

Capture of di-protonated [2.2.2]cryptand in the cavity of two *p*-sulfonated calixarenes as part of 2-D bi-layer lanthanide coordination polymers

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Received (in Columbia, MO, USA) 8th August 2002, Accepted 23rd August 2002

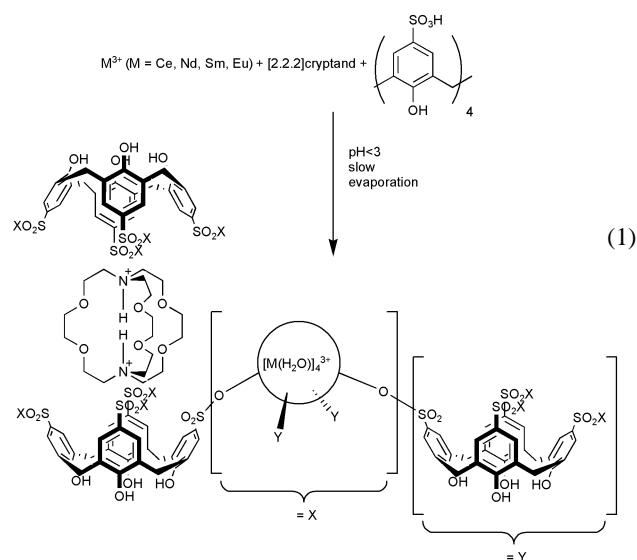
First published as an Advance Article on the web 11th September 2002

Treating *p*-sulfonatocalix[4]arene with lanthanide ions, Ln³⁺ (Ln = Ce, Nd, Sm and Eu), in the presence of [2.2.2]cryptand results in a 2-D bi-layer coordination polymer with axially elongated diprotonated cryptand in the cavity of two *p*-sulfonatocalix[4]arenes.

Water soluble calix[*n*]arenes have been widely investigated, and are becoming increasingly important tectons in the field of supramolecular chemistry and crystal engineering, showing interesting inclusion properties and a wide range of metal coordination complexes both in solution and in the solid state.^{1–9} In this context, *p*-sulfonatocalix[4]arene is a highly versatile tecton, assembling in several different structural motifs which include ‘Russian dolls’ or ‘molecular capsules’, ‘ferris wheels’, hydrogen bonded polymers, and 2-D coordination polymers.^{1,10} Then there are the spectacular structures of Atwood *et al.*, where twelve of these calixarenes are in a spherical like arrangement with the cavities directed away from the centre of the sphere, or are arranged into nano-tubes with the cavities of the calixarenes directed outwards, each formed reproducibly, depending on the reaction conditions.¹¹ Both structures incorporate trivalent lanthanide ions and each calixarene has pyridine N-oxide in its cavity. All of the above structural types have the calixarenes in the cone conformation, with the exception of a 4,4′-bipyridinium salt of the calixarene where it is in the 1,3-alternate conformation.¹²

Continuous structures based on inclusion phenomena of metal complexes of [2.2.2]cryptand (cryptates) with *C*-methylcalix[4]resorcinarene,¹³ cyclotrimeratrylene (CTV)¹⁴ and Ni(TMTAA) [5,7,12,14-tetramethyldibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradecinenickel(*n*)],¹⁵ have recently been reported. Complete encapsulation of the cryptand and the corresponding K⁺, Sr²⁺ and Ba²⁺ cryptates by two upper rim modified hydrogen bonded calix[4]resorcinarene molecules has been established in solution.¹⁶ There has been no structural authentication of a ‘molecular capsule’ within which the bi-cyclic cryptand resides, either neutral or as cryptates, or protonated. In contrast there have been extensive studies on the monocyclic 18-crown-6 analogue, and also protonated cyclam.¹ Recently, we reported the structures of 2-D coordination polymers incorporating *p*-sulfonatocalix[4]arene and early trivalent lanthanide metal ions (Ce, Pr) in the absence of potential guest molecules,¹⁰ along with the formation of a hydrogen bonded polymer of *p*-sulfonatocalix[4]arene and late trivalent lanthanide metal ions (Gd, Tb, Tm) in the presence of [2.2.2]cryptand or indeed 1-aza-18-crown-6, but these are not incorporated in the structure. Herein we report the synthesis and structure of a cryptand inclusion complex, **1**, with the *p*-sulfonatocalix[4]arene for some early trivalent lanthanide metal ions (Ce, Nd, Sm, Eu), eqn. 1.† This was achieved following reaction optimisation techniques which we have previously used to good effect.¹⁷

