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FULL PAPER

Strontium complexes of calixarene amides in the solid state: structural dependence on the ligand size and on the counter ions

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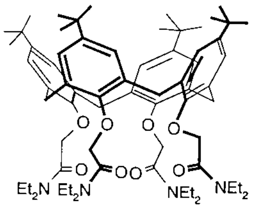
For the first time, crystal structures of three strontium complexes of calixarene amides have been determined. A *p-tert*-butylcalix[6]arene hexaamide forms a 1 : 1 complex with $Sr(Pic)_2$ (Pic = picrate), whereas *p-tert*-butylcalix[8]arene and *p*-methoxycalix[8]arene octaamides encapsulate two strontium cations each. The binding geometries of the metal cations depend on the ligand size and on the counter anion used (chloride or picrate).

Introduction

Calixarene-based ionophores have been of a great interest in the last few years in several fields such as membrane transport,[1,2] selective electrodes[3] and optodes,[4,5] and luminescent probes.[6,7] Calix[4]-crowns[8,9] and CMPO-like[10–12] calixarenes (CMPO being (diisobutylcarbamoyl)ocylphenyl phosphine oxide) have been used in radioactive waste treatment for the extraction of caesium and actinides, respectively. Very recently calix[6]- and calix[8]-arene amides were found to be efficient ionophores for the selective extraction of strontium from highly acidic radioactive solutions.[13] Despite the low concentration of strontium ion present (*ca.* 10^{-3} M), sodium is much more concentrated ($[NaNO_3] = 4$ M) and therefore ligands with high Sr^{2+}/Na^+ selectivity are desired.[14,15] Tetraamides (*e.g.* **1**)[16,17] of calix[4]arenes fixed in the *cone* conformation show a remarkable efficiency in binding alkali and alkaline-earth metal ions,[14] but selectivity within the alkali and alkaline-earth metal ions is for sodium and calcium, respectively. Contrary to tetraamide **1**, whose complexes with several metal ions such as Na^+,[18] K^+,[16,19] Sr^{2+},[20] Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}[21] were structurally characterised by X-ray diffraction, very few data are available for the complexes of calix-[6]- and -[8]-arene amides **2**–**4**.[22–24] Also with the aim of studying the origin of the observed strontium over sodium selectivity, we determined three crystal structures of strontium complexes with hexa- and octa-amides of calixarenes, which are the first examples of complexes between neutral calix[6]- or calix[8]-arene ligands and a main group metal ion.



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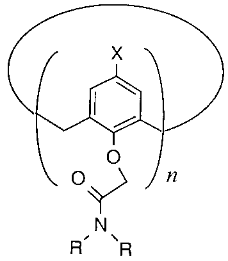

2a: *n* = 6, X = *tert*-Bu, R = Et
2b: *n* = 6, X = H, R = Et
3 : *n* = 8, X = *tert*-Bu, R = Et
4 : *n* = 8, X = OMe, R = Et

Experimental

Synthesis

The synthesis of hexaamide **2a** and octaamide **3** were carried out by alkylation of *p-tert*-butyl-calix[6]- and -calix[8]-arene, respectively, as reported.[23] Octaamide **4** was synthesized by methylation of *p*-hydroxycalix[8]arene octaamide[24] and its characterisation will be reported elsewhere. Complexes **I**–**III** were synthesized starting from the corresponding ligands (L) as follows and characterised by elemental analysis, electrospray mass spectrometry (ESI, ZMD Micromass) and X-ray diffraction on single crystals.

Complex I, $[Sr_2(4)(CH_3CO_2H)_4][Pic]_4\cdot 6CH_3CO_2H$ (Pic = picrate). Yellow crystals were obtained by slow evaporation at room temperature (48 h) of 3.5 ml of an ethyl acetate–methanol–diethyl ether–acetic acid (1:1:1:0.5) solution of octaamide **4** (15 mg, 7.5 μmol) and $Sr(Pic)_2$ (4 mg, 7.5 μmol). Yield (45%) (Found: C, 50.75; H, 5.53; N, 7.70. $C_{78}H_{100}N_{10}O_{36}Sr$ requires C, 50.88; H, 5.47; N, 7.61%). MS (ESI, methanol): 1040.4 ($[L + Sr]^{2+}$, 100), 571.5 ($[L + 2Sr + 2CH_3CO_2H]^{4+}$, 50), 602.0 ($[L + 2Sr + 4CH_3CO_2H]^{4+}$, 30), 798.8 ($[L + 2Sr + Pic]^{3+}$, 14), 1313.0 ($[L + 2Sr + 2Pic]^{2+}$, 8) and 2310.5 ($[L + Sr + Pic]^{+}$, 3%).

