Lanthanum(III) capture of 18-crown-6 in the cavity of *p*-sulfonatocalix[4]arene

Alexander Drljaca,[a] Michaele J. Hardie,[a] Julian A. Johnson,[b] Colin L. Raston[a] and Helen R. Webb[a]

[a] *Department of Chemistry, Monash University, Clayton, Melbourne, Victoria, 3168, Australia. E-mail: c.raston@sci.monash.edu.au*

[b] *CSIRO Minerals, Clayton, Melbourne, Victoria, 3168, Australia*

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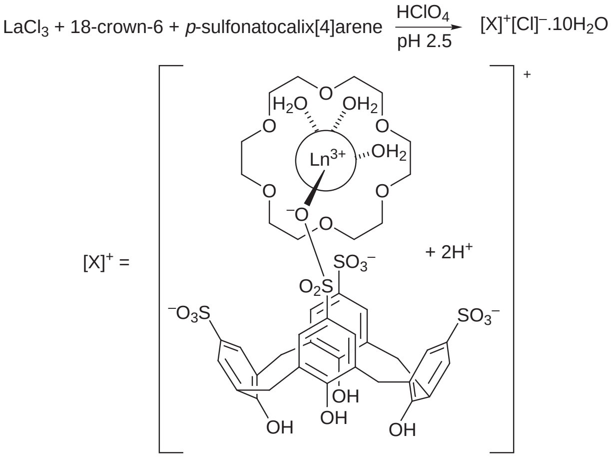
Aqueous solutions of sodium *p*-sulfonatocalix[4]arene, 18-crown-6 and lanthanum(III) trichloride at pH 2.5 afford the 'ferris wheel' type supercation: $[\{Ln^{3+}\subset(18\text{-crown-}6)(OH_2)_3\}\cap\{(p\text{-sulfonatocalix}[4]\text{arene}^{4-} + 2H^+)\}]^+$ isolated as the chloride with numerous waters of crystallisation.

The coordination selectivity exhibited by calixarenes toward rare earth cations has been widely investigated because of its implications for separation science.[1] Of particular interest are the interactions with the highly charged and water-soluble sodium *p*-sulfonatocalixarenes.[2–5] These show remarkable inclusion properties for both ionic and neutral molecules (especially the smaller sized calix[4 and 5]arenes).[5–8] As crown ethers are good lanthanide complexants[9] it was anticipated that they would also be useful supramolecular synthons. Thus the species formed when combining a rare earth cation, crown ether, and sodium *p*-sulfonatocalixarene was explored. Whilst these systems may ultimately prove important for the separation of lanthanides, the assembly of such multicomponent arrays is of interest in itself.

Herein we report the results of the interaction between the cone-shaped sodium *p*-sulfonatocalix[4}arene, 18-crown-6, and lanthanum(III) chloride in aqueous media. The interplay between the two macrocycles has proved effective in stabilising, and in some cases selectively crystallising, a broad range of highly charged polynuclear aqua cations. Specifically, $[Cr_2(OH)_2(H_2O)_8]^{4+}$, $[Cr_3(OH)_4(H_2O)_{10}]^{5+}$ and $[Cr_4(OH)_6(H_2O)_{12}]^{6+}$, and $[Al_3O_4(OH)_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ have been identified.[10] The main counterions are globular-like ionic capsules or superanions $[\{Na^+\subset(18\text{-crown-}6)(OH_2)_2\}\subset\{(p\text{-sulfonatocalix}[4]\text{arene}^{4-})_2\}]^{7-}$ (Θ^{7-}), which vary their crown ether conformation and degree of protonation with the polynuclear cation. A variety of cohesive forces are present in these solid-state ionic capsules, including hydrogen bonding, electrostatic, π-stacking, and van der Waals interactions. Additionally, the crown ether and the calixarene exhibit a complementarity of curvature, albeit after some geometric pre-organisational requirements. In the present study a new type of assembly results whereby the crown ether (containing a lanthanide and three water molecules) resides in one calixarene, as a perched structure, like a 'ferris wheel' with the rotation axis about a metal to O-centre of a sulfonate group. This supercation has a single positive charge and hence two of the sulfonate groups are protonated, as $[\{Ln^{3+}\subset(18\text{-crown-}6)(OH_2)_3\}\cap\{(p\text{-sulfonatocalix}[4]\text{arene}^{4-} + 2H^+)\}]^+$ ($[X]^+$). It is noteworthy that the formation of an ionic capsule, Θ^{7-} or the partially protonated forms, is precluded in the present study by (i) the lanthanide ions effectively competing with sodium to form the central ionic 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 the ionic capsule (at least for the pH of the solutions studied).

