Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Structure of a Discrete 8:6 La(Iii): P-Sulfonatocalix[4]Arene Complex

Yaël Israeli[ab]; Glenn P. A. Yap[a]; Christian Detellier[a]
[a] Ottawa-Carleton Chemistry Institute, University of Ottawa Campus, Ottawa, Ontario, Canada [b] Thermodynamique des Solutions et des Polymères, Université Blaise Pascal, Aubière, France

To cite this Article Israeli, Yaël , Yap, Glenn P. A. and Detellier, Christian(2001) 'Structure of a Discrete 8:6 La(Iii): P-Sulfonatocalix[4]Arene Complex', Supramolecular Chemistry, 12: 4, 457 — 464

To link to this Article: DOI: 10.1080/10610270108027478

URL: http://dx.doi.org/10.1080/10610270108027478

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 457-464
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Harwood Academic Publishers imprint,
part of the Gordon and Breach Publishing Group.
Printed in Malaysia

Structure of a Discrete 8:6 La(Iii): P-Sulfonatocalix[4]Arene Complex

YAËL ISRAELI[a][b], GLENN P. A. YAP[a] and CHRISTIAN DETELLIER[a]*

[a]*Ottawa-Carleton Chemistry Institute, University of Ottawa Campus, Ottawa, Ontario K1N 6N5, Canada and* [b]*Thermodynamique des Solutions et des Polymères, Université Blaise Pascal, 24 avenue des Landais, 63170 Aubière, France*

(Received August 09, 2000)

The crystal structure of a complex formed between La(III) and p-sulfonatocalix[4]arene is reported. The complex cristallizes in the monoclinic space group $P2_1/n$, a = 15.091(1), b = 28.550(3), c = 30.167(3) Å, β = 90.008(2)°, V = 12997(2) Å^3, $\rho_{calc.}$ (g cm^{-3}) = 1.792, Z = 2. Refinement led to R_1 value of 0.0961 for 13930 unique reflections. It forms discrete units with 8 La(III) cations coordinated by 6 calixarene ligands. The calixarenes are organized in an up-down configuration, bridged by La(III), forming layers of 3 repeating calixarene units and channels along the a axis. The units are linked by hydrogen-bonds.

Keywords: Calixarenes, Lanthanum, Complexes, La(III) coordination, water soluble calixarene

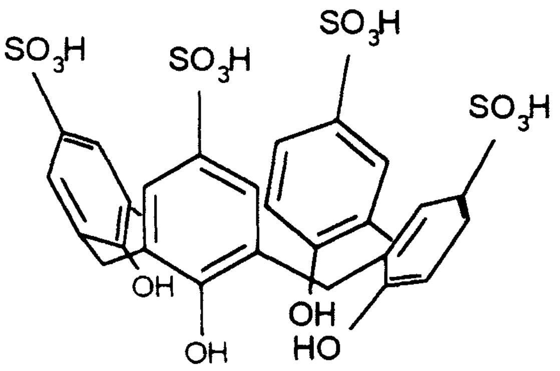
INTRODUCTION

The calixarenes, macrocyclic molecules composed of phenolic groups linked by methylenic bridges, contain an hydrophobic cavity suitable for host-guest interactions with organic or inorganic ions and molecules. These compounds are widely studied [1,2] because of their relatively facile syntheses, ease of cavity modifications to satisfy guest molecule requirements and ease of functionalization [2]. In an effort to understand the factors and mechanisms responsible for the observed selectivity of the host-guest complexation in solution, our group is engaged in kinetic and mechanistic studies of complexation and dissociation processes in solution [3–7]. Whereas the mechanistic studies have almost entirely focussed so far on non-aqueous solvents, it would be very valuable to obtain information on these processes in aqueous solutions. Most calixarene derivatives are not water soluble. However, the substitution at the para position to the phenolic groups by sulfonate groups (Scheme 1) affords an aqueous solubility of at least 0.1 mol dm^{-3}[8]. The structure of crystalline complexes of La(III) with p-sulfonatocalix[4]arene was studied in the context of a mechanistic study of the formation and dissociation of their complexes in aqueous solutions [9].

In the solid state, in the presence of organic or inorganic ions, the water soluble p-sulfonatocalix[4]arene generally forms a bilayered structure, with an up-down arrangement of the calixarene molecules. Yb(III) [10, 11], Cu(II) in presence of pyridine [12], La(III) with pyridine N-oxide [13] are bound to one of the calixarene layers through one sulfonate oxygen atom. In the latter case, a pyridine N-oxide molecule is inserted into the

---

* Corresponding Author.