Complex II $[Sr_2(3)Cl]Cl_2\cdot 3CH_3OH\cdot 7H_2O$. Colourless crystals of complex **II** were obtained by slow evaporation (48 h) at room temperature of 4 ml of a dichloromethane–methanol (1:1) solution of octaamide **3** (15 mg, 7.5 μmol) and $SrCl_2$ (2 mg, 7.5 μmol). Yield (40%) (Found: C, 60.79; H, 8.37; N, 4.16. $C_{139}H_{226}Cl_4N_8O_{26}Sr_2$ requires C, 60.88; H, 8.31; N, 4.09%). MS (ESI, methanol): 1144.6 ($[L + Sr]^{2+}$, 100), 594.1 ($[L + 2Sr]^{4+}$, 25), 804.0 ($[L + 2Sr + Cl]^{3+}$, 20), 1224.0 ($[L + 2Sr + 2Cl]^{2+}$, 5) and 2324.9 ($[L + Sr + Cl]^{+}$, 1%).

Complex III $[Sr(2a)][Pic]_2\cdot CH_3C_6H_5$. Yellow crystals of complex **III** were obtained by slow evaporation (48 h) at room temperature of 4 ml of a dichloromethane–methanol–toluene

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Table 1 Crystal data and experimental parameters for the crystallographic study of complexes **I**–**III**

	I	**II**	**III**
Empirical formula	$C_{156}H_{200}N_{20}O_{72}Sr_2$	$C_{139}H_{226}Cl_4N_8O_{26}Sr_2$	$C_{121}H_{162}N_{12}O_{26}Sr$
Formula weight	3682.63	2742.40	2288.30
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1n$ (no. 15)
a/Å	16.045(2)	16.553(2)	20.766(5)
b/Å	16.769(3)	16.602(8)	28.012(5)
c/Å	18.527(2)	19.139(4)	23.306(5)
a/°	101.11(1)	72.19(3)	—
β/°	111.01(1)	69.87(1)	91.61(2)
γ/°	104.36(1)	60.09(3)	—
V/Å^3	4284(1)	4222(3)	13552(5)
Z	1	1	4
μ/cm^{-1}	7.24	7.54	11.06
T/K	173	173	295
Reflections measured	11188	10627	11380
Independent reflections	10195 ($R_{int} = 0.040$)	10061 ($R_{int} = 0.071$)	10981 ($R_{int} = 0.038$)
Observed reflections [$F_o \geqslant 4.0\sigma(F_o)$]	6002 (F)	5149	9576
Final $R1$, $wR2$	0.0526, 0.1088	0.091, 0.293	0.082, 0.215

(1:1:1) solution of hexaamide **2a** (11.25 mg, 7.5 μmol) and Sr(Pic)$_2$ (4 mg, 7.7 μmol). Yield (85%) (Found: C, 63.42; H, 7.19; N, 7.46. $C_{121}H_{162}N_{12}O_{26}Sr$ requires C, 63.51; H, 7.14; N, 7.35%). MS (ESI, methanol): 869.5 ([L + Sr]$^{2+}$, 100) and 1967.0 ([L + Sr + Pic]$^+$, 2%).

X-Ray crystallography

Data for the three structures were measured using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The most significant experimental details and structure analysis and refinement are collected in Table 1.