The structure of **1**, M = Nd³⁺, was determined using single crystal diffraction data. Cell dimensions for crystals obtained for the other metals, eqn. 1, showed that they are all isostructural.† The extended structure determined for the neodymium analogue has a 2-D coordination polymer with the calixarenes packed into a bi-layer arrangement. However, the bi-layer itself is distinctly different to that reported previously



for complexes of *p*-sulfonatocalix[4]arene. Rather than having π -stacking from one calixarene to another within the bi-layer, the primary hydrophobic interplay is C–H \cdots aromatic ring involving the methylene groups of the calixarenes (C–H \cdots centroid 3.377 Å).¹⁸ This appears to be without precedent in calixarene bi-layer arrays. π -Stacking is a feature of the related complexes of *p*-sulfonatocalix[4]arene and 18-crown-6, whereas in the present structure, each cavity faces the cavity of another calixarene, both shrouding a di-protonated cryptand, in the form of ‘molecular capsules’, Fig. 1.† In the absence of large guest molecules, bi-layer structures based on 2-D lanthanide coordination polymers are distinctly different with each cavity of a calixarene facing the base of a calixarene from another bi-layer.¹⁰ The structure also possesses several disordered water molecules which reside in the hydrophilic layers generated by the sulfonate groups at the upper rims of the calixarenes.

To our knowledge, this is the first example of establishing encapsulation of [2.2.2]cryptand by a calix[4]arene in the solid state, albeit as the diprotonated form. Previous attempts to encapsulate cryptand using *p*-sulfonatocalix[4]arene were unsuccessful.¹⁰ This was ascribed to a shape mismatch of the globular like nature of the macrobicyclic compound relative to the calixarene (complexation in the present study is driven by a large excess of the lanthanide). In contrast, 18-crown-6 has complementary of size and shape with *p*-sulfonatocalix[4]arene but requires splaying apart of two opposite phenol rings within each calixarene.¹⁷ Close analysis of the structure of **1** shows that di-protonation of the cryptand results in elongation of its structure along the N \cdots N vector, and concomitant reduction in diameter normal to this vector. This then enhances complementarity of shape for binding of the calixarenes, at least where the N \cdots N vector of the cryptand is normal to the cavity of the calixarenes, which is the case.

In selectively forming a coordinated polymer, the layers arrange themselves in the bi-layer structure, as expected, to

optimise hydrophilic–hydrophilic and hydrophobic–hydrophobic interactions between the layers whilst at the same time accommodating the cryptand molecules within the cavities. The dihedral angle between the aromatic rings and the plane of the four phenolic oxygens is 130.1° which is much greater than that corresponding to the coordination polymer in the absence of cryptand (125.6°). This is consistent with the aromatic rings of the calixarenes being splayed to accommodate the cryptand yet whilst retaining their coordination interplay with the lanthanide metals. Indeed, when 18-crown-6 is incorporated, pinching of the calixarene to accommodate the curvature of the guest molecule is prevalent with typical dihedral angles of 108.8 and 135.1° .¹ This, coupled with the splaying effect for the encapsulation of cryptand, demonstrates the flexibility of *p*-sulfonatocalix[4]arene to act as a host molecule.

The above skewed arrangement of bi-layers incorporating C–H⋯aromatic ring interplay is in association with all the metal centres sitting directly above and below each other. Each metal centre is bound to four sulfonate groups from the four nearest neighbouring calixarenes and also possesses four ligated water molecules which point into the hydrophilic layers whilst also hydrogen bonding to an oxygen of the nearest sulfonate group, NdO–OS distance of 2.764 Å, Fig. 1 and 2.

It should be noted that the N⋯N distance in the present

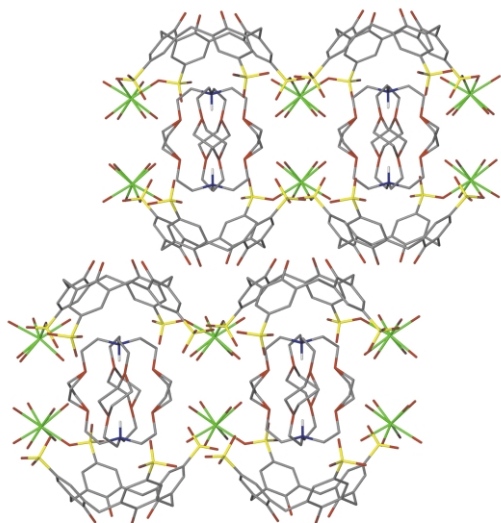


Fig. 1 Cross section of the structure of **1**, $M = \text{Nd}^{3+}$, showing the bi-layer arrangement and the encapsulation of cryptand (non-coordinated water molecules and hydrogens [with exception of NH] have been omitted for clarity).