SCHEME 1

cavity, while the other is located between the calixarene bilayers. However, the presence of greater amount of the pyridine N-oxide coligand can distort the structure of the layers, inducing an up-up orientation of the cavities of the calixarenes, and the formation of extended tubules [14]. In this case, La(III) cations bridge the layers. Unlike the corresponding calix[4]arene, the p-sulfonatocalix[5]arene binds to La(III) in its second coordination sphere [15]. In the cases of Gd(III) and Eu(III), the cations are associated with two calixarenes by direct coordination to the sulfonate groups, while Yb(III) is coordinated to the sulfonate group of a single calixarene ligand [15]. Mn(II) cross-links the sulfonate groups, leading to a biscalix[4]arene with a larger inner cavity [16]. Very recently, a cationic organic substrate, L-lysine, was shown to span the hydrophobic part of the sulfonatocalix[4]arene bilayer [17].

Cu(II) shows versatility in its binding abilities, since four modes of interaction have been observed so far. The copper ion can be bound to one calixarene in the presence of pyridine [12]. It can act as a spanner between sulfonate groups of different calixarenes [10, 11] and it can bridge the layers, or be intercalated between them [10, 11, 18].

Interactions of the calixarene ligand with the second coordination sphere of metallic cations have also been reported for pyridino Ni(II) ions [19] and Zn(II)-pyridine N-oxide [13]. Ionic species such as pyridinium, morpholinium [10, 18], methyl sulfate [20], choline [21] and tetramethylammonium ions [22] can be inserted inside the hydrophobic cavity of the calixarene.

Crystallographic structures of complexes of p-sulfonatocalix[4]arene or p-sulfonatocalix[5]arene with lanthanide cations have previously been reported but exclusively in presence of a co-ligand. This paper describes the X-ray crystal structure of the complex formed between p-sulfonatocalix[4]arene (1) and La(III), in the absence of coligands. The structure presents an interesting bilayer packing arrangement, in which the bilayers are formed of discrete units of stoechiometry 8:6, containing three different coordination environments of La(III) ions, some of which act as bridges between layers. The units are linked through hydrogen bonding interactions.

RESULTS AND DISCUSSION

The crystal analyzed by X-ray crystallography was obtained by slow evaporation from a 10 mM HCl solution of $LaCl_3$ (14.3 mM) and of p-sulfonatocalix[4]arene (13.9 mM). The cell contains two units (Figure 1). Each unit can be described as an up-down arrangement of 6 p-sulfonatocalix[4]arene molecules bridged by 8 La(III) cations, with 54 water molecules coordinated to La(III) (Figure 2), giving the complex (p-sulfonatocalix[4]arene)$_6$ (La(III))$_8$ $(H_2O)_{54}$ (**2**). This arrangement leads to a crystal packing of the bilayer type. Bilayered structures have been described for other complexes of sulfonatocalix[4]arene with metallic cations, for example with sodium and other alkali metal cations [10,23]. The calix[4]arenes are tetraanionic, all the hydroxyl groups being protonated. The (p-sulfonatocalix[4]arene)$^{4-}$ anions are in the cone conformation, as expected, since the sulfonatocalixarenes adopt generally the bowl geometry [24]. This is also the case for the p-sulfonatocalix[5]arene [15], due to intramolecular hydrogen bonding [1, 10]. However, the (sulfonatocalix[6]arene)$^{8-}$ anion adopts a double partial cone conformation [25].

