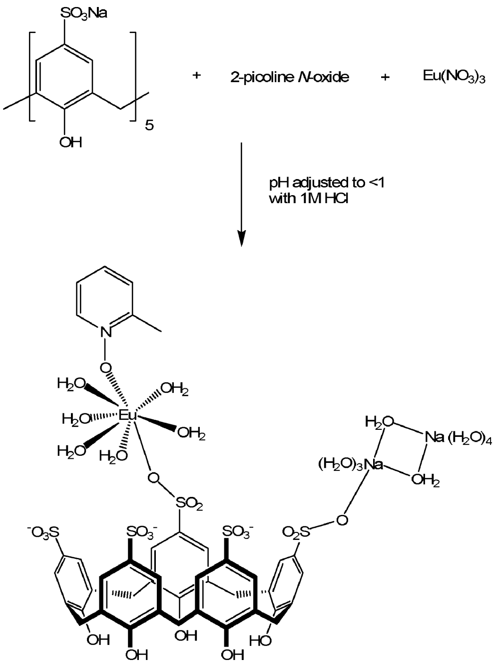


Fig. 2 Part of the asymmetric unit in **1** showing the metal coordination spheres and the binding of 2-picoline *N*-oxide to the europium centre. Waters of crystallisation have been omitted for clarity. Disordered europium ligands, 2-picoline *N*-oxide, sodium centres and aquo ligands are only shown in one position.



(1)

Examination of the coordination sphere of the europium centre shows the metal to be octa-coordinate and of square anti-prismatic geometry. The two sodium centres (and aquo ligands) are badly disordered over a number of positions, although both are hexa-coordinate and are of near octahedral geometry (Fig. 2).

The calixarene is in a slightly distorted cone conformation with dihedral angles (between the plane of the calixarene defined by the five phenolic oxygen centres and the five phenol rings) in the range of ~95–149°. For the 2-PicNO molecule, it was to some extent unexpected to find the ligand directed away from the $SO_3[5]$ cavity in the asymmetric unit (Fig. 2). Symmetry expansion around the 2-PicNO revealed that the molecule resides in the cavity of a neighbouring assembly as part of a bi-layer arrangement (Fig. 3 and 4). Close examination of the contacts between two interacting assemblies reveals a number of influential (and crystallographically unique) interactions in the form of $EuOH_2\cdots OS$ hydrogen bonds and $CH\cdots\pi$ interactions. The former are from europium aquo ligands to $SO_3[5]$ sulfonate groups, and five unique interactions have $EuO\cdots OS$ distances ranging from 2.706 to 2.802 Å. The $CH\cdots\pi$ interactions are from the 2-PicNO guest molecules, and in one of two disordered positions, there are two $CH\cdots$aromatic centroid distances of 3.09 and 3.12 Å.

Further symmetry expansion of the asymmetric unit reveals that these interacting assemblies form host–guest chains as part of a bilayer arrangement (Fig. 4). This occurs through numerous other hydrogen bonding interactions between europium aquo ligands and symmetry equivalent $SO_3[5]$ sulfonate groups or waters of crystallisation (the distances for which are all of a magnitude similar to those discussed above).

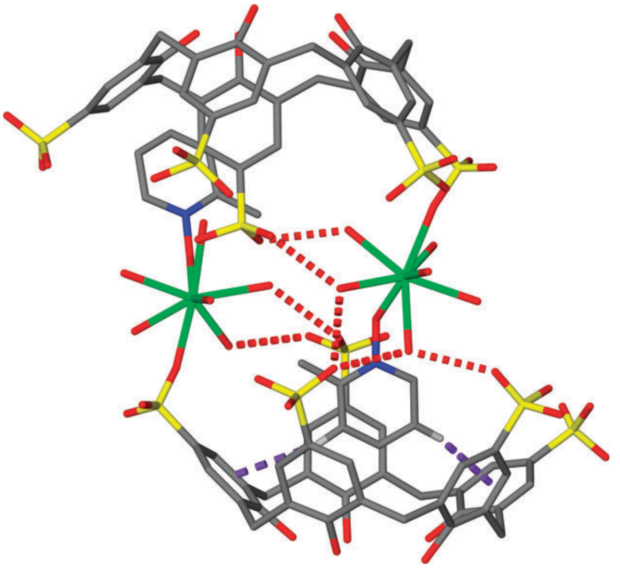


Fig. 3 Some intermolecular interactions found between two interlocking complexes in **1**. Hydrogen bonds and $CH\cdots\pi$ interactions are shown as dashed red and purple lines respectively. Polyaquo sodium centres, non-participating hydrogen atoms and waters of crystallisation have been omitted for clarity. Disordered europium aquo ligands and 2-picoline *N*-oxides are only shown in one position.

