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Zouhair Asfari[a]; Jack Harrowfield[b]; Pierre Thuéry[c]; Jacques Vicens[a]
[a] ECPM, Université Louis Pasteur de Strasbourg, Strasbourg Cedex 2, France [b] School of Biomedical and Chemical Sciences, University of Western Australia, Crawley, WA, Australia [c] CEA/Saclay, DSM/DRECAM/SCM, Gif-sur-Yvette, France

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Calixarenes as Polyhapto-aromatic Ligands: Alkali Metal Ions and Sulfonated Calixarenes

ZOUHAIR ASFARI[a,*], JACK HARROWFIELD[b], PIERRE THUÉRY[c] and JACQUES VICENS[a]

[a]*ECPM, Université Louis Pasteur de Strasbourg, 25, rue Becquerel, Cronenbourg, F-67087, Strasbourg Cedex 2, France;* [b]*School of Biomedical and Chemical Sciences, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia;* [c]*CEA/Saclay, DSM/DRECAM/SCM (CNRS URA 331), Bât. 125, 91191 Gif-sur-Yvette, France*

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Crystal structure determinations for the hexarubidium and octacesium derivatives of calix[6]arene hexasulfonic acid, as well as of a new solvate of the pentasodium derivative of calix[4]arene tetrasulfonic acid, and comparison with structural data from the literature for alkali metal complexes of sulfonated calixarenes, have provided further evidence for the importance of interactions with aromatic π-electrons for the heavier alkali metal cations. There is evidence as well that this interaction can be enhanced by extended ionization of the sulfonated calixarene.

Keywords: Calixarene sulfonates; Alkali metals; π-Donation; Crystal structures

INTRODUCTION

Binding of the alkali metals, and of cesium in particular, by calixarenes has been a topic of particular interest due to its possible exploitation in ligands suitable for separation of these elements and especially for the treatment of nuclear waste [1,2]. There is extensive structural evidence for polyhapto binding of cesium to the aromatic rings of calixarenes (the "cation–π interaction") [3–5], and this has frequently been nominated as a source of the selectivity observed in the binding and extraction of Cs^+ by neutral "calixcrown" ligands capable of extraction of Cs^+ in the presence of vastly greater amounts of Na^+ [2,6]. Though characterized in some anionic derivatives of calix[4]arene [3,4], it is not evident for the monoanion of *p*-*t*-butyltetrathiacalix[4]arene [7], perhaps because interaction with more than one aromatic unit may be necessary to overwhelm other influences and dimensional differences prevent this. In the case of sulfonated calixarenes, π-basicity has been demonstrated by the inclusion of small molecules within the cavity of cone-form calix[4]arene sulfonate [8,9]. The known structures of alkali metal ion complexes of sulfonated calixarenes [9–18], however, have not been interpreted as providing evidence for polyhapto-aromatic coordination of the metal ion, although many of these are of complexes of Na^+, a cation which has been found to bind in various ways to different calixarenes [19–21], but rarely through polyhapto-π coordination [22,23]. Whether the remarkably high formal negative charges that may be associated with sulfonated calixarene anions might be a factor to use in control of π-basicity is unknown, though the fascinating structures of numerous solids incorporating these anions indicate certainly that novel characteristics might be anticipated [9].

In an attempt to study and compare the structures of all alkali metal derivatives of a sulfonated calixarene, we chose to expand the structural studies of the hexasulfonate of calix[6]arene [17]. In the event, this proved to be a complicated task, less successful in fact than early studies of sulfonated calix[4]arene, where only the Li complex was missing [10,11]. The structures of the Rb and Cs derivatives, however, do provide an interesting illustration of changes in bonding proclivities. As a useful comparison, we include discussion of the structure of the previously structurally uncharacterized ethanol solvate of the pentasodium derivative of calix[4]arene sulfonate.

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*Corresponding author.

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EXPERIMENTAL

Syntheses

Ethanol/water Solvate of the Pentasodium Complex of Calix[4]arene Tetrasulfonate (L_1), $Na_5(L_1-5H)\cdot 9H_2O\cdot EtOH$, 1

This compound was obtained by vapor diffusion of ethanol into an aqueous solution of the simple hydrate obtained by known procedures [11].