The structures were solved by Direct Methods in the WinGX[25] suite for complexes **I** and **II** and with SIR 92[26] for **III**. They were refined by full matrix least-squares methods on F^2 using SHELXL 97[27] (**I** and **II**) and SHELXL 93[28] (**III**). All the non-hydrogen atoms were refined with anisotropic thermal parameters excepting those involved in the static disorder which were treated with isotropic thermal parameters. The hydrogen atoms were included in the last stage of the refinement in their calculated positions according to the hybridisation of the atoms to which they were bonded and treated in the "riding" model. Geometrical parameters have been calculated by PARST.[29]

In the structure **II** the presence in the lattice of the water molecules is affected by severe static disorder that could be fitted by seven H_2O molecules distributed over eleven positions. After this, some further residual peaks remained in the final Fourier ΔF maps but they could not be fitted by a rational structural model.

CCDC reference numbers 186/2136.

See http://www.rsc.org/suppdata/dt/b0/b004402o/ for crystallographic files in .cif format.

Results and discussion

Despite the several crystal structures obtained with parent calix[6]arenes and calix[8]arenes with different metal ions,[30,31] where the macrocycle is acting as an ionisable ligand giving rise to complexes which are stable under restricted pH conditions or in a moisture excluded atmosphere, to the best of our knowledge there are no examples of complexes between a calix[8]arene neutral ligand and metal ions, while only two examples are reported with neutral calix[6]arene ligands and transition metal ions.[32,33] No crystal data are, however, known for complexes of alkali or alkaline-earth metal ions and modified calix[6]- or calix[8]-arene ligands despite several examples being available with tetrameric neutral ligands.

The strontium complexes of *p*-methoxycalix[8]arene octaamide **I**, *p*-*tert*-butylcalix[8]arene octaamide **II** and *p*-*tert*-butylcalix[6]arene hexaamide **III** have been characterised by X-ray diffraction.

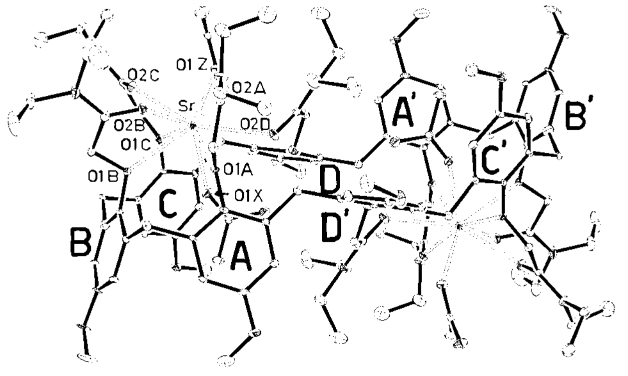

Fig. 1 An ORTEP[34] view of the structure of the cationic complex **I** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

The picrate complex **I** consists of two Sr^{2+} cations co-ordinated by the ligand, four picrate anions and ten CH_3CO_2H molecules from the mixture of solvents. The shape of the cationic complex, illustrated in Fig. 1, resembles that of a chair formed by two tetrameric sub-units co-ordinating the two metal cations and related to each other by a centre of symmetry. The Sr···Sr separation between the two strontium cations is 10.346(1) Å. In each tetrameric sub-unit three adjacent phenolic units (A,B,C) are mutually oriented as in a *cone* conformation. The fourth phenolic unit (D) is oriented as in a classical *flattened partial cone* conformation and lies almost parallel to the plane passing through the three bridging CH_2 groups of the cone. The D sub-unit (and its centrosymmetric equivalent) participates in the co-ordination of the cation only with its amide oxygen atom and acts as a connector between the two centrosymmetric trimeric subunits in the cone conformation. The most significant bond distances and angles are summarised in Table 2. The whole calix[8]arene conformation is unequivocally described by the conformational parameters[35] reported in Table 5 which lead to the C_i +−,+−,+−, symbolic representation. Table 7 reports the orientations of the four symmetry independent phenolic rings with respect to the conventional reference plane R[36] of the macrocycle.

