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Hydrogen-bonded arrays of a ytterbium(III) *p*-sulfonatocalix[6]arene complex

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A novel *p*-sulfonatocalix[6]arene/ytterbium(III) pyridine *N*-oxide inclusion complex has been structurally authenticated by X-ray diffraction studies and shows the self-assembly of the large calixarene tectons into extended sheets through intricate hydrogen bonding.

In recent years, the supramolecular host–guest chemistry of water-soluble calixarenes, including that of *p*-sulfonatocalix[*n*]arenes, in both solution and the solid state, has received considerable attention.[1–11] This is in part due to their ability to interact in a variety of ways with a number of organic or inorganic species to generate interesting and often spectacular new complexes and/or extended structures.

In particular, the readily accessible *p*-sulfonatocalix[4]arene has been shown to be particularly versatile in its ability to assemble complex supramolecular architectures around many different guests of varied charge, in the presence of suitable counterions.[12–17] This versatility extends to inclusion of water molecules deep within the cavity and accommodation of globular like guests such as diprotonated [2.2.2]cryptand.[18,19] Whilst this area of supramolecular chemistry is well documented, that of the higher charged and more fluxional *p*-sulfonatocalix[6]arene remains in its infancy. This is presumably related to the formidable challenge of gaining control over the conformation of such a flexible molecule.[20–23] To date, the handful of reported structures determined based on this calixarene show either an '*up–down*' double partial cone conformation of the calixarene or an '*up–up*' double cone conformation. Despite the ability to form multiple guest inclusion compounds with 18-crown-6, until now, there have been no reported examples of *p*-sulfonatocalix[6]arene associating with a metal complex through both coordinating a sulfonate group and binding to a ligand within the molecular cavity. The current study shows that a new host–guest assembly is indeed accessible and demonstrates the structural versatility of the calixarene thus showing promise for formation of more complex supramolecular architectures.

Pyridine *N*-oxide in the presence of *p*-sulfonatocalix[4]arene and a lanthanide metal forms remarkable nano-spheroidal and tubular arrays.[24] Similar chemistry with the larger and more synthetically challenging cone shaped calix[5]arene analogue generates capsule like arrangements, but larger supramolecular arrays have not yet been formed with this tecton.[25] The present contribution reports the formation of a *p*-sulfonatocalix[6]arene/pyridine *N*-oxide/ytterbium(III) complex, **1**, with the calixarene in the '*up–down*' conformation and demonstrates the potential for such species to assemble multifaceted supramolecular arrays in a manner reminiscent to that for the smaller calix[4]arene analogue.

Single-crystal X-ray diffraction studies reveal the asymmetric unit of the complex to be composed of two half calixarene molecules, two ytterbium centres that are bound to sulfonate groups of the calixarenes, three pyridine *N*-oxide molecules that are bound to the lanthanide metal centres, two free molecules of pyridine *N*-oxide (one of which is disordered over two positions) and a total of nine solvent water molecules. Both metal centres are eight coordinate and have distorted square antiprismatic geometry. For clarity, each of the calixarene moieties shall initially be discussed individually as they self-assemble in a markedly different manner, with later discussion highlighting the packing of complex self-assembled sheets.

Each of the calixarenes resides around a centre of inversion with, the first, **A**, bound by two ytterbium centres through opposing sulfonate groups within the calixarene. In addition, each of these lanthanide ions has six aquo ligands and is coordinated by the oxygen atom of one pyridine *N*-oxide molecule which resides in the partial cone generated by the '*up–down*' conformation of the calixarene and displays a CH···π interaction with the CH···π centroid distance of 3.091 Å.

This supramolecular tecton self-assembles into a sheet arrangement through several intra- and inter-molecular interactions. Primarily, these consist of hydrogen bonding from aquo ligands of the lanthanide centre to sulfonate groups of adjacent tectons at YbO···OS distances ranging from 2.733 to 2.882 Å. In addition, hydrogen bonding is evident from a hydroxyl group at the base of the calixarene to a sulfonate group of the nearest adjacent calixarene within the sheet with the O···OS distance at 2.783 Å, Fig. 2.

The second supramolecular tecton, **B**, consists of one calixarene, again with two lanthanide metal centres coordinated to opposing sulfonate groups within the calixarene, but with two pyridine *N*-oxide ligands rather than one, as found in **A**, resulting in five aquo ligands around the metal centre. Of the two pyridine *N*-oxide molecules tethered to each lanthanide, one resides in one partial cone of the calixarene whilst the other resides in a partial cone of the nearest identical tecton (Figs. 3 and 4).