Calix[6]arene Hexasulfonic Acid (L_2)

The hexasulfonate of calix[6]arene was obtained by reaction of *p-t*-butylcalix[6]arene with concentrated H_2SO_4, following essentially a literature procedure [17]. Thus, a vigorously stirred mixture of *p-t*-butylcalix[6]arene (6.0 g) and concentrated H_2SO_4 (60 ml) was heated at 60°C for 6 h. The mixture was filtered to remove the last traces of unreacted calixarene and, after cooling to room temperature, the brown filtrate was added drop-by-drop to diethyl ether (1 l). The ethereal solution was decanted from the partially oily precipitate and the latter converted to a slightly discolored white powder (~8 g) by crystallization from the minimum volume of ethanol by addition of ether. Repeated crystallization did not result in a completely colorless product but the extremely simple ^1H NMR spectrum, provided no evidence of significant levels of a (proton containing) contaminant. The material was assumed to have the previously established [17] composition of calix[6]arene hexasulfonic acid tricosahydrate.

Alkali Metal Ion Complexes of Calix[6]arene Hexasulfonate

In the hope of obtaining derivatives of the hexaanion (where only the sulfonate groups are deprotonated), an aqueous solution of the acid was first reacted with either a sixfold molar amount of MOH (M = Na, K) or a threefold molar amount of M_2CO_3 (M = Li, Rb, Cs). In all cases, a clear solution results rapidly, any obtained using the carbonates being heated gently until CO_2 evolution appeared complete. Although partial crystallization from these solutions occurred readily for K, Rb and Cs, all solutions were taken to dryness prior to systematic efforts at crystallization. Note that evaporation of the Li solution gave an oily residue, which was solidified by trituration with ethanol. After exploring a wide variety of crystallization methods, vapor diffusion of ethanol into aqueous solutions (~20 mg ml^{-1}) of the solid residues was found to be the most readily reproducible method of crystal formation, though it failed completely in the case of the Li complex, for which no satisfactory method was obtained. Crystals obtained from the Na compound appeared to be those of the known (and structurally characterized) octasodium species, while none of the crystals of the K compound were found suitable for diffraction studies. Successful studies were, however, possible, albeit with difficulty, of the Rb and Cs compounds, the crystallized materials proving to be the hexarubidium **2** and octacesium **3** complexes, of composition determined from the crystal structure solutions, of $Rb_6(\mathbf{L}_2-6H)\cdot 10H_2O$ and $Cs_8(\mathbf{L}_2-8H)\cdot 13H_2O\cdot EtOH$, respectively.

Crystallography

The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer [24] using graphite-monochromated Mo Kα radiation (0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The unit cell parameters were determined from the reflections collected on ten frames and were then refined on all data (90 frames, ϕ-scans, 2° steps). The data were processed with DENZO-SMN [25]. The structures were solved by direct methods with SHELXS-97 [26] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97 [27]. Absorption effects were corrected empirically with the program DELABS from PLATON [28]. Special features for each structure were:

> Complex **1**. The hydrogen atoms of the phenolic oxygen atoms and those of water and ethanol oxygen atoms were found on the Fourier-difference map (except the second proton of the water oxygen atom O26, probably disordered) and were introduced as riding atoms.
>
> Complex **2**. The hydrogen atoms of the phenolic and water oxygen atoms were not found on the Fourier-difference map. Two of the water molecules, whose oxygen atoms were too close one to the other and which behave badly on refinement (O17 and O18), were refined with partial occupancies constrained to sum to unity.
>
> Complex **3**. The hydrogen atoms of the phenolic, water and ethanol oxygen atoms were not found on the Fourier-difference map. The ethanol molecule is disordered over two positions sharing the oxygen and terminal carbon atoms (hydrogen atoms not introduced). One of the cesium atoms (Cs6) has been included with a 0.5 occupancy factor in order to keep a physically acceptable displacement factor.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Apart from those indicated above, all hydrogen atoms were

TABLE I Crystal data and structure refinement details

	1	2	3
Empirical formula	$C_{30}H_{43}Na_5O_{26}S_4$	$C_{42}H_{50}O_{34}Rb_6S_6$	$C_{44}H_{60}Cs_8O_{38}S_6$
$M/\mathrm{g\,mol}^{-1}$	1062.83	1804.00	2452.56
T/K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/c$	$P2_1/n$	$P2_1/m$
$a/\text{Å}$	16.9112(12)	13.743(3)	13.3220(8)
$b/\text{Å}$	14.1106(10)	11.493(2)	19.2779(6)
$c/\text{Å}$	18.1933(10)	19.068(4)	14.5822(9)
$\beta/°$	106.227(4)	104.346(8)	91.663(2)
$V/\text{Å}^3$	4168.5(5)	2917.8(9)	3743.4(3)
Z	4	2	2
μ/mm^{-1}	0.377	5.306	4.104
Reflections collected	28159	18405	28760
Independent reflections	7544	5266	3588
Observed reflections [$I > 2\sigma(I)$]	5115	2447	3024
R_{int}	0.093	0.123	0.105
Parameters	587	408	460
R_1	0.049	0.078	0.073
wR_2	0.109	0.226	0.181
S	1.021	0.930	1.001

introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Crystal data and structure refinement details are given in Table I. The material for publication and molecular plots were obtained with SHELXTL [29]. All calculations were performed on a Silicon Graphics R5000 workstation.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC no. 182143 (**1**), 182144 (**2**) and 182145 (**3**). Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033;. E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