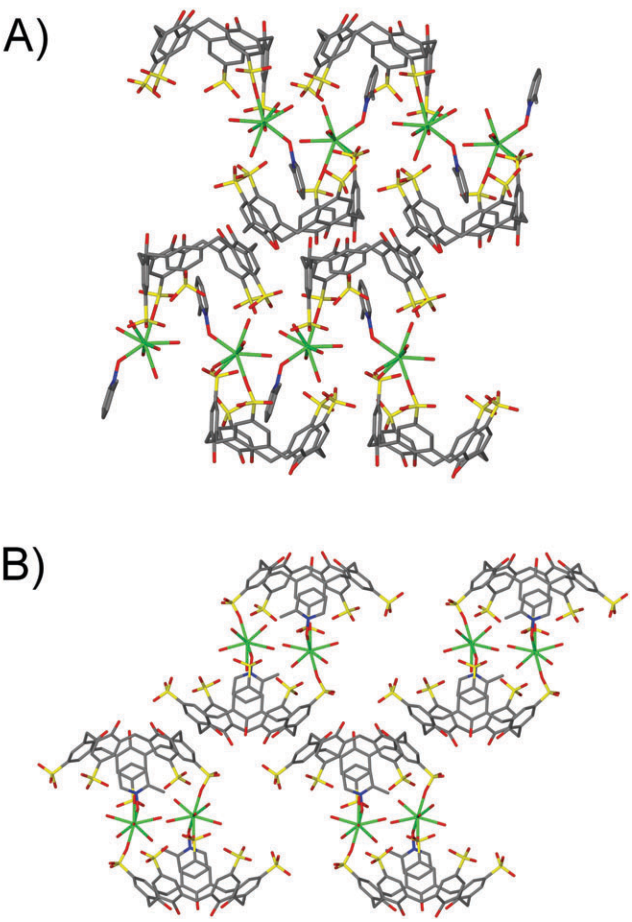
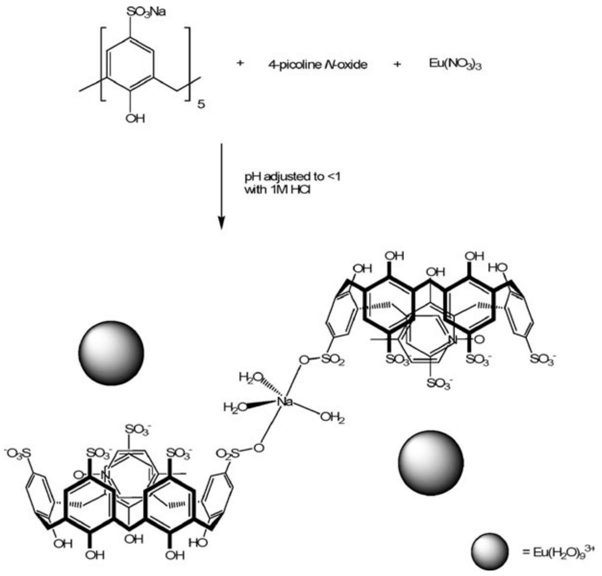


Fig. 4 Two views of the extended bi-layer structure in **1**. (A) Discrete complexes pack in a host–guest fashion within one another to form non-covalent chains running the width of the page. (B) Non-covalent chains (running into and out of the page) pack into a bilayer arrangement through hydrophobic interactions. Disordered ligands/groups, all sodium aquo cations, and waters of crystallisation have been omitted for clarity.

There are three crystallographically unique interactions between the $SO_3[5]$ molecules in the bi-layer array. There is one π-stacking interaction with an aromatic centroid⋯aromatic centroid distance of 3.774 Å, and three $CH\cdots\pi$ interactions with $CH\cdots$aromatic centroid distances in the range of 3.00–3.36 Å. In order to examine the effect of the methyl group on the picoline *N*-oxide guest, we employed the 3- and 4-PicNO derivatives in an analogous manner to that used in the formation of complex **1**. Single crystals of a europium complex were not formed when 3-PicNO was used. When 4-PicNO was used however, single crystals formed of a europium complex that has a non-coordinated guest molecule residing in the $SO_3[5]$ cavity.