Thus each metal cation is co-ordinated by nine oxygen atoms disposed in the form of a distorted capped square antiprism and is shielded from interactions with the counter anions. The three phenolic units in the cone conformation chelate the metal centre by their phenolic oxygen atoms O1A, O1B, O1C and their amide oxygen atoms O2A, O2B, O2C, whereas the fourth "flattened" phenolic unit binds the cation only through the

Table 2 Selected bond distances (Å) and angles (°) for complex **I**

Sr–O1A	2.691(4)	Sr–O2A	2.566(4)
Sr–O1B	2.737(4)	Sr–O2B	2.559(3)
Sr–O1C	2.753(3)	Sr–O2C	2.596(3)
Sr–O2D	2.840(4)	Sr–O1X	2.569(5)
Sr–O1Z	2.457(3)		
O1A–Sr–O2A	60.2(1)	O1A–Sr–O1B	77.4(1)
O1A–Sr–O2B	71.7(1)	O1A–Sr–O1C	138.1(1)
O1A–Sr–O2C	137.5(1)	O1A–Sr–O2D	82.6(1)
O1A–Sr–O1X	140.8(1)	O1A–Sr–O1Z	71.3(1)
O2A–Sr–O1B	117.7(1)	O2A–Sr–O2B	65.3(1)
O2A–Sr–O1C	161.7(1)	O2A–Sr–O2C	109.6(1)
O2A–Sr–O2D	80.7(1)	O2A–Sr–O1X	87.5(1)
O2A–Sr–O1Z	125.5(1)	O1B–Sr–O2B	58.9(1)
O1B–Sr–O1C	73.0(1)	O1B–Sr–O2C	72.5(1)
O1B–Sr–O2D	139.0(1)	O1B–Sr–O1X	141.0(1)
O1B–Sr–O1Z	70.3(1)	O2B–Sr–O1C	114.72(9)
O2B–Sr–O2C	67.2(1)	O2B–Sr–O2D	144.3(1)
O2B–Sr–O1X	116.7(1)	O2B–Sr–O1Z	121.8(1)
O1C–Sr–O2X	57.6(1)	O1C–Sr–O2D	100.9(1)
O1C–Sr–O1X	76.1(1)	O1C–Sr–O1Z	71.1(1)
O2C–Sr–O2D	139.1(1)	O2C–Sr–O1X	71.1(1)
O2C–Sr–O1Z	123.1(1)	O2D–Sr–O1X	69.8(1)
O2D–Sr–O1Z	69.5(1)	O1X–Sr–O1Z	120.4(1)

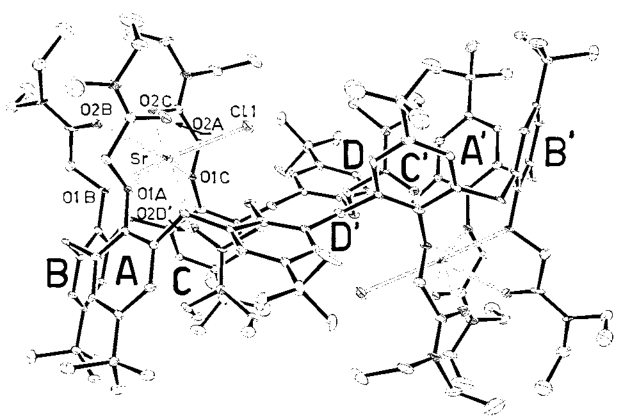

Fig. 2 An ORTEP view of the structure of the cationic complex **II**. Details as in Fig. 1.

amide oxygen O2D. Moreover none of the oxygen atoms O3 of the methoxy groups in the *para* positions is co-ordinated. The two remaining "axial" co-ordination positions are occupied by two acetic acid molecules: one lies inside the intramolecular cavity of the trimer and chelates the strontium cation through O1X and the second is hosted in the niche created by the terminal C_2H_5 groups of the amide chains and is bonded to the metal cation through O1Z. So the lower face (in Fig. 1) of the co-ordination polyhedron is formed by O1A, O1B, O1C and O2D and the extra position is occupied by the oxygen atom O1X of the acetic acid molecule inside the intramolecular cavity of the cone. The vertices of the upper face of the co-ordination polyhedron are occupied by the oxygen atoms of the three adjacent amide chains of the trimer (O2A, O2B, O2C) and by the oxygen atom of the second acetic acid molecule (O1Z). In the crystal lattice a complicated network of hydrogen bonds links the picrate anions to the acetic acid molecules not co-ordinated to the cations.