DISCUSSION

As ligands for metal ions, calix[6]arene derivatives resist facile classification, since despite instances where these potentially multidentate species have been found to bind as merely unidentate [30] or at best bidentate [31] ligands, there are other instances where especially strong interactions appear to occur [32–38]. In comparison to calix[4]arene derivatives, of course, those of the larger calixarenes have yet been only superficially studied [38] and the present work simply adds to what is known of the possibilities with calix[6]arene compounds, rather than defining a specific exploitation of anticipated properties. The only prior structural study of an alkali metal complex of calix[6]arene hexasulfonate [17] has shown the formally octa-anionic form of the ligand to adopt the commonly encountered *1,2,3-alternate* conformation, and the present work shows this to be the case for a hexa-anionic form as well. In general, the focus of prior studies of alkali metal ion derivatives of sulfonated calixarenes has not been upon the coordination modes of the alkali metals, though it has been noted that, as with other metals, sulfonate-*O* coordination is prominent even when phenoxide-*O* coordination is possible [9–18]. Nonetheless, as far as is known, phenoxide ion formation does not occur until all sulfonate protons have been removed, and a derivative with more than partial removal of phenoxide protons is yet to be structurally characterized.

In the present compounds, the ligand, both as formally hexanegative and octanegative forms, again adopts the *1,2,3-alternate* conformation. This seeming independence of the conformation on the formal charge on the ligand has also been observed for calix[5]arene pentasulfonate [18], though it is not always the case with calixarenes in general [39]. As is discussed in detail below, metal ion coordination in both the present hexarubidium and octacesium compounds involves complicated polymeric structures, with the metals showing an assortment of unsymmetrical high coordination numbers. In addition, as is often the case for the heavier alkali metals [40,41], definition of the coordination sphere involves a decision as to the separation taken to define a bond which may leave several additional atoms at only slightly longer distances.

The crystal structure of $Na_5(\mathbf{L}_1{-}5H)\cdot 9H_2O\cdot EtOH$, **1**, is very similar to that previously reported for $Na_5(\mathbf{L}_1{-}5H)\cdot 12H_2O$ [10,11], with, in particular, the same -5 charge for the calixarene, indicating deprotonation of one phenolic group. The five sodium ions in **1** are distributed over six sites, two of which (Na3 and Na5) are located on a twofold axis (Fig. 1). The coordination number is five (Na2, Na6) or six (all the other ions). The five ions Na1–Na5 are bound to two, three or four oxygen atoms from the sulfonate groups, with Na–O bond lengths ranging from 2.307(3) to 2.827(3) Å [mean value 2.48(14) Å]. Not more than two sulfonate groups bound to one sodium ion pertain to the same calixarene, so that polymeric arrangements are formed. The overall three-dimensional arrangement can again be sensibly described as a bilayer system [9,11]. The sulfonate oxygen atoms are unidentate or bridging, such that different sulfonate groups are bound to between two and five cations. The coordination spheres are completed by two, three or four water molecules, with Na–O bond lengths ranging from 2.318(3) to 2.483(3) Å [mean value 2.39(5) Å]. Na6 presents a singular and interesting mode of coordination, since it is bound to two adjacent phenolic groups from the same calixarene [Na6–O1 2.349(3) Å, Na6–O13 2.642(3) Å; both O1 and O13 are protonated, the phenoxide oxygen atom being O5], just as is sodium bound to the monoanions of both *p*-*t*-butylcalix[4]arene [42] and *p*-*t*-butyltetrathiacalix[4]arene [7], and to one oxygen atom from each of three sulfonate groups pertaining to three different neighboring calixarenes [2.289(3)–2.344(3) Å]. As in $Na_5(\mathbf{L}_1{-}5H){\cdot}12H_2O$ [10,11], the sodium ion bound to the phenolic groups is located inside the calixarene layer, the three sulfonate-*O*-coordinated macrocycles being inverted with respect to the phenol-*O*-coordinated one. It may be noticed that phenol-coordination is not universal in these sodium–sulfonatocalixarene complexes: it is present in $Na_5(\mathbf{L}_1{-}5H){\cdot}12H_2O$, as well as in $Na_{10}(\mathbf{L}_3{-}5H)_2{\cdot}33.5H_2O$ [18] ($\mathbf{L}_3$ = calix[5]arene pentasulfonic acid), $Na_7(\mathbf{L}_3{-}7H){\cdot}18H_2O$ [12] and $Na_8(\mathbf{L}_2{-}8H){\cdot}20.5H_2O$ [17], but it is absent in $Na_5(\mathbf{L}_1{-}5H){\cdot}8H_2O{\cdot}(CH_3)_2CO$ [10,11]. When it occurs, it involves only one or two cations (bound to one or two phenolic groups from the same molecule), the other cations being embedded in the hydrophilic layer. In one case [12], such a phenol-coordinated sodium ion is also bound to a sulfonate group from the next layer. The *cone* conformation of ($\mathbf{L}_1$–5H) in **1** is quite unremarkable, with dihedral angles between the four aromatic rings and the mean plane defined by the four methylene links of 54.00(9), 56.25(9), 40.30(8) and 69.82(9)°. Three intramolecular hydrogen bonds are formed in the mono-deprotonated lower rim, the phenoxide oxygen atom being an acceptor in two of them. An intricate hydrogen bonding pattern links the water and ethanol molecules in the hydrophilic layer between them and also with sulfonate and phenolic oxygen atoms. The ethanol molecule is further included in the calixarene cavity, with its oxygen atom directed outwards (shortest C···C contact 3.65 Å). The Na···Na separations in **1** are in the range 3.49–4.16 Å, comparable to those in the complexes cited above (3.33–4.20 Å).