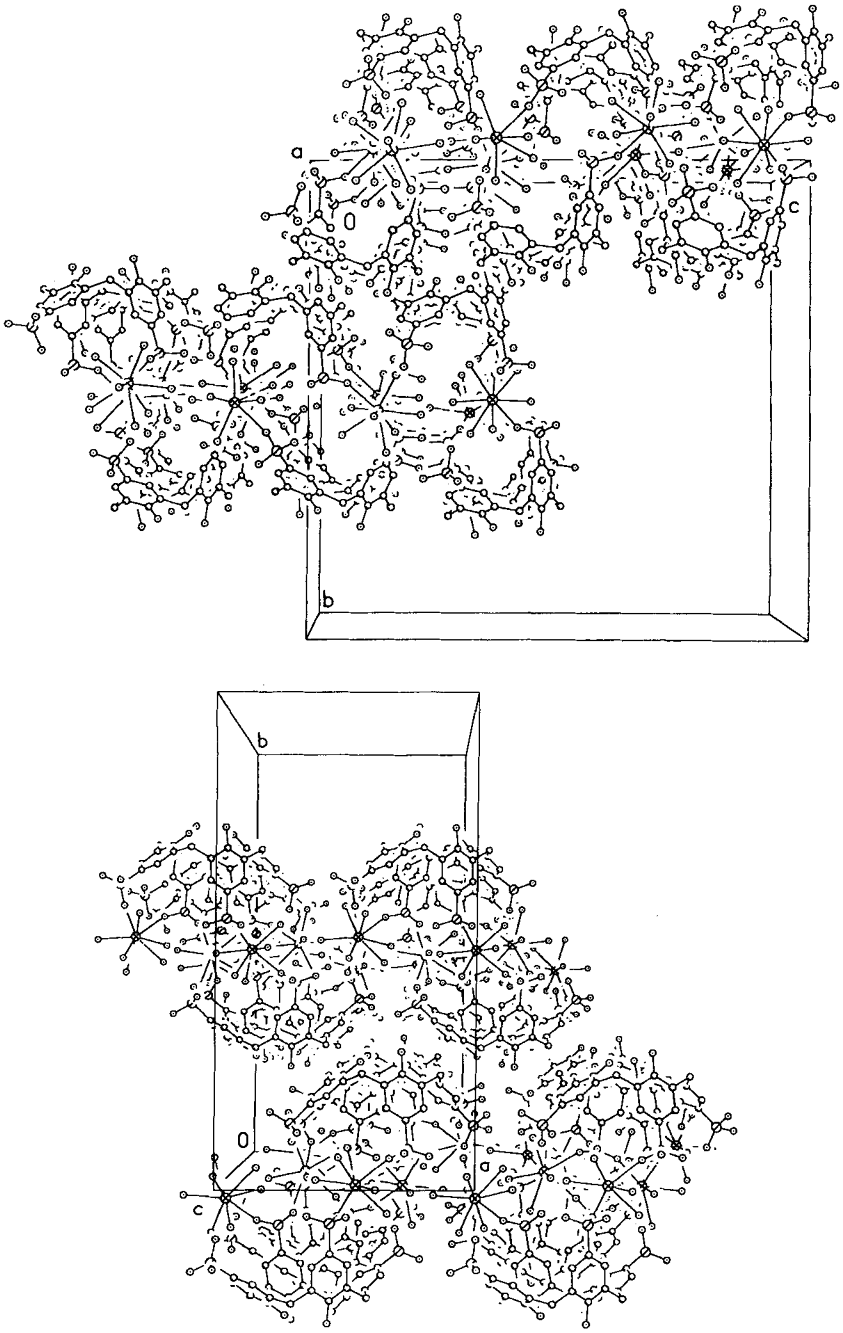


FIGURE 1 Bilayer structure of $La_8[p\text{-sulfonatocalix[4]arene}]_6$ viewed down the crystallographic a axis (a), and down the crystallographic c axis (b)