The *p*-*tert*-butylcalix[8]arene octaamide complex **II** is centrosymmetric and consists of two Sr^{2+} cations co-ordinated by the ligand, four chloride anions, three methanol molecules and seven H_2O molecules from the solvent. The most significant bond distances and angles are summarised in Table 3. The structure of the cationic complex (see Fig. 2) resembles that of **I**: the calix[8]arene surrounds the two cations as in **I** with three adjacent phenolic units as in a cone and the fourth one as in a flattened partial cone conformation, but the Sr ··· Sr separation between the two metal cations is now shortened to 9.650(4) Å.

Table 3 Selected bond distances (Å) and angles (°) for complex **II**

Sr–O1A	2.630(5)	Sr–O1B	2.634(8)
Sr–O1C	2.752(8)	Sr–O2A	2.524(10)
Sr–O2B	2.582(7)	Sr–O2C	2.529(6)
Sr–O2D′	2.461(9)	Sr–Cl1	2.888(3)
Cl–Sr–O1A	131.4(1)	Cl–Sr–O1B	149.9(1)
Cl–Sr–O1C	73.7(1)	Cl–Sr–O2A	85.3(2)
Cl–Sr–O2B	132.0(2)	Cl–Sr–O2C	82.3(2)
Cl–Sr–O2D′	92.4(2)	O1B–Sr–O2B	59.9(2)
O1B–Sr–O1A	77.1(2)	O1B–Sr–O2A	122.7(3)
O1B–Sr–O2D′	86.0(2)	O1B–Sr–O1C	76.6(3)
O1B–Sr–O2C	78.1(2)	O2B–Sr–O1A	69.9(2)
O2B–Sr–O2A	69.9(3)	O2B–Sr–O2D′	135.0(2)
O2B–Sr–O1C	117.4(2)	O2B–Sr–O2C	68.9(2)
O1A–Sr–O2A	60.4(3)	O1A–Sr–O2D′	74.7(2)
O1A–Sr–O1C	142.4(2)	O1A–Sr–O2C	138.5(2)
O2A–Sr–O2D′	114.6(3)	O2A–Sr–O1C	156.7(3)
O2A–Sr–O2C	108.8(3)	O2D′–Sr–O1C	77.0(3)
O2D′–Sr–O2C	135.6(2)	O1C–Sr–O2C	59.2(2)

However, the different counter anion induces a significant stereochemical change in the complex. Differently to that observed in **I**, here each Sr^{2+} cation is eight-co-ordinated in the form of a distorted square antiprism whose vertices are occupied by the three phenolic oxygen atoms O1A, O1B, O1C, by the three amide oxygen atoms O2A, O2B, O2C of the trimeric subunit and by the amide oxygen of the fourth phenolic unit O2D′. The eighth co-ordination position is filled by one of the two chloride ions at Sr–Cl1 2.888(3) Å. The other chloride ion is in the crystal lattice at 8.746(8) Å from the strontium cation. Thus the lower face of the antiprism (although distorted) is defined by O1A, O1B, O1C and O2D′ (the latter being responsible for the distortion), whereas the upper face of the co-ordination polyhedron is defined by O2A, O2B, O2C and Cl1.

Also quite different in complex **II** is the orientation of the fourth phenolic unit with respect to the cone trimeric subunit as indicated by the conformational parameters[35] in Table 5 (the symbolic representation for the molecular conformation of the cationic complex is C_i ++,+−,+−,+−) and by the dihedral angles between the least-squares plane through the phenolic rings and the molecular reference plane R.[36] Comparison with the corresponding values of **I** evidences the larger tilting of the fourth phenolic unit [127.6(2)° in **II** *vs.* 98.1(1)° in **I**] whereas the conformations of the trimeric cone subnunits are similar in the two complexes. Moreover, significant differences exist in the orientations of the terminal ethyl groups of the amide chains with respect to the corresponding ones in complex **I** although it is not easy to separate the contributions due to the different counter anions from that due to the different packing forces. Interestingly, both complexes **I** and **II** crystallised as dinuclear strontium complexes (Sr : L = 2 : 1) although equimolar amounts of strontium salt and ligand were used. This indicates a strong tendency of the first strontium ion to preorganise the chelating groups to host the second cation and therefore the existence of a positive cooperative effect between the two binding regions. Although such effects are not very frequent due to unfavourable Coulomb interactions between two cations, it has been shown by ^1H NMR[23] and mass spectrometry[37] that amide ligands derived from large calixarenes (*e.g.* **2a**) can form complexes with 2 : 1 (metal to ligand) stoichiometry.