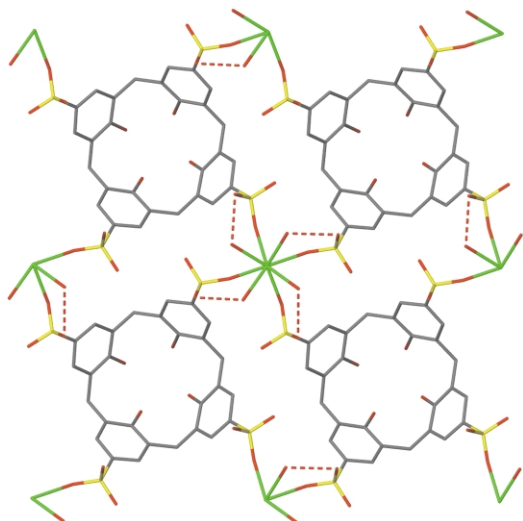


Fig. 2 Projection of the 2-D coordination polymer and associated hydrogen bonding between the ligated water molecules and SO_3 groups.

structure is 6.07 Å, close to the value of 6.33 Å previously reported by Atwood *et al.*,¹⁹ also for a di-protonated form of [2.2.2]cryptand but with the hydrogens on the nitrogen pointing away from the cavity, unlike in the present structure. Even though the cryptand is disordered, around a four fold symmetry axis, the protons, also on the four fold symmetry axis, are directed towards the core of the molecule (not located, but is consistent with the disorder model).

In conclusion, we have succeeded in encapsulating [[2.2.2]cryptand + 2H^+] by exploiting the formation of coordination polymers which incorporate *p*-sulfonatocalix[4]arene and lanthanide ions, at the same time establishing unexpected C–H⋯aromatic interplay within the bi-layers.

Notes and references

† *p*-Sulfonatocalix[4]arene was synthesised by literature methods.²⁰ X-Ray crystallographic studies were performed on a Nonius Kappa CCD instrument.

Synthesis of $(2\text{H}[2.2.2]\text{cryptand})^{2+} \subset (\textit{p}\text{-sulfonatocalix[4]arene})^{4-} \cdot 2(\text{M}(\text{H}_2\text{O})_4)^{3+}$, **1**: *p*-Sulfonatocalix[4]arene (10 mg, 13.4 μmol), [2.2.2]cryptand (10 mg, 26.5 μmol), and lanthanide(m)chloride (> 10 molar equiv.) were dissolved in distilled water (1 cm³). Over two days, colourless plates formed which were suitable for X-ray diffraction studies. CCDC 191753. See <http://www.rsc.org/suppdata/cc/b2/b207922b/> for crystallographic files in CIF or other electronic format. *Crystal data*. $\text{C}_{9.25}\text{H}_{10.75}\text{N}_{0.25}\text{Nd}_{0.25}\text{O}_{6.38}\text{S}_1$, $M = 295.55$, tetragonal, $a = 11.9026(17)$, $c = 32.876(7)$ Å, $U = 4657.6(13)$ Å³, $\mu = 1.686$ mm⁻¹, $T = 150$ K, space group $P4/mnc$ (no. 126), $Z = 16$, Mo-K α radiation ($\lambda = 0.71073$ Å), Final GOF = 1.186, $R_1 = 0.0686$, 17329 reflections measured, 2701 unique ($R_{\text{int}} = 0.1563$) which were used in all calculations. The final $wR(F^2)$ was 0.2046 (all data). Both solvated water molecules in the asymmetric unit were refined isotropically with partial occupancy (0.5), one residing on a special position. Thermal parameters of the non-hydrogen atoms in the cryptand were fixed.

For Ce^{3+} , unit cell measurements were $a = 11.9527(3)$, $b = 11.9558(6)$, $c = 32.9301(8)$ Å, $\alpha = 90.004$, $\beta = 90.022$, $\gamma = 90.008^\circ$. For Sm^{3+} , unit cell measurements were $a = 11.8453(2)$, $b = 11.8625(3)$, $c = 32.4934(9)$ Å, $\alpha = 90.047$, $\beta = 90.104$, $\gamma = 90.048^\circ$. For Eu^{3+} , unit cell measurements were $a = 11.9291(5)$, $b = 11.9464(3)$, $c = 32.6602(7)$ Å, $\alpha = 89.961$, $\beta = 89.931$, $\gamma = 90.061^\circ$.

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