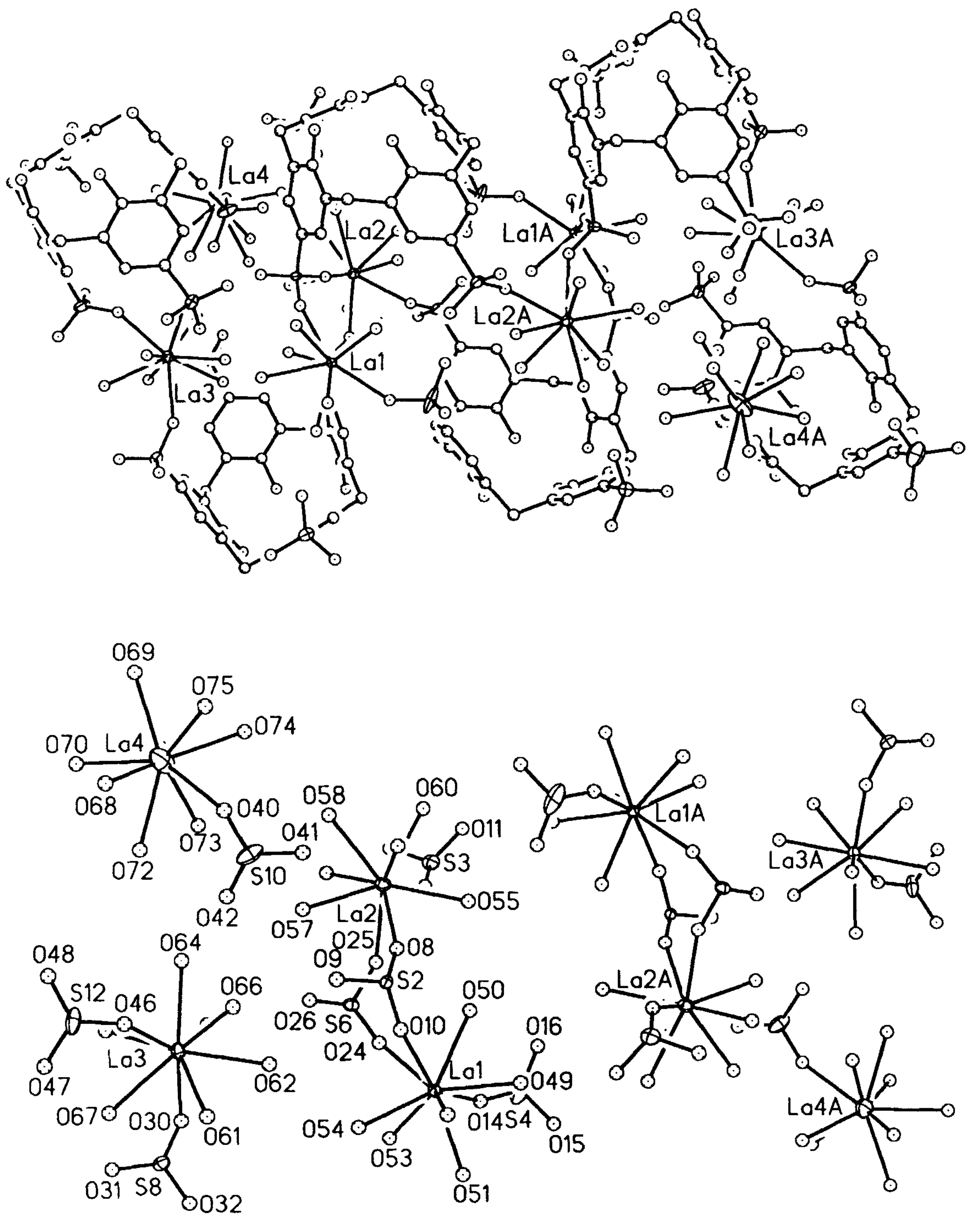


FIGURE 2 (a) View of the molecular unit and (b) coordination environment of the La(III) cations in La_8[p-sulfonatocalix[4]arene]$_6$ showing the atom numbering scheme

All the La (III) cations are nonacoordinated in the complex **2**. It is generally accepted that, in aqueous solution, La(III) is coordinated by 9 molecules of water [26–29]. In the crystal structure of **2**, some of the water molecules have been replaced by oxygens of the sulfonate groups. There are three symmetry-unique coordination environments for the La(III) cations (Figure 2). La_4 and $La_{4A}$are associated with one calixarene via one sulfonate S_{10} oxygen atom. La_3 and La_{3A} act as bridges for two independent calixarene anions through one of the oxygens of S_{12} and S_8. (La_1, La_{1A}) and (La_2, La_{2A}) are coordinated with three different calixarenes through one of the oxygens of (S_2, S_4 and S_6) and (S_2, S_3 and S_6), respectively. The atoms S_4 and S_6 (or S_3 and S_6) belong to two neighbouring calixarenes while S_2 belongs to a calixarene of the opposite layer. La_1 and La_2 share the same sulfonate groups of S_2 and S_6. The calixarene molecules are all coordinated to the first coordination sphere of the metallic cation through at least one sulfonate group. This is in contrast with the case of the p-sulfonatocalix[5]arene which occupies exclusively the second sphere of coordination of La(III) [15].

To verify that the characteristics of the crystallized compound described above did not depend on the initial crystallization conditions several crystallization experiments were performed (Table I). Regardless of the value of the ratio $[\text{calixarene}]_{\text{total}}$ / $[\text{La(III)}]_{\text{total}}$, or of the presence of HCl, the unit cell parameters of the grown crystals were consistently the same.