The *p*-*tert*-butylcalix[6]arene complex **III** (see Fig. 3) consists of one Sr^{2+} cation co-ordinated by the ligand, two picrate anions and one toluene molecule from the crystallisation solvent. The most significant bond distances and angles are reported in Table 4. The metal ion is hosted in the polar niche created by the phenolic and amide oxygen atoms of five of the six phenolic subunits of the calixarene. The metal cation is eight-co-ordinated in the form of a distorted square antiprism.

Table 4 Selected bond distances (Å) and angles (°) for complex **III**

Sr–O2A	2.503(6)	Sr–O2C	2.439(7)
Sr–O1D	2.703(5)	Sr–O2D	2.485(7)
Sr–O1E	2.736(5)	Sr–O2E	2.538(7)
Sr–O1F	2.626(6)	Sr–O2F	2.573(6)
O2A–Sr–O2C	81.6(2)	O2A–Sr–O1D	102.2(2)
O2A–Sr–O2D	85.4(2)	O2A–Sr–O1E	162.5(2)
O2A–Sr–O2E	138.2(2)	O2A–Sr–O1F	107.9(2)
O2A–Sr–O2F	72.6(2)	O2C–Sr–O1D	76.0(2)
O2C–Sr–O2D	130.2(2)	O2C–Sr–O1E	82.0(2)
O2C–Sr–O2E	138.4(2)	O2C–Sr–O1F	87.1(2)
O2C–Sr–O2F	127.5(2)	O1D–Sr–O2D	60.1(2)
O1D–Sr–O1E	67.6(1)	O1D–Sr–O2E	100.2(2)
O1D–Sr–O1F	142.8(2)	O1D–Sr–O2F	153.1(2)
O2D–Sr–O1E	100.5(4)	O2D–Sr–O2E	75.8(2)
O2D–Sr–O1F	142.4(2)	O2D–Sr–O2F	93.0(2)
O1E–Sr–O2E	59.3(2)	O1E–Sr–O1F	77.4(2)
O1E–Sr–O2F	123.0(2)	O2E–Sr–O1F	71.1(2)
O2E–Sr–O2F	71.5(2)	O1F–Sr–O2F	60.1(2)

Table 5 Conformational parameters (°) for complexes **I** and **II**

	I		**II**	
	ϕ	χ	ϕ	χ
D–C	72.6(7)	−7.4(8)	37.6(1)	56.1(2)
C–B	68.9(6)	−83.4(6)	84.7(1)	−69.0(1)
B–A	78.0(6)	−70.8(7)	74.5(1)	−76.8(1)
A–D′	−32.8(8)	−68.3(7)	43.4(2)	−89.1(1)

[a] Centrosymmetric ring. Symmetry operations: $1 - x$, $1 - y$, $1 - z$ for complex **I** and $-x$, $1 - y$, $2 - z$ for **II**.

Table 6 Conformational parameters (°) for complex **III**

	ϕ	χ
A–B	96.9(1)	−54.7(1)
B–C	148.5(8)	125.1(9)
C–D	122.9(9)	−20.2(1)
D–E	79.4(1)	−84.0(1)
E–F	84.2(1)	−71.5(1)
F–A	25.1(1)	−81.0(1)

Table 7 Dihedral angles (°) between the least-squares reference molecular plane and the least-squares planes through the aromatic rings in complexes **I**–**III**

	I	II	III
R–A	116.5(1)	113.3(3)	154.8(2)
R–B	110.5(1)	112.5(2)	89.5(2)
R–C	98.1(1)	127.6(2)	124.8(2)
R–D	154.8(1)	151.1(3)	122.7(2)
R–E			105.3(2)
R–F			98.2(2)