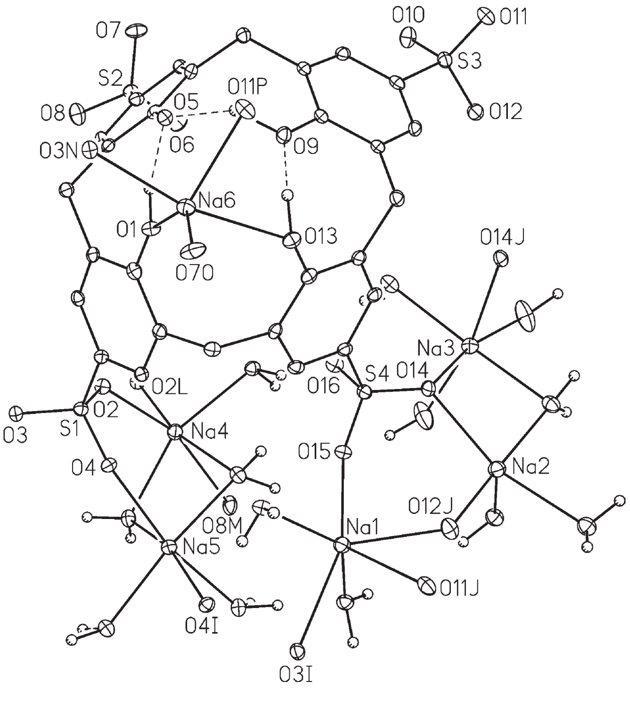

FIGURE 1 View of the repeat unit in the penta-sodium complex **1**. Hydrogen bonds represented as dashed lines. Hydrogen atoms of the calixarene skeleton omitted for clarity. Ellipsoids drawn at the 30% probability level. Symmetry codes: I = −*x*, *y*, 0.5 − *z*; J = 1 − *x*, *y*, 0.5 − *z*; K = 1 − *x*, 1 − *y*, 1 − *z*; L = −*x*, 1 − *y*, −*z*; M = *x*, 1 − *y*, 0.5 + *z*; N = −*x*, 2 − *y*, −*z*; O = *x*, 2 − *y*, 0.5 + *z*; P = 1 − *x*, 2 − *y*, −*z*.

Compound **2**, $Rb_6(\mathbf{L}_2{-}6H){\cdot}10H_2O$, is the first rubidium ion complex of $\mathbf{L}_2$, the only complex with a sulfonatocalixarene reported up to now being $Rb_5(\mathbf{L}_1{-}5H){\cdot}5H_2O$ [11]. The calixarene in **2**, which is likely to have no deprotonated phenolic group, presents the centrosymmetrical *1,2,3-alternate* or *three-up, three-down* conformation (Fig. 2), which is the conformation observed in the two isostructural compounds $\mathbf{L}_2{\cdot}23H_2O$ and $Na_8(\mathbf{L}_2{-}8H){\cdot}20.5H_2O$ [17]. The Cambridge Structural Database (Version 5.22, [43]) gives only one more structure of a sulfonatocalix[6]arene, which is that of the cobalt(III) sepulchrate complex of O-hexamethylated $\mathbf{L}_2$ [44], which presents an essentially similar, but less regular, conformation. None of the three Rb^+ ions in the repeat unit of the structure of compound **2** is bound to a phenolic oxygen atom (Fig. 3). This is at variance with what is observed in $Rb_5(\mathbf{L}_1{-}5H){\cdot}5H_2O$ [11], in which one of the cations is bound to two adjacent phenolic oxygen atoms from the same calixarene, the resulting location of this cation with respect to the bi-layer arrangement being similar to that previously described in the case of Na^+. The cations in **2** are bound to seven (Rb1), five (Rb2) and two (Rb3) sulfonate oxygen atoms, with Rb–O distances in the range 2.861(9)–3.266(9) Å [mean value 3.02(14) Å], less extended than that in $Rb_5(\mathbf{L}_1{-}5H){\cdot}5H_2O$, 2.758–3.629 Å [mean value 3.1(2) Å].