TABLE I Initial crystallisation conditions for **2**

Solution of $LaCl_3$	*$[calixarene]_{total}$ / $[La(III)]_{total}$*
7.1 mM in absence of HCl	0.80
7.1 mM in absence of HCl	1.22
7.1 mM in absence of HCl	1.55
14.8 mM in absence of HCl	0.79
14.3 mM in 10 mM HCl	0.97

The range of values of the bond lengths between La(III) and the sulfonate oxygen atoms, 2.500–2.571 Å, overlap with the range of the La(III) to water oxygen atoms bond lengths, 2.508–2.646 Å. This is also observed for the S-O-La angles which are found in a relatively narrow range, 141.1° to 158.1° (Table II). The La-O distances, from 2.50 to 2.65 Å, are comparable with distances previously reported for complexes of p-sulfonatocalix[4]arene with $Yb\text{-}O_{sulfonate}$ (2.33 Å) [11], $Cu\text{-}O_{sulfonate}$ (2.55 Å) [12] and $Mn\text{-}O_{sulfonate}$(2.39–2.47 Å) [16]. In the case of p-sulfonatocalix[5]arene, values of 2.35 and 2.31 Å have been observed for $Gd\text{-}O_{sulfonate}$, $Eu\text{-}O_{sulfonate}$ and $Yb\text{-}O_{sulfonate}$, respectively [15].

TABLE II Selected La-O bond lengths (Å) and angles (deg.)

$La_{(1)} - O_{(10)}{}^{a}$	2.536(8)	$La_{(4)} - O_{(40)}{}^{a}$	2.513(9)
$La_{(1)} - O_{(14)}{}^{a}$	2.500(11)	$La_{(4)} - O_{(68)}$	2.508(11)
$La_{(1)} - O_{(24)}{}^{a}$	2.547(8)	$La_{(4)} - O_{(69)}$	2.539(11)
$La_{(1)} - O_{(50)}$	2.560(11)	$La_{(4)} - O_{(70)}$	2.590(11)
$La_{(1)} - O_{(51)}$	2.558(11)	$La_{(4)} - O_{(71)}$	2.555(11)
$La_{(1)} - O_{(52)}$	2.567(11)	$La_{(4)} - O_{(72)}$	2.536(11)
$La_{(1)} - O_{(53)}$	2.581(11)	$La_{(4)} - O_{(73)}$	2.646(11)
$La_{(1)} - O_{(54)}$	2.564(11)	$La_{(4)} - O_{(74)}$	2.567(11)
$La_{(2)} - O_{(8)}{}^{a}$	2.571(8)	$La_{(4)} - O_{(75)}$	2.547(11)
$La_{(2)} - O_{(13)}{}^{a}$	2.509(11)		
$La_{(2)} - O_{(25)}{}^{a}$	2.557(8)	$S_{(2)}O_{(10)}La_{(1)}$	155.0(6)
$La_{(2)} - O_{(55)}$	2.559(11)	$S_{(4)}O_{(14)}La_{(1)}$	146.6(8)
$La_{(2)} - O_{(56)}$	2.548(11)	$S_{(6)}O_{(24)}La_{(1)}$	157.1(7)
$La_{(2)} - O_{(57)}$	2.538(11)	$S_{(2)}O_{(8)}La_{(2)}$	158.1(7)
$La_{(2)} - O_{(58)}$	2.593(11)	$S_{(3)}O_{(13)}La_{(2)}$	142.8(7)
$La_{(2)} - O_{(59)}$	2.576(11)	$S_{(6)}O_{(25)}La_{(2)}$	141.1(6)
$La_{(2)} - O_{(60)}$	2.556(11)	$S_{(8)}O_{(30)}La_{(3)}$	150.0(6)
$La_{(3)} - O_{(30)}{}^{a}$	2.525(8)	$S_{(12)}O_{(46)}La_{(3)}$	145.8(7)
$La_{(3)} - O_{(46)}{}^{a}$	2.514(9)	$S_{(10)}O_{(40)}La_{(4)}$	154.9(8)
$La_{(3)} - O_{(61)}$	2.543(11)		
$La_{(3)} - O_{(62)}$	2.565(11)		
$La_{(3)} - O_{(63)}$	2.577(11)		
$La_{(3)} - O_{(64)}$	2.554(11)		
$La_{(3)} - O_{(65)}$	2.546(11)		
$La_{(3)} - O_{(66)}$	2.590(11)		
$La_{(3)} - O_{(67)}$	2.563(11)		
$La_{(3)} - O_{(68)}$	2.508(11)		