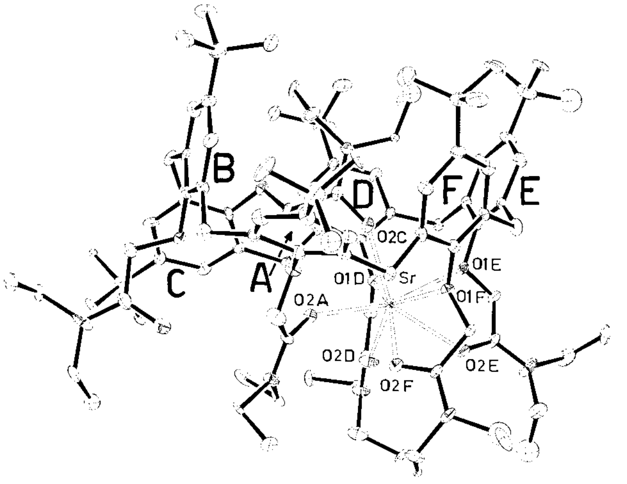

Fig. 3 An ORTEP view of the structure of the cationic complex **III**. Details as in Fig. 1.

Three adjacent phenolic subunits of the calix[6]arene D, E, F are mutually oriented as in a cone conformation and chelate the metal cation with their phenolic oxygen atoms O1D, O1E, O1F and their amide oxygen atoms O2D, O2E, O2F. The other two calixarene subunits A and C chelate the metal ion only through their amide oxygen atoms O2A, O2C. The remaining phenolic subunit B does not participate in the co-ordination. The conformational parameters[35] reported in Table 6 together with the dihedral angles[36] reported in Table 7 completely describe the conformation of the macrocyclic ligand in the cationic complex and suggests the C_1 +−,++,+−,+−,+−,+− symbolic representation. The vertices of one face of the distorted square antiprism are occupied by O1D, O2D, O1E, O2E, and those of the second face by O2C, O2A, O1F, O2F.

Comparison of these structural results with the structure of the *p-tert*-butylcalix[4]arene tetraamide **1** complex strontium previously reported[14] indicates that, among the ligands series, it is the latter that is more efficient: it binds the Sr^{2+} more strongly as shown by the shortest Sr–O distances and by the more regular co-ordination polyhedron. The Sr–O distances in the lower face (phenolic oxygen atoms) of the co-ordination polyhedron range from 2.556(5) to 2.592(6) Å [av. 2.577(5) Å] and those in the upper face (amide oxygen atoms) from 2.489(6) to 2.530(5) Å [av. 2.502(6) Å]. In the two calix[8]arene complexes the metal cation is more strongly bonded to the amide oxygen atoms and the av. Sr–O distances are identical, within the estimated standard deviations, [2.573(4) in **I** and 2.545(8) in **II**], and comparable to those in the calix[4]arene. On the contrary, quite longer, and spread over a larger range, are the $Sr–O_{Ph}$ bond distances in the two calix[8]arene complexes. For example in **I** the average Sr–O bond distance in the lower face of the co-ordination polyhedron is 2.755(4) Å. Such longer Sr–O values are attributable to the conformational constraints of the calix[8]arene which prevent the approach to the metal especially of the phenolic oxygen atoms as its size increases and the creation of a closed and symmetric polar cage of well defined dimensions as that in the calix[4]arene. In fact, for example, the acetic acid molecule (X) in **I** inside the aromatic cavity of each cone which has no steric constraints is free to approach the metal cation at 2.457(3) Å. Also in complex **II** the three $Sr–O_{Ph}$ distances show the same trend [av. 2.672(7) Å], whereas the fourth co-ordination site (O2D′) in the lower face of the co-ordination polyhedron is at 2.461(9) Å close to the Sr^{2+} ion. Interestingly, the acetic acid molecule X in **I** and the amide chain attached to the phenolic unit D′ in **II** are included in the calixarene lipophilic cavity created by the aromatic nuclei in what has been defined as "co-ordinative inclusion" by Harrowfield *et al.*[38]

The structure of the calix[6]arene complex **III** shows a similar trend; the Sr^{2+} ion is preferably bonded to the amide oxygen atoms [O2A, O2C, O2D, O2E, O2F, av. Sr–O 2.507(7) Å] than to the phenolic ones [O1D, O1E, O1F, av. Sr–O 2.688(6) Å], because of conformational constraints. However the higher number of OCH_2CO groups and the larger size of the macrocycle in the calix[8]arenes compared to those in the calix[6]arene allow the former to host two metal cations and the electrostatic repulsion between the two metal cations is compensated in **I** by the presence of four acetic acid molecules, which have access to the co-ordination spheres, and in **II** by the presence of two counter anions between them. On the contrary the calix[6]arene ligand is oversized for the complexation of one metal cation and undersized for two.