Structure of the complex $[((4\text{-picoline } N\text{-oxide})\subset(p\text{-sulfonatocalix}[5]\text{arene}))_2 + 3H^+)(Na(H_2O)_3)][(Eu(H_2O)_9)_2]\cdot 16.5\ H_2O$, 2

Crystals of complex **2** grew upon slow evaporation of an acidic aqueous solution containing a 1 : 3 : 1 mixture of $Na_5SO_3[5]$, 4-picoline *N*-oxide and europium(III) nitrate (pH adjusted to be <1 with 1 M HCl, eqn (2)). Complex **2** crystallises in an orthorhombic cell and the structural solution was performed in the space group *Pbcn*. The asymmetric unit consists of one *p*-sulfonatocalix[5]arene, one 4-picoline *N*-oxide, one disordered nonaaqua europium cation, one half of a sulfonate bound tris-aquo sodium centre (residing on a special position) and a total of eight and a quarter water molecules that are disordered over fifteen positions.



(2)

The calixarene is also in a distorted cone conformation with similar dihedral angles to those in complex **1**, with values of ~94–150°. This is related to the orientation of the 4-PicNO molecule in the $SO_3[5]$ cavity (Fig. 5), and the nature of the interaction with the internal walls of the calixarene, notably involving π-stacking through one of the phenyl rings with an aromatic centroid···centroid distance of 3.885 Å. Although there are no other interactions between the 4-PicNO molecule and the calixarene, the guest interacts with a water of crystallisation that hydrogen bonds to both the *N*-oxide of the guest and an $SO_3[5]$ sulfonate group (O···ON and O···OS distances of 2.514 and 2.691 Å, respectively), Fig. 5. Although the nona-aqua europium cation is disordered, it is of near tricapped trigonal prismatic geometry. Symmetry expansion of the coordination sphere of the sodium atom in complex **2** shows the metal centre to be five coordinate and of trigonal bipyramidal geometry, Fig. 5. Further symmetry expansion around the sodium coordination sphere reveals a bis-$SO_3[5]$ arrangement that is linked *via* calixarene sulfonate groups through the penta-coordinate sodium centre that spans the hydrophilic layer, Fig. 5.

Examination of the extended structure (Fig. 6) reveals the calixarenes to pack in a bilayer arrangement that is similar to complex **1** and both the Ln/PyNO/$SO_3[5]$ series of complexes described by Atwood and co-workers,[5a,b] and the crown ether complexes described above.[5d] The calixarene molecules in the bilayer arrangement of **2** pack through two crystallographically unique interactions. There is one π-stacking interaction between aromatic groups of neighbouring calixarenes (aromatic centroid···centroid distance of 3.803 Å) and one CH···π interaction from a methylene bridging group to an aromatic ring of a neighbouring calixarene (CH···aromatic centroid distance of 2.77 Å). Given the extent of the disorder associated with the homoleptic europium cation and calixarene sulfonate groups, coupled with the locally disordered water molecules, numerous possible EuO···OS or EuO···O hydrogen bonding interactions are evident.

Some ambiguity arises when the overall charge of the arrangement is considered. In one 'bis-asymmetric unit' arrangement, there are two $SO_3[5]$ molecules presenting a 10− charge. This charge is partially counterbalanced by the presence of two nona-aqua europium cations and a tris-aqua sodium metal centre, all of which have a cumulative charge of 7+. Hence there is an overall charge deficit of 3−. This deficit may be balanced by sulfonate group protonation or the