a. oxygen atom of SO_3^- groups

The closest O...O interunit, end to end distance, 2.7 Å, is consistent with the presence of hydrogen bonding interactions between the unit ends. These hydrogen bonds organize the crystal into an extended bilayer structure made of repeating units, each unit being composed of 6 calixarenes coordinating 8 La(III) (Figure 3). The units are linked also by H-bonds between sulfonate groups and water molecules of the La(III) first coordination sphere from vicinal units. The distance between two layers of the 8:6 complex is 14.1 Å while the hydrophilic layer is 8.4 Å wide. These values are similar to the 13.7 and 8.3 Å, respectively, associated to the sodium salt analogue [23]. An hydrophilic layer width of 7.51 Å is observed for the ytterbium salt analogue [11]. The difference can be attributed to the fact that Yb(III) is bound to only one sulfonate group while La(III) bridges the layers. Similarly, for the p-sulfonatocalix[5]arene anions, the lanthanide cations Gd(III), Eu(III) and Tb(III), in the presence of pyridine N-oxide, bridge two independent anions, producing hydrophilic layer widths ranging from 8.5 to 9.9 Å [15]. Bilayer repeat distances of 10.0, 12.1, 13.7, 14.7 and 19.1 Å have been obtained for tetramethylammonium [22], manganese [16], sodium [23], lanthanum [15] and adeninium salt [30], respectively.

It is also worth noting that the sulfonate groups form cavities leading to the formation of channels in the a axis direction. The up and down position of the bowl cavity of the calixarenes also allows the formation of channels along the a axis (Figure 1a).

An interesting feature of the complex formed between the p-sulfonatocalix[4]arene and La(III) cations in the solid state resides in its bilayer packing arrangement. The bilayers are formed of units containing three different coordination environments of La(III) ion, some of which act as bridges between layers. No La(III) ions act as spanners. Layers are formed mainly through hydrogen bonding interactions between units. In contrast to the solid state results, ^{139}La solution NMR and microcalorimetry studies of the complexation between p-sulfonatocalix[4]arene and La(III) have identified the exclusive formation of a 1:1 complex in aqueous solution [9].