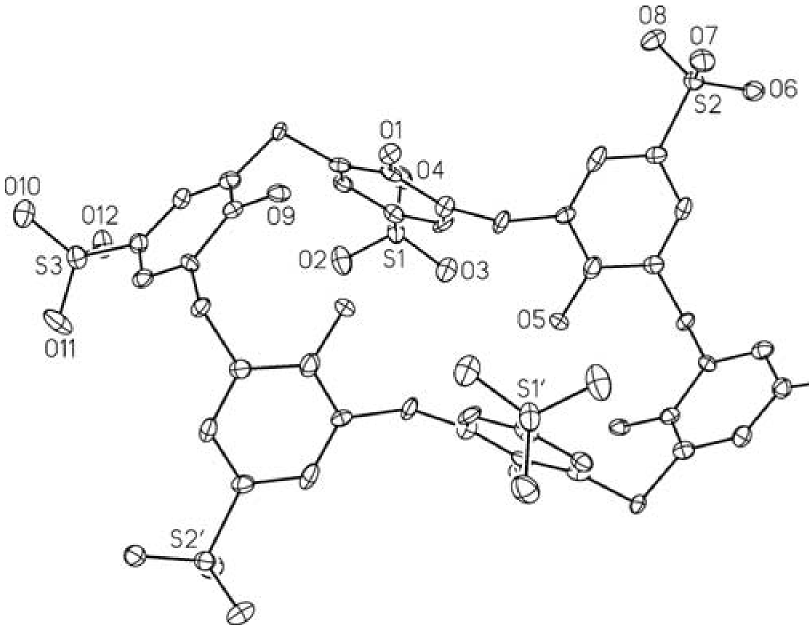

FIGURE 2 View of the calixarene in the hexa-rubidium complex **2**. Hydrogen atoms omitted for clarity. Ellipsoids drawn at the 30% probability level. Primed atoms are related to unprimed ones by the symmetry center.

The sulfonate oxygen atoms are bound to a maximum of three cations, the maximum coordination for one sulfonate group being to five different cations. Two to five water molecules are also coordinated in **2**, with Rb–O distances in the range 2.71(3)–3.527(15) Å [mean value 3.0(2) Å] {2.714–3.587 Å [mean value 3.2(2) Å] in $Rb_5(\mathbf{L}_1{-}5H)\cdot 5H_2O$}. A new trend, that was absent with Na^+, appears with Rb^+, which is the existence of cation-π interactions, as evidenced by short contacts between Rb2 and Rb3 and some aromatic rings (shortest Rb···C distance 3.34 Å). Note that these interactions involve only one aromatic ring for each cation. Cation-π interactions are also present in $Rb_5(\mathbf{L}_1{-}5H)\cdot 5H_2O$, with a shortest Rb···C distance of 3.45 Å. The conformation of the calixarene in **2** can be described by the dihedral