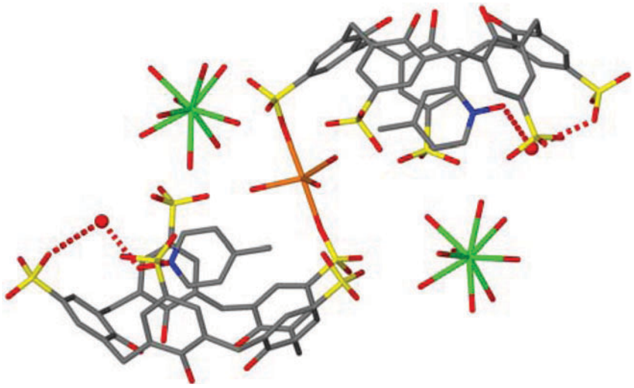


Fig. 5 Expansion of the asymmetric unit around the trigonal bipyramidal sodium centre in complex **2**. The hydrogen bonding between waters of crystallisation and $SO_3[5]$ sulfonate groups and 4-picoline *N*-oxide are shown as dashed red lines. The homoleptic nona-aqua europium cations reside at the $SO_3[5]$ upper rims and partake in extensive hydrogen bonding (not shown).

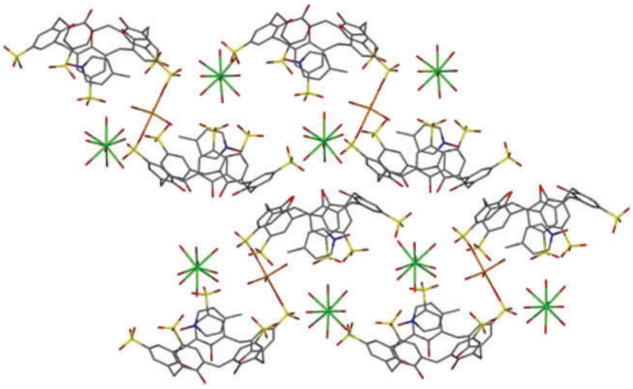


Fig. 6 Extended symmetry expansion of the crystal structure of complex **2** showing the bilayer arrangement of *p*-sulfonatocalix[5]-arenes, the $SO_3[5]$ coordination dimers, and the positioning of the nona-aqua europium cations. Waters of crystallisation, some disordered calixarene sulfonate oxygen atoms, and disordered europium aquo ligands have been omitted for clarity.

presence of H_3O^+ given that the pH adjusted solution ($pH < 1$) undergoes slow evaporation to achieve crystal growth. This phenomenon has been observed by us on a number of previous occasions.[5f]

The host–guest behaviour of non-coordinated 4-PicNO in complex **2** is partly reminiscent of a PyNO/La/Na/SO_3[5] complex that was reported by Atwood and co-workers, in which PyNO occupied the molecular cavity and was also non-coordinating.[5a] When 4-PicNO in the above ternary system is replaced with the significantly larger 4,4′-dipyridine *N*,*N*′-dioxide, a host–guest Eu/SO_3[5]/DiPyNO complex forms. The complex shows partial inclusion of the guest within the SO_3[5] cavity and a dimerisation across the hydrophilic layer with neighbouring assemblies *via* numerous intermolecular interactions.

Structure of the complex [((4,4′-dipyridine *N*,*N*′-dioxide)⊂(*p*-sulfonatocalix[5]-arene))$_2$ + $4H^+$][(Eu(H_2O)$_9$)$_2$]·17H_2O, 3

Crystals of complex **3** grew upon slow evaporation of an acidic aqueous solution containing a 1 : 3 : 1 mixture of Na_5SO_3[5], DiPyNO and europium(III) nitrate (pH adjusted to be <1 with 1 M HCl, eqn (3)). The crystals are in a monoclinic cell and the structural solution was performed in the space group $P2_1/c$. The asymmetric unit consists of two *p*-sulfonatocalix[5]arenes, two 4,4′-dipyridine *N*,*N*′-dioxides, two nona-aqua europium cations (one of which is disordered) and a total of seventeen water molecules that are disordered over twenty four positions. The calixarenes are in a more distorted cone conformation which relates to the orientation of the 4,4′-dipyridine *N*,*N*′-dioxide and the nature of the interactions with the walls of the calixarene (see below, Fig. 7). In this case the dihedral angles between the plane of the calixarene are dissimilar to those in complexes **1** and **2**, with values in the ranges of ~92–156 and 96–155°.