The higher Sr^{2+}/Na^{+} selectivity shown by calix[8]arene derivatives compared to those of calix[6]- and calix[4]-arene amides

[**4** ≈ **3** > **2a** > **1**] is mainly linked to the low binding ability of the larger calixarene ligands towards the sodium cation[13] and has a structural basis. Each polar niche for cation co-ordination in the calix[8]arenes is too large and cannot result in all the oxygen atoms being at 2.45–2.53 Å from the metal cation as required for co-ordination of Na$^+$ to *p-tert*-butylcalix[4]arene tetraamide **1**,[39] whereas those of the calix[6]- and calix[4]arenes can realise the fine-tuning of the Na–O distances needed for strong bonding of the sodium cation.

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References

1 F. de Jong and H. C. Visser, in *Comprehensive Supramolecular Chemistry*, ed. D. N. Reinhoudt, Pergamon Press, Oxford, 1996, vol. 1, pp. 13–51.
2 H. C. Visser, D. N. Reinhoudt and F. de Jong, *Chem. Soc. Rev.*, 1994, **23**, 75.
3 D. Diamond and M. A. McKervey, *Chem. Soc. Rev.*, 1996, **25**, 15.
4 T. Hayashito and M. Takagi, in *Comprehensive Supramolecular Chemistry*, ed. G. W. Gokel, Pergamon Press, Oxford, 1996, vol. 1, pp. 635–669.
5 M. Pietraszkiewicz, in *Comprehensive Supramolecular Chemistry*, ed. D. N. Reinhoudt, Pergamon Press, Oxford, 1996, vol. 10, pp. 225–266.
6 N. Sabbatini, M. Guardigli and I. Manet, *Adv. Photochem.*, 1997, **23**, 213.
7 N. Sabbatini, M. Guardigli and I. Manet, in *Handbook on the Physics and Chemistry of Rare Earths*, eds. K. A. Gschneider and L. Eyring, Amsterdam, 1996, vol. 23, p. 69.
8 A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M. J. Schwing, R. J. M. Egberink, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 2767.
9 J.-F. Dozol, V. Lamare, N. Simon, R. Ungaro and A. Casnati, in *Proceedings ACS Symposium* "*Calixarene Molecules for Separation*", 217 ACS Meeting, Anaheim, CA, 21–25 March, 2000, in press.
10 L. H. Delmau, N. Simon, M. J. Schwing-Weill, F. Arnaud-Neu, J. F. Dozol, S. Eymard, B. Tournois, V. Böhmer, C. Gruttner, C. Musigmann and A. Tunayar, *Chem. Commun.*, 1998, 1627.
11 S. Barboso, A. G. Carrera, S. E. Matthews, F. Arnaud-Neu. V. Böhmer, J. F. Dozol, H. Rouquette and M. J. Schwing-Weill, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 719.
12 L. H. Delmau, N. Simon, M. J. Schwing-Weill, F. Arnaud-Neu, J. F. Dozol, S. Eymard, B. Tournois, C. Gruttner, C. Musigmann, A. Tunayar and V. Böhmer, *Sep. Sci. Technol.*, 1999, **34**, 863.
13 J. F. Dozol, R. Ungaro and A. Casnati, *Fr. Pat.*, 99 10480, 17 August, 1999.
14 M. A. McKervey, M. J. Schwing-Weill and F. Arnaud-Neu, in *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. McNicol and F. Vögtle, Pergamon, New York, 1996, vol. 1, ch. 15, pp. 537–603.
15 R. Ungaro, A. Arduini, A. Casnati, A. Pochini and F. Ugozzoli, *Pure Appl. Chem.*, 1996, **68