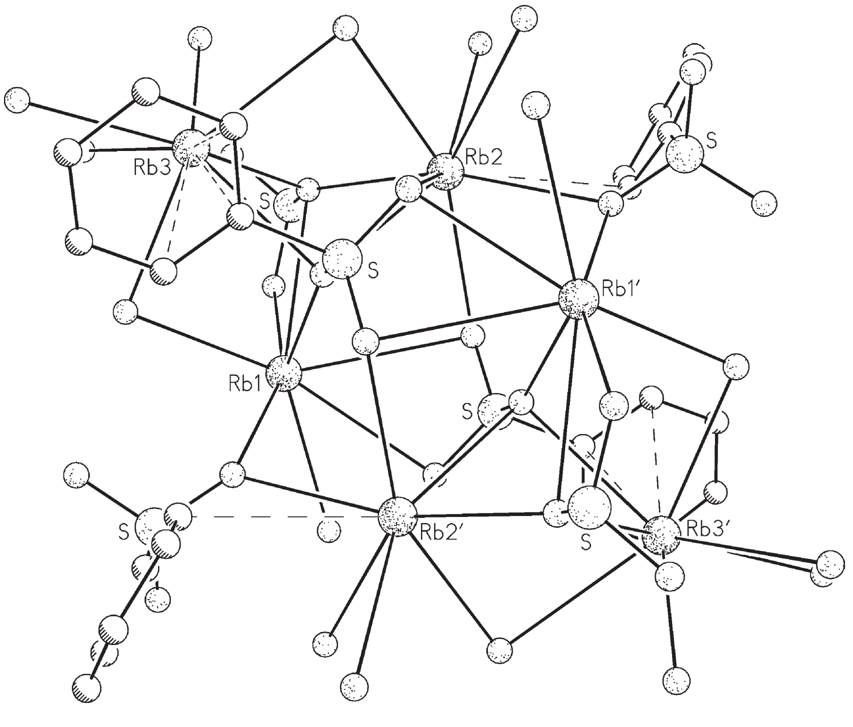

FIGURE 3 View of the hexa-rubidium assemblage in complex **2**. The aromatic rings involved in polyhapto bonding are represented (interactions as dashed lines). Primed atoms are related to unprimed ones by the symmetry center.

angles between the aromatic rings and the mean plane defined by the six methylene carbon atoms, in spite of the high rms deviation of fitted atoms in the latter (0.59 Å). These angles are 72.3(1), 60.5(1) and 39.1(1)° for the three aromatic rings of each half-cone subunit, indicating a somewhat irregular geometry. The ϕ and χ torsion angles [45] define the sign sequence ($+-$, $+-$, $++$) in the half-cone subunit, the last $++$ corresponding to the link between the two reversed half-cones (with one of the values in this case as low as 39.5°). The calixarenes are arranged in layers, with each calixarene tilted so that three sulfonate groups face one interlayer space and the reversed three other ones face the opposite space. The cations and water molecules are located between the calixarene layers, as usual in such complexes, and an extensive hydrogen bonding pattern unites water and sulfonate oxygen atoms. The Rb···Rb distances are in the range 4.13–4.48 Å.

The crystal structure of $\mathrm{Cs_8}(\mathbf{L}_2-8\mathrm{H})\cdot 13\mathrm{H_2O}\cdot\mathrm{EtOH}$ **3** is the second case of a cesium sulfonatocalixarene complex, the other one, which involves $\mathbf{L}_1$ (as in the case of rubidium), being $\mathrm{Cs_5}(\mathbf{L}_1-5\mathrm{H})\cdot 4\mathrm{H_2O}$ [11]. Compound **3** shares some common features with **2**, in particular the *1,2,3-alternate* conformation of the calixarene. However, whereas **2** is a centrosymmetric complex, **3** has a symmetry plane bisecting the two opposite central aromatic rings of the half-cone subunits. Furthermore, two phenolic groups are probably deprotonated in **3**. The repeat unit contains six cesium ions, three of them (Cs1, Cs3 and Cs5) being located on the symmetry plane, and Cs6 being seemingly half-occupied (see "Experimental" Section). All cations but Cs1 are bound to sulfonate oxygen atoms, with Cs–O bond lengths in the range 3.016(12)–3.57(2) Å [mean value 3.24(15) Å], in agreement with the range 2.920–3.637 Å [mean value 3.23(18) Å] in $\mathrm{Cs_5}(\mathbf{L}_1-5\mathrm{H})\cdot 4\mathrm{H_2O}$. All cations but Cs5 are bound to water (and one to ethanol) molecules {2.70(2)–3.81(5) Å [mean value 3.2(3) Å]; 3.022–3.805 Å [mean value 3.4(2) Å] in $\mathrm{Cs_5}(\mathbf{L}_1-5\mathrm{H})\cdot 4\mathrm{H_2O}$}. Some differences arise between these two cesium complexes regarding phenol complexation. Whereas only one cation is bound to two phenolic oxygen atoms of one calixarene in $\mathrm{Cs_5}(\mathbf{L}_1-5\mathrm{H})\cdot 4\mathrm{H_2O}$, giving an arrangement similar to that observed in sodium and rubidium complexes, two cations (Cs1 and Cs5) are bound to four and three phenol groups, respectively, in **3** (Fig. 4). Cs1 is embedded in the calixarene cavity (in which it is closer to one subunit than to the other) and bound to the two lateral oxygen atoms of each half-cone subunit [Cs1–O4 3.630(10), Cs1–O8 3.218(10) Å, to be compared with 3.002 and 3.247 Å in $\mathrm{Cs_5}(\mathbf{L}_1-5\mathrm{H})\cdot 4\mathrm{H_2O}$]. This cation is further bound to three water molecules included in the calixarene cavity (O15, O16) and it displays short contacts with the three aromatic rings of one half-cone subunit (shortest contact 3.53 Å) [loose water···π hydrogen bonds [46] involving O16 and its symmetry-related counterpart and the closest aromatic rings are possible, with an O···centroid distance of 3.58 Å]. The second cation, Cs5, is located out of