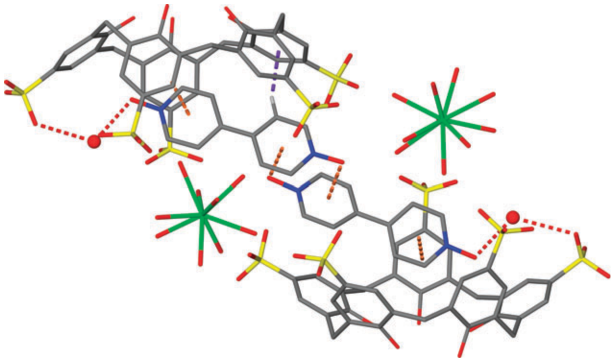
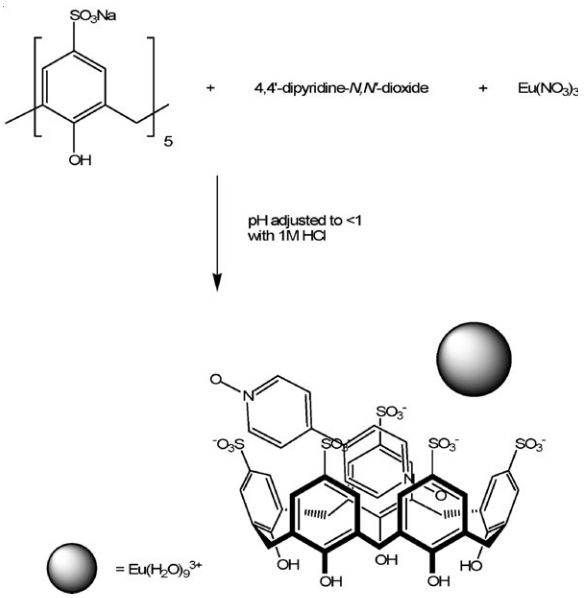


Fig. 7 The asymmetric unit found in the crystal structure of **3** and the various intermolecular interactions between the SO_3[5]/DiPyNO dimeric assembly. Hydrogen bonds, π-stacking (and DiPyNO···DiPyNO), and CH···π interactions are shown as dashed red, orange or purple lines respectively. Waters of crystallisation proximate to the DiPyNO guests are shown in ball representation. Other waters of crystallisation and non-participating hydrogen atoms have been omitted for clarity. A disordered europium aquo ligand is only shown in one position.



(3)

A striking feature of **3** is that the DiPyNO molecules in the large asymmetric unit are non-coordinating and form a dimer like arrangement that spans the hydrophilic layer. This is facilitated through a series of cooperative inter-molecular interactions between SO_3[5], DiPyNO, and waters of crystallisation, Fig. 7. There are two π-stacking interactions and one CH···π interaction between the DiPyNO guest molecules and the SO_3[5] hosts (aromatic centroid···centroid and CH···centroid distances of 3.687, 3.843 and 2.76 Å). The DiPyNO molecules also interact with the SO_3[5] hosts *via* hydrogen-bonding from the waters of crystallisation to both *N*-oxide (DiPyNO) and sulfonate (SO_3[5]) functionalities (two O···ON distances of 2.486 and 2.516 Å, and two O···OS distances of 2.886 and 2.773 Å). The dimerisation through the hydrophilic layer occurs *via* two O···aromatic centroid interactions between two DiPyNO *N*-oxide groups and their opposing aromatic rings (two NO···aromatic centroids distances of 3.226 and 3.284 Å). In addition to all of the above, there are several hydrogen bonds between the europium aquo ligands and the oxygen atoms of calixarene sulfonate groups, the distances of which are all of typical magnitude for such arrangements.[2s]

Symmetry expansion shows the *p*-sulfonatocalix[5]arenes to assemble in a bilayer arrangement, Fig. 8. Each calixarene from the asymmetric unit forms uni-composite neighbouring bilayers. The calixarene packing within each uni-composite layer is similar and both layer types are formed through two CH···π and one π-stacking interaction. For one SO_3[5], the two CH···aromatic centroid and aromatic centroid···centroid distances are 2.65, 2.77 and 3.691 Å, respectively. For the other, respective CH···aromatic centroid and aromatic centroid···centroid distances are 2.99, 2.87 and 3.598 Å. In addition to all of the aforementioned interactions, the numerous disordered waters of crystallisation reside in the hydrophilic layer and are in positions consistent with hydrogen bonding with appropriate functional groups as expected.