The complex $[X]^+[Cl]^-.10H_2O$ crystallised from an aqueous solution of sodium *p*-sulfonatocalix[4]arene,[11,12] 18-crown-6, and lanthanum trichloride hexahydrate[12] at pH 2.5 (which was adjusted using perchloric acid) (Scheme 1).† Using small-scale reactions varying in 0.5 pH units, it was established that crystallisation occurred over a narrow pH range (2.5–3). The proposed composition of this structure is reinforced by electron microprobe results which show that lanthanum and chloride are present, and in an equivalent stoichiometric ratio.



Scheme 1

Crystals suitable for X-ray diffraction‡ deposited over several days. They crystallised in the space group $P3_1$ with the supercation $[X]^+$, the counter ion, and ten water molecules in the asymmetric unit. Results are reported in Fig. 1 and 2. As can be

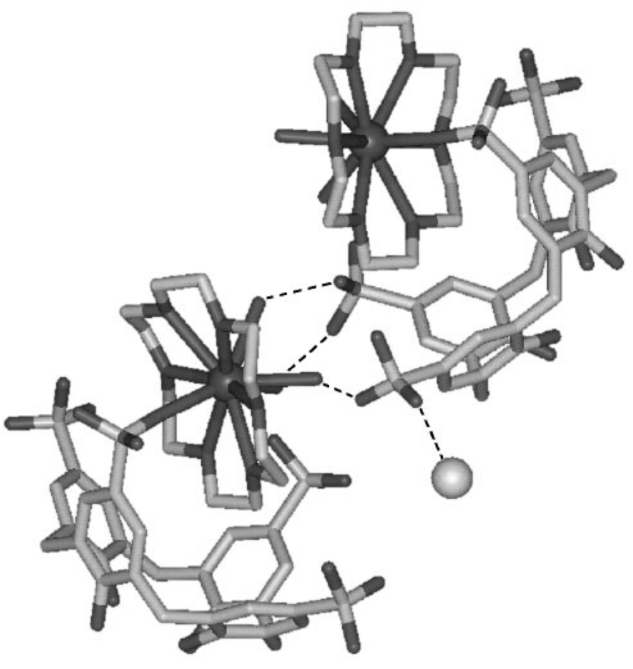


Fig. 1 Projection of two supercations $[X]^+$ in **1** showing associations between sulfonate groups and coordinated waters and sulfonate groups and chloride ions; hydrogen atoms have been removed for clarity and implied hydrogen-bonding interactions are represented by dashed lines.

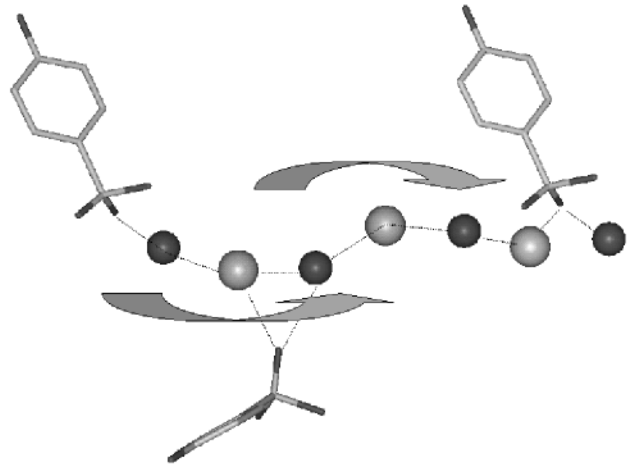


Fig. 2 Hydrogen bonded helical array of supercations, chlorides and waters of crystallisation. Only one phenyl group of each supercation is shown for clarity.