The assembly of tecton **B** shows intramolecular CH···π interactions between an aryl hydrogen of the pyridine *N*-oxide in the partial cone and one phenyl ring of the calixarene at a distance of 2.742 Å. In addition, the same pyridine *N*-oxide π-stacks with another phenyl ring of the same partial cone with an aryl centroid···centroid distance at 3.748 Å. As mentioned above, self-assembly of this complimentary tecton into a sheet arrangement results in the second pyridine *N*-oxide residing in

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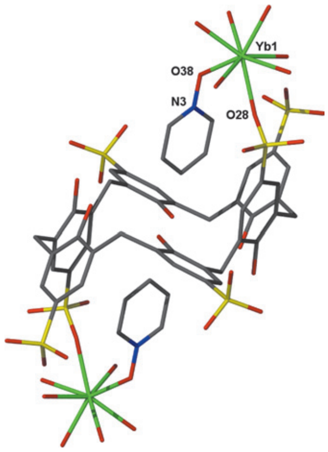


Fig. 1 Sulfonated calixarene tecton **A** in **1**, showing lanthanide coordination by both sulfonate groups and pyridine *N*-oxide molecules.

the nearest partial cone of an adjacent tecton with three primary intermolecular interactions. There are two hydrogen bonds from water ligands of the penta-aquo ytterbium to one sulfonate group of the nearest neighbouring calixarene (YbO···OS distances 2.707 and 2.829 Å); and CH···π bonding from an aryl hydrogen of the second pyridine *N*-oxide to the nearest phenyl ring of the adjacent calixarene (CH···π distance 2.659 Å).

Both supramolecular tectons **A** and **B** form sheet arrangements through complex hydrogen bonding and CH···π interaction regimes. Despite the presence of excess pyridine *N*-oxide, the ytterbium centres in **A** only coordinate to one of the potential guest molecules. Clearly the resulting supramolecular architecture demands mono-coordination and the excess pyridine *N*-oxide molecules reside in and around the partial cones of **A** forming, through CH···π, π–π, and hydrogen bonding interactions, a link between alternating sheets of **A** and **B**. Only one hydrogen bond from an aquo ligand of a lanthanide centre from sheet **B** to a sulfonate group of sheet **A** is evident (YbO···OS distance 2.688 Å). The numerous solvent water molecules reside around the hydrophilic regions of the structure and form an intricate hydrogen bonding regime between adjacent dissimilar sheets.

p-Sulfonatocalix[4]arene assembles, as mentioned earlier, into spheroidal and tubular arrays through formation of a crucial C-shaped dimer by coordination of a lanthanide to sulfonate groups of calixarenes and to pyridine *N*-oxide molecules in each of the calixarene cavities (**2**).[24] The present structure, in particular that of tecton **B**, shows potential for construction of extended supramolecular arrays by possible formation of a dimer-like arrangement which can be envisaged forming with the calixarene in the double cone conformation in a double capsule motif similar to that formed in the presence of 18-crown-6 (**2**).[23] Such an architecture would perhaps mimic the C-shaped dimer and may introduce the curvature necessary to overcome the favourable bi-layer arrangements seen for *p*-sulfonatocalix[4,5,6]arenes in the presence of a suitable guest molecule to build up larger supramolecular arrays.[5,23,25]

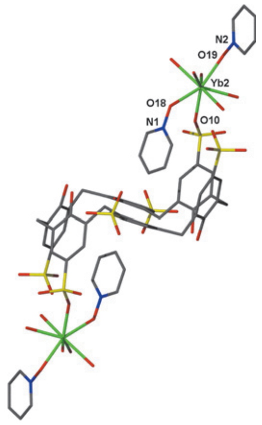
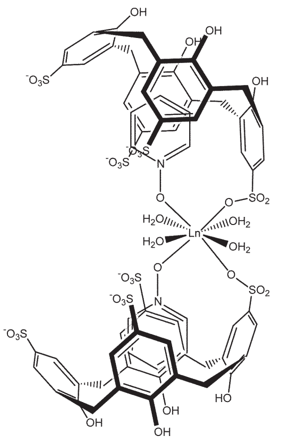


Fig. 3 Calixarene tecton **B** in **1** showing coordination of each lanthanide by a sulfonate group and two pyridine *N*-oxide molecules.