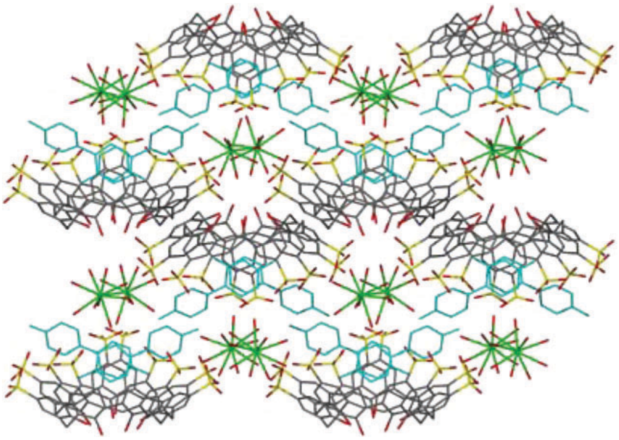


Fig. 8 The extended structure of complex **3** showing the bilayer arrangement of *p*-sulfonatocalix[5]arene and the DiPyNO dimerisation that spans the hydrophilic layer generated by the SO_3[5] packing. The DiPyNO molecules are shown in pale blue for clarity. All waters of crystallisation have been omitted and disordered europium aquo ligands are only shown in one position.

Although the guest is clearly too large to be completely inserted in a single SO_3[5] cavity without causing significant conformational distortion, the non-coordinative dimerisation in **3** was (to some extent) unexpected given that *p*-sulfonatocalix[6]arene (SO_3[6]) forms an interesting coordination polymer with Eu(III) and DiPyNO. In the latter complex, DiPyNO completely spans the hydrophilic layer and coordinates to two SO_3[6] sulfonate bound europium centres to form a zigzag coordination polymer chain.[7] Furthermore, this guest has also been used in the formation of a complex europium coordination polymer with *p*-sulfonatocalix[8]arene.[8]

Critical analysis of the organisation of *p*-sulfonatocalix[5]arene anions

Analysis of the packing of *p*-sulfonatocalix[5]arene in all structures reported to date (18),[9] and those reported here (3), shows that the molecule often packs in essentially identical bi-layer structures (16 of total 21) with variations in the properties of the hydrophilic layers (Fig. 9).[5] Indeed, the bilayer is remarkably versatile, persisting with or without organic moieties in the cavity. In this typical arrangement, alternating 'up–down' chains of SO_3[5] pack very efficiently through a limited number of crystallographically unique CH···π and π-stacking interactions, some of which are shown in Fig. 9. Although the number of interactions can vary slightly in each structure, as can the length of the contacts, slight changes in the cone angles do not cause deviation from this highly favourable structure. Space filling of the bilayer shows tight packing with no scope for communication (through molecular transport) from one side of the bilayer to the other. This is in contrast to the capabilities of SO_3[4] and is particularly noteworthy in assembling bilayers onto surfaces to form impervious films. This has been recently highlighted in the context of SO_3[5] stabilising nanoparticles of β-carotene, but not so the smaller and larger analogous calixarenes.[10] In this case the calix[5]arenes are devoid of included organic molecules. The enhanced stability is with respect to both protecting particles from extraction of the carotenoid by organic solvents, and also in their stability towards reaction with osmium tetroxide vapours. The present bilayer arrangements are different in the nature of the C–H···π interactions (now involving aromatic H-atoms, compared to methylene H-atoms in other structures. Moreover, the presence of organic molecules serves as a refined model for a bilayer arrangement of calixarenes locking together forming stable nano-particles. In the present examples the presence of organics in the calixarene cavities may model the interplay of organic molecules in a nanoparticle with the inner wall of the calixarene bilayer.