seen, the lanthanide is bound symmetrically by the six crown ether oxygen atoms [La–O = 2.654(5) to 2.733(5) Å] (Fig. 1). Assisted by the complementarity of curvature, this moiety resides in the cavity of the calixarene *via* a La–sulfonate linkage [La–O = 2.418(5) Å] and van der Waals interactions. The metal centre also has three water molecules attached at 2.557(5), 2.558(5) and 2.542(5) Å, on the opposite side to the sulfonate group relative to the plane of the crown ether, and these hydrogen bond to a single adjacent supercation (Fig. 1, O···O distances = 2.696, 2.799, 2.916 Å). The coordination environment around the lanthanide is unexceptional.[13]

Complementarity of curvature of the crown ether with that of the calixarene is achieved by the splaying of two opposite phenol groups (with torsion angles between the opposite phenol groups of 140.5 and 79.9°). In comparison the analogous angles in the ionic capsules Θ^{7-} range from 93–100°, and 46–59° respectively.[10] Due to the linkage between the metal and the calixarene, in the present structure the plane of the crown ether is rotated towards the cavity of the calixarene by 51.6° with respect to the vector of symmetrical approach. Within the crystal lattice an infinite helical array of the supercations, chloride counterions and water is formed through hydrogen bonding associations (Fig. 2).

In conclusion, using a combinatorial approach we have gained access to a novel supercation comprised of four components. By varying the pH in a systematic way, there is scope for constructing a wide range of structural types for such multicomponent systems.

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Notes and references

† *Synthesis*: Using an excess of the metal salt, 13 mg of $LaCl_3.6H_2O$ (3.8×10^{-2} mmol), 15.5 mg of *p*-sulfonatocalix[4]arene (1.89×10^{-2} mmol) and 5 mg of 18-crown-6 (1.89×10^{-2} mmol) were dissolved in *ca.* 1 ml of water and the pH adjusted to 2.5 using a few drops of concentrated perchloric acid (65%). A yield of 13% was obtained (*ca.* 3 mg). Electron microprobe: lanthanum and chlorine are present in an equal ratio.

‡ *Crystal data* for **1**: $C_{40}H_{72}ClLaO_{35}S_4$, $M_r = 1415.59$; trigonal (hexagonal setting), $P3_1$, $a = b = 20.1097(3)$, $c = 13.2080(3)$ Å, $V = 4625.7$ Å^3, $Z = 3$, $\mu = 0.963$ mm^{-1} (no correction), 25935 data collected, 12878 unique ($R_{int} = 0.044$), number of parameters = 729, final GoF = 1.038, $R_1 = 0.0591$ [on 11332 observed data with $I > 2\sigma(I)$], $wR_2 = 0.1720$, (all data). Data were collected at 123(1) K on an Enraf-Nonius KappaCCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS-97) and refined using full-matrix least-squares on F^2 (SHELXL-97). All nonhydrogen atoms were refined anisotropically except for two disordered water positions that were refined isotropically, and all C-H hydrogens were fixed at geometrically estimated positions. Interestingly, a crystal with a corresponding unit cell [trigonal (hexagonal setting), $P3_1$, $a = b = 20.0838(3)$, $c = 13.1953(2)$ Å] was also isolated from a solution prepared in an analogous way using lanthanum *tris*(trifluoromethanesulfonate) nonahydrate. Perchloric acid was not required to acidify the solution to *ca.* pH 2.5. Electron microprobe results indicate that lanthanum and fluorine are present, but not chlorine. CCDC 182/1251. See http://www.rsc.org/suppdata/cc/1999/1135/ for crystallographic data in .cif format.

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