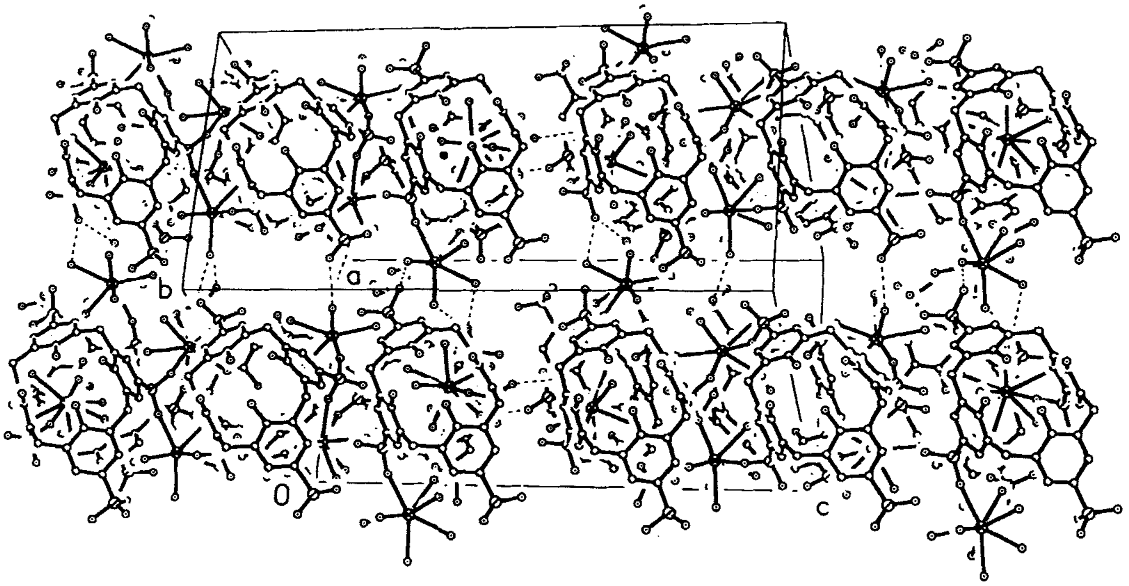


FIGURE 3 Crystal packing arrangement of La_8[p-sulfonatocalix[4]arene]$_6$

EXPERIMENTAL

Chemicals

The 5, 11, 17, 23-tetrasulfonic calix[4]arene hexahydrate and lanthanum(III) chloride heptahydrate (purity 99%) were purchased from Acros Organics and Aldrich, respectively. The lanthanum chloride was used without further purification. The calixarene was purified by recrystallization from an aqueous solution and dried 24 hours in an oven at 80–90 °C. An amount of 11 ± 1 molecules of cocrystallized water was quantified by ^{1}H NMR using a 1.77×10^{-2} mol dm^{-3} solution of dioxane as internal reference.

X-ray crystallographic analysis

A suitable crystal of $0.4 \times 0.3 \times 0.1$ mm^3 was selected, mounted on a thin, glass fibre using epoxy cement. The intensities of 102097 reflections were collected on a BRUKER SMART 1k CCD diffractometer using monochromatized MoK$_\alpha$radiation ($\lambda = 0.71073$ Å), 0.3° ω-scans at 0, 90, and 180°, at 293(2) K. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. A semi-empirical absorption correction from equivalents was applied (absorption coefficient = 15.98 cm^{-1}) [31]. Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structure was solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. The lanthanum and the sulfur atoms were refined with anisotropic displacement parameters. Oxygen atoms were refined with a common isotropic parameter and carbon atoms were refined isotropically to conserve a favourable data/parameter ratio. All hydrogen atoms were treated as idealized contributions except those on water molecules which were ignored. A void space analysis suggested 27 interstitial water molecules per molecular complex and final refinement was performed on diffraction data modified by Squeeze bypass filter in PLATON (Spek, A. L., Utrecht University, The Netherlands, 1997). The final difference map had features in close association to the heavy atom positions and were considered as artifacts resulting from less than perfect absorption corrections. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library (Sheldrick, G. M., Bruker AXS, Madison, WI, 1997). Crystallographic details are reported in Table III.

TABLE III Crystal data and structure refinement for the La(III) – p-sulfonatocalix[4]arene complex

Formula	$C_{168}H_{282}La_8O_{177}S_{24}$
formula weight	7014.66
crystal system	Monoclinic
space group	$P2_1/n$
cell dimensions:	
a (Å)	15.091(1)
b (Å)	28.550(3)
c (Å)	30.167(3)
β (deg.)	90.008(2)
volume (Å^3)	12997(2)
Z	2
ρ_{calc}. (g cm^{-3})	1.792
F(000)	7092
2θ range (deg.)	3.06 – 42.00
N° reflections collected	102097
N° unique reflections	13930
GoF	1.04
$R1$, $wR2$	0.09, 0.257
Largest peak (e Å^{-3})	7.443

$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. based on [I>2σ(I)];

$wR2 = \left(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\right)^{1/2}$

Acknowledgements

The Natural Sciences and Engineering Research Council of Canada, NSERC, is gratefully acknowledged for a research grant (CD).

References

[1] Pocchini, A.; Ungaro, R.; "Calixarenes and Related Hosts", in *Comprehensive Supramolecular Chemistry*, Vögtle, F. (Ed.), Elsevier Sc. Ltd., Oxford, 1996, p. 103.

[2] Perrin, R.; Harris, S.; in *Calixarenes: A versatile Class of Macrocyclic Compounds*, Vicens, J. and Böhmer, V. (Eds.), Kluwer Acad. Pubs., Dordrecht, 1991, p. 235.

[3] Israëli, Y.; Detellier, C.; *J. Phys. Chem. B*, **1997**, *101*, 1897–1901.

[4] Meier, U.C.; Detellier, C.; *J. Phys. Chem. A*, **1999**, *103*, 3825–3829.

[5] Blixt, J.; Detellier, C.; *J. Am. Chem. Soc.* **1995**, *117*, 8536–8540.

[6] Meier, U.C.; Detellier, C.; *J. Phys. Chem. A*, **1998**, *102*, 1888–1893.

[7] Meier, U.C.; Detellier, C.; *Supramolecular Chem.*, **1998**, *9*, 289–295.