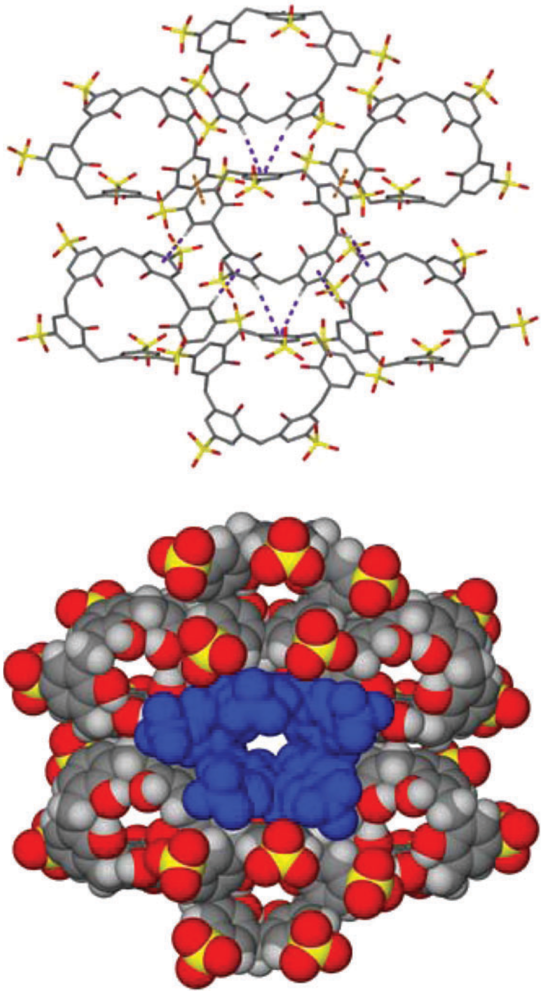


Fig. 9 Stick (top) and space filling (bottom) representations of the favourable packing motif formed by 'up–down' alternating chains of *p*-sulfonatocalix[5]arene. (a) Some of the typically observed π-stacking and CH···π interactions are shown as dashed orange and purple lines respectively. (b) Space-filling representation emphasises the 'good fit' of six neighbouring SO_3[5] molecules around one central host (blue) within the favourable bilayer motif.

While the calixarene has five-fold symmetry in the symmetrical cone conformation, and the packing of such symmetrical molecules in 2D has limitations, the alternative arrangement of the five-membered rings and distortion of the cone conformation nevertheless results in very efficient packing.

For the remaining five structures containing $SO_3[5]$, deviation from the common bilayer is associated with a significant departure from the cone conformation of the molecule (a feature prevalent in all the above bilayer structures),[5g] the presence of protonated organic cations that span or insert within atypical $SO_3[5]$ layers,[5e,g,i] or co-crystallised sulfuric acid.[5c] Co-crystallisation with charged organic species was covered in the Introduction. Distortion of the calixarene cavity by co-crystallisation with additional species causes the expected disruption to the common bilayer. In all cases of bilayer deviation, these interactions must therefore be significant in order to disturb the seemingly favourable bilayer packing motif.

Experimental

Synthesis of the complex $[(Eu(H_2O)_6(2\text{-picoline-}N\text{-oxide}))(p\text{-sulfonatocalix-[5]arene})(Na_2(H_2O)_9)]\cdot 2.75H_2O$, 1

Pentasodium *p*-sulfonatocalix[5]arene (10 mg, 10 μmol), 2-picoline *N*-oxide (3 mg, 30 μmol) and europium(III) nitrate hexahydrate (5 mg, 10 μmol) were dissolved in distilled water (2 cm^3). Upon slow evaporation, a small number of very small crystals that were suitable for synchrotron diffraction studies formed. Given the fragility of the crystals and small quantity grown, it was not possible to harvest an adequate amount for manipulation, yield calculation and further IR analysis.

Synthesis of the complex $[((4\text{-picoline }N\text{-oxide})\subset(p\text{-sulfonatocalix[5]arene}))_2 + 3H^+)(Na(H_2O)_3)][(Eu(H_2O)_9)_2]\cdot 16.5\ H_2O$, 2.

Pentasodium *p*-sulfonatocalix[5]arene (10 mg, 10 μmol), 4-picoline *N*-oxide (3 mg, 30 μmol) and europium(III) nitrate hexahydrate (5 mg, 10 μmol) were dissolved in distilled water (2 cm^3). Upon slow evaporation, crystals that were suitable for X-ray diffraction studies formed. Yield 8 mg, 51%. IR (solid phase, ν/cm^{-1}): 3365s, 2926s, 1608m, 1583m, 1519m, 1472m, 1336s, 1160s, 1107s, 1043s. This analysis confirms the presence of groups indicative of molecular components.

Synthesis of the complex $[((4,4'\text{-dipyridine }N,N'\text{-dioxide})\subset(p\text{-sulfonatocalix[5]-arene}))_2 + 4H^+][(Eu(H_2O)_9)_2]\cdot 17H_2O$, 3.