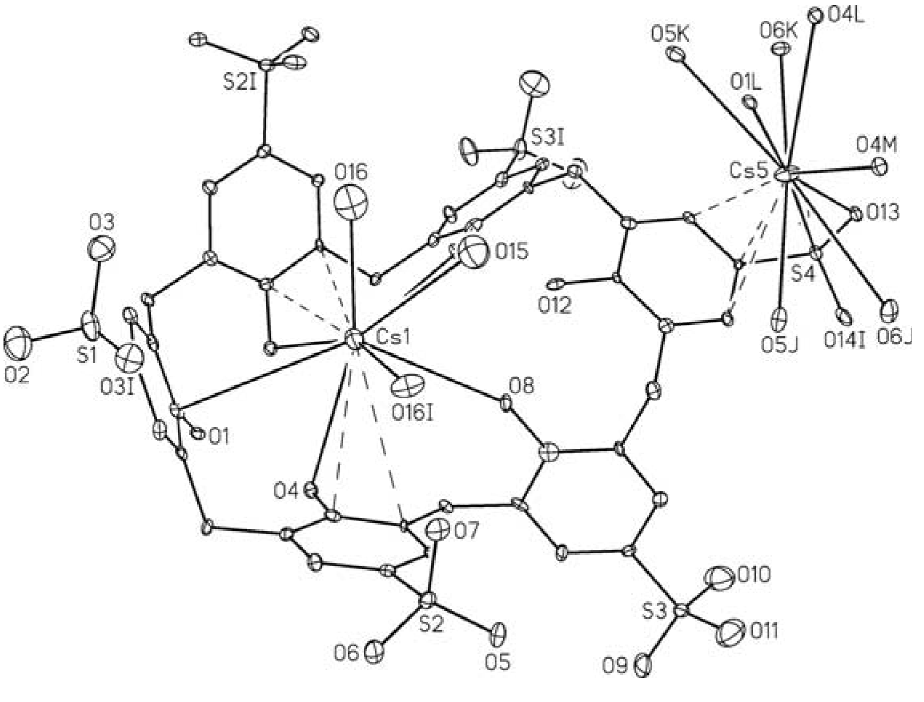

FIGURE 4 View of the calixarene and the two phenol-bound cesium cations Cs1 and Cs5 in the octa-cesium complex **3**. Hydrogen atoms omitted for clarity. Ellipsoids drawn at the 20% probability level. Symmetry codes: I = x, 1.5 − y, z; J = −x, 1 − y, −z; K = −x, 0.5 + y, −z; L = x − 1, y, z; M = x − 1, 1.5 − y, z.

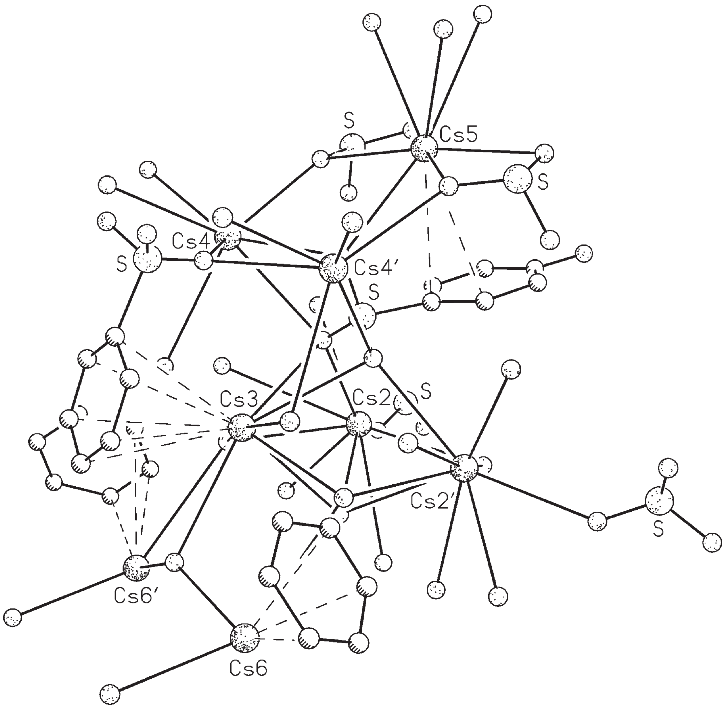

FIGURE 5 View of the cesium assemblage in complex **3**. Cs1 omitted for clarity. The aromatic rings involved in polyhapto bonding are represented (interactions as dashed lines). Primed atoms are related to unprimed ones by the symmetry plane.