(2)

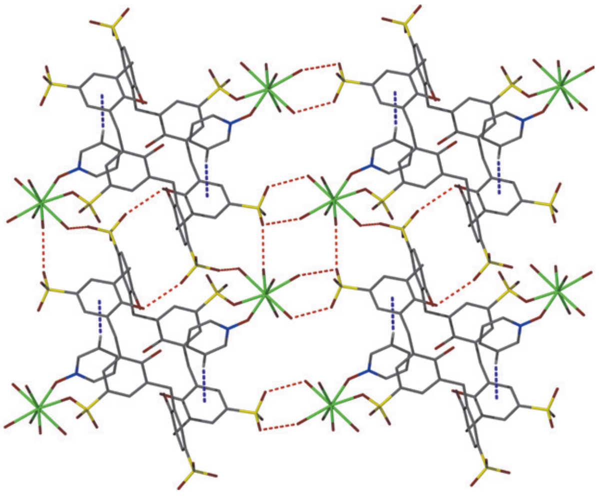


Fig. 2 Extended sheet arrangement of **A** showing both intramolecular (CH···π, blue dotted lines) and intermolecular (YbO···OS, dotted red lines) interactions.

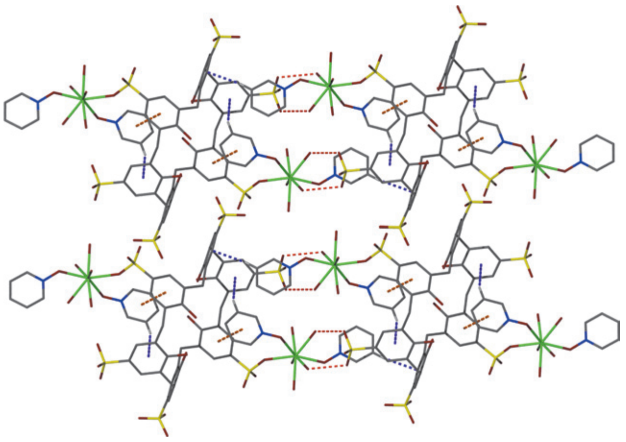


Fig. 4 Extended sheet arrangement in **B** showing intra-molecular π–π and CH···π interactions (orange and blue dotted lines, respectively) and intermolecular hydrogen bonding and CH···π interactions (red and purple dotted lines, respectively).

In summary, we have reported the formation of a novel *p*-sulfonatocalix[6]arene inclusion complex, **1**, which assembles into complex sheet-like arrangements. Such supramolecular tectons show potential for formation of larger and more complex tectons which would be a pre-requisite for formation of nanometre scale supramolecular architectures. Clearly for large supramolecular arrays to form, the challenge of overcoming the affinity for the calixarene to form a bilayer type arrangement, as for *p*-sulfonatocalix[4,5]arenes must be overcome. For this to be achieved, pyridine *N*-oxide or larger variances thereof (in the presence of lanthanide ions) may prove useful in achieving this goal.

Experimental

Synthesis of 1, [Yb(H_2O)$_6$(pyridine *N*-oxide)(*p*-sulfonatocalix[6]arene)$_{0.5}$][Yb(H_2O)$_5$(pyridine *N*-oxide)$_2$(*p*-sulfonatocalix[6]arene)$_{0.5}$] · 9H_2O · 2pyridine *N*-oxide

Sodium *p*-sulfonatocalix[6]arene (30 mg, 23 μmol), pyridine *N*-oxide (5 mg, 53 μmol), and ytterbium(III) nitrate pentahydrate (21 mg, 46 μmol) were dissolved in distilled water (1.5 cm^{-3}). Over three days, large colourless plates formed which were suitable for X-ray diffraction studies. Yield 19 mg (dried), 37%. *Crystal data.* $C_{67}H_{95}N_5O_{49}S_6Yb_2$, $M = 2292.92$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.487(4)$, $b = 17.799(5)$, $c = 20.803(6)$ Å, $\alpha = 113.601(4)$, $\beta = 91.155(5)$, $\gamma = 91.297(5)°$, $U = 4234(2)$ Å^3, $\mu = 1.799$ mm^{-1}, $T = 173$ K, $Z = 2$, Mo-Kα radiation ($\lambda = 0.71073$ Å), Final GOF = 1.028, $R_1 = 0.0440$, 37 445 reflections measured, 18 422 unique ($R_{int} = 0.0434$) which were used in all calculations. The final $wR(F^2)$ was 0.1089 (all data). All hydrogen atoms were fixed at geometrically calculated positions with the exception of those of the hydroxy groups of the calixarenes which were located and refined. The crystals are susceptible to solvent loss upon removal from the mother-liquor thus microanalyses were not performed.

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See http://www.rsc.org/suppdata/nj/b3/b311288h/ for crystallographic data in CIF or other electronic format.

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