Pentasodium *p*-sulfonatocalix[5]arene (10 mg, 10 μmol), 4,4′-dipyridine *N*,*N*′-dioxide (6 mg, 30 μmol) and europium(III) nitrate hexahydrate (5 mg, 10 μmol) were dissolved in distilled water (2 cm^3). Upon slow evaporation, crystals that were suitable for X-ray diffraction studies formed. Yield 7 mg, 43%. IR (solid phase disc, ν/cm^{-1}): 3373s, 2879s, 1698m, 1610m, 1588m, 1514m, 1470m, 1338s, 1273m, 1162s, 1102s, 1042s, 1034s. This analysis confirms the presence of groups indicative of molecular components.

Crystallography

X-Ray data for complex **1** were collected using synchrotron radiation (wavelength λ = 0.69030 Å) and a Bruker 1000 SMART diffractometer. Data for complexes **2** and **3** were collected using a Kappa CCD diffractometer using Mo-Kα radiation (wavelength λ = 0.71073 Å). Due to the solvent dependent nature of the crystals, microanalyses were not performed.

Crystal data for 1. $C_{41}H_{65.5}N_1O_{37.75}S_5EuNa_2$, M = 1534.68, orthorhombic, space group $P2_12_12_1$, a = 11.3889(10), b = 19.1696(17), c = 29.359(3) Å, U = 6409.8(10) Å^3, μ = 1.590 mm^{-1}, T = 123 K, Z = 4, Final GOF = 1.031, R_1 = 0.0542, 43343 reflections measured, 15 887 unique (R_{int} = 0.0429) which were used in all calculations. The final $wR(F^2)$ was 0.1521 (all data). Flack parameter = 0.581(10). A number of restraints were applied to disordered groups.

Crystal data for 2. $C_{41}H_{79.5}N_1O_{41.25}S_5EuNa$, M = 1554.78, orthorhombic, space group $Pbcn$, a = 19.1391(3), b = 21.8802(3), c = 29.5140(5) Å, U = 12359.5(3) Å^3, μ = 1.671 mm^{-1}, T = 150 K, Z = 8, Final GOF = 1.038, R_1 = 0.0686, 47 652 reflections measured, 13 417 unique (R_{int} = 0.0978) which were used in all calculations. The final $wR(F^2)$ was 0.2144 (all data).

Crystal data for 3. $C_{90}H_{120}N_2O_{80}S_{10}Eu_2Na$, M = 3157.39, monoclinic, space group $P2_1/c$, a = 30.0333(4), b = 19.4301(3), c = 21.3461(7) Å, β = 92.9400(10)°, U = 12440.1(5) Å^3, μ = 1.686 mm^{-1}, T = 150 K, Z = 4, Final GOF = 1.169, R_1 = 0.1115, 77243 reflections measured, 15039 unique (R_{int} = 0.0998) which were used in all calculations. The final $wR(F^2)$ was 0.2776 (all data).

Conclusions

In examining europium complexes of *p*-sulfonatocalix[5]arene in the presence of pyridine *N*-oxide based ligands, the versatility of the host nature of the calixarene as part of a common bilayer motif has been highlighted. The study builds upon work previously reported by Atwood and co-workers[5a,b] and Makha *et al.*,[5h] and examines the effect of varying the *N*-oxide guest properties. Of the picoline *N*-oxides, only 2- and 4-PicNO were found to be incorporated in the $SO_3[5]$ cavity, and single crystals could not be grown when 3-PicNO was incorporated as a potential guest/ligand. The presence of the larger DiPyNO guest resulted in the formation of a dimeric arrangement of these molecules incorporated in the otherwise hydrophilic layer *via* a number of intermolecular interactions, as an expanded bilayer. Interestingly, this dipyridine dioxide has proved useful in forming coordination polymers with $SO_3[6]$ and $SO_3[8]$ as europium complexes,[7,8] but this is not the case in the present study where it prefers to be non-coordinating under these conditions. Work continues on the formation of supramolecular architectures with $SO_3[5]$ focusing on determining the requirements to overcome the favourable alternating chain bilayer arrangement with an ultimate goal of assembling large nano-metre scaled spheroidal arrays (among other things) as is possible for $SO_3[4]$.

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