the calixarene to which it is bound through the three phenolic oxygen atoms of the subunit which contains Cs1 [Cs5–O1 3.272(15) Å, Cs5–O4 3.211(10) Å] and it is further bound to five sulfonate oxygen atoms pertaining to two laterally neighboring calixarenes and one other located on top of it. Some short Cs5···C contacts (shortest value 3.48 Å) exist with the aromatic ring bound to the latter coordinating sulfonate group. As a unique occurrence in this series of alkali metal ion complexes, Cs5 is bound to no water molecule. Some short contacts indicative of cation-π interactions are also present for the cations Cs3 (shortest value 3.69 Å) and Cs6 (3.44 Å) (Fig. 5). One cation in the structure of $Cs_5(\mathbf{L}_1{-}5H){\cdot}4H_2O$ is held in the calixarene cavity by cation-π interactions, with a shortest Cs···C contact of 3.59 Å, slightly longer than the shortest ones observed in compound **3**. Cesium polyhapto binding has also been described in calixcrown complexes, in which Cs···C contacts as short as 3.09 Å have been reported [5]. The sulfonate oxygen atoms are bound to a maximum of six different cations, which is also the maximum number of cations per sulfonate group. The conformation of the calixarene in compound **3** can be described by the dihedral angles between the aromatic rings and the mean plane defined by the six methylene carbon atoms, although, as in compound **2**, the latter is far from a well-defined plane (rms deviation 1.11 Å). These angles are 84.5(1), 50.3(1), 53.7(1) and 23.6(1)° for the four aromatic rings of the repeat unit, the first and last ones being those bisected by the symmetry plane. A possible better choice is to consider the dihedral angles between the aromatic rings and the mean planes defined by the three phenolic oxygen atoms in each subunit, i.e. 66.1 and 43.9° in the first subunit and 52.7 and 48.8° in the second. However, whereas the mean planes defined by the three phenolic oxygen atoms of each subunit were parallel in compound **2**, they define a dihedral angle of 47.6° in **3**. This conformation brings the adjacent terminal oxygen atoms of both subunits closer to one another than they were in compound **2**, with a separation O4···O8 of 4.48 Å, to be compared to a distance O1···O5 of 5.49 Å in **2**. It is likely that this conformation change is related to the bonding of Cs1 to these four oxygen atoms, bringing them in closer contact than in the more regular centrosymmetric *1,2,3-alternate* conformation. This, rather irregular geometry is also apparent from the ϕ and χ torsion angles, which define the sign sequence $(-\,+,-\,+,+\,-)$ in the repeat unit, with a value of $-12.7°$ for one angle of the central $-\,+$ which corresponds to the joining of the two reversed halves of the whole calixarene. The calixarenes in **3** are arranged in bi-layers of "up" and "down" units, separated by hydrophilic sheets. The hydrogen bonding pattern links water molecules between them and with phenolic and sulfonate groups. The Cs···Cs distances are in the range 4.71–5.67 Å.

These detailed structural analyses highlight the subtleties that are involved in attempting to define the bonding proclivities of the alkali metal ions when in interaction with ambidentate ligands. Clearly, these depend not only upon the nature of the different possible binding sites in ligands such as the sulfonated calixarenes but also upon the simple solvent molecules incorporated in the crystalline lattice and the way they interact not only with the cations but also with the ligands. The inability to prepare suitable crystals for structure determinations on all possible species in a series frustrates definitive interpretations but the weight of present evidence certainly supports the notion that cation-π interactions become increasingly important, relative to other possible donor interactions, with the heavier alkali metal ions. In the particular case of the formally octanegative anion derived from calix[6]-arene hexasulfonic acid in its complexes with Na^+ and Cs^+, the lack of obvious π-interactions with Na^+ suggests that it must be a weaker Lewis acid in this sense than is Cs^+. This may, however, be simply a consequence of the conformation of the calixarene and the geometric fit of the cation to the cavity defined by three aromatic rings, evidence from study of thiacalixarene complexes [7], for example, showing that π-interactions with Cs^+ may well be sensitive to such factors. Comparison of Rb^+ and Cs^+ in the present systems is complicated by the different charges on the calixarene in the two systems studied but it is clear that both cations are involved in interactions with the aromatic group π electrons to some extent, and the higher electron density that might be expected on an 8− anion by comparison with a 6− is possibly the explanation of the seemingly greater importance of these interactions in **3** than in **2**.

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