[8] Gutsche, C.D.; in *Calixarenes*, Stoddart, J. F. (Ed.), Royal Society of Chemistry, London, 1989, Chapter 3, p. 67.

[9] Israëli, Y.; Bonal, C.; Detellier, C.; Morel, J.-P.; Morel-Desrosiers, N. *To be submitted for publication.*

[10] Atwood, J.L.; Bott, S.G.; in *Calixarenes: A versatile Class of Macrocyclic Compounds*, Vicens, J. and Böhmer, V. (Eds.), Kluwer Acad. Pubs., Dordrecht, (1991) p. 199.

[11] Atwood, J.L.; Orr, G.W.; Means, N.C.; Hamada, F.; Zhang, H.; Bott, S.G.; Robinson, K.D.; *Inorg. Chem.* **1992**, *31*, 603–606.

[12] Atwood, J.L.; Orr, G.W.; Hamada, F.; Bott, S.G.; Robinson, K.D.; *Supramolecular Chem.* **1992**, *1*, 15–17.

[13] Atwood, J.L.; Orr, G.W.; Robinson, K.D.; Hamada, F.; *Supramolecular Chem.* **1993**, *2*, 309–317.

[14] Orr, G.W.; Barbour, L.J.; Atwood, J.L.; *Science* **1999**, *285*, 1049–1052.

[15] Steed, J.W.; Johnson, C.P.; Barnes, C.L.; Juneja, R.K.; Atwood, J.L.; Reilly, S.; Hollis, R.L.; Smith, P.H.; Clark, D.L. *J. Am. Chem. Soc.* **1995**, *117*, 11426–11433.

[16] Iki, H.; Tsuzuki, H.; Kijima, H.; Hamachi, I.; Shinkai, S.; *Supramolecular Chem.*, **1995**, *4*, 223–228.

[17] Selkti, M.; Coleman, A.W.; Nicolis, I.; Douteau-Guével, N.; Villain, F.; Tomas, A.; de Rango, C.; *J. Chem. Soc., Chem. Commun.* **2000**, 161–162.

[18] Barbour, L.J.; Damon, A.K.; Orr, G.W.; Atwood, J.L. *Supramolecular Chem.* **1996**, *7*, 209–213.

[19] Atwood, J.L.; Orr, G.W.; Hamada, F.; *J. Am. Chem. Soc.* **1991**, *113*, 2760–2761.

[20] Bott, S.G.; Coleman, A.W.; Atwood, J.L.; *J. L.; J. Am. Chem. Soc.* **1988**, *110*, 610–611.

[21] Lehn, J.-M.; Meric, R.; Vigneron, J.-P.; Cesario, M.; Guilhem, J.; Pascard C.; Asfari, Z.; Vicens, J.; *Supramolecular Chem.* **1995**, *5*, 97–103.

[22] Atwood, J.L.; Barbour, L.J.; Junk, P.C.; Orr, G.W.; *Supramolecular Chem.* **1995**, *5*, 105–108.

[23] Coleman, A.W.; Bott, S.G.; Morley, C.M.M.; Robinson, K.D.; Zhang, H.; Atwood, J.L.; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1361–1362.

[24] Shinkai, S.; Araki, K.; Matsuda, T.; Nisiyama, N.; Ikeda, H.; Takasu, I.; Iwamoto, M.; *J. Am. Chem. Soc.* **1990**, *112*, 9053–9058.

[25] Atwood, J.L.; Clark, D.L.; Juneja, R.K.; Orr, G.W.; Robinson, K.D.; Vincent, R.L.; *J. Am. Chem. Soc.* **1992**, *114*, 7558–7559.

[26] Habenschuss, A.; Spedding F.H.; *J. Chem. Phys.* **1980**, *73*, 442–450.

[27] Kanno H.; *J. Phys. Chem.* **1988**, *92*, 4232–4236.

[28] Cossy, C.; Merbach, A.E.; *Pure Appl. Chem.* **1988**, *60*, 1785–1796.

[29] Chen, Z.; Detellier, C.; *J. Solution Chem.* **1992**, *21*, 941–951.

[30] Atwood, J.L.; Barbour, L.J.; Dawson, E.S.; Junk, P.C.; Kienzle, J.; *Supramolecular Chem.* **1996**, *7*, 271–274.

[31] Blessing, R.; *Acta Cryst.* **1995**, *A51*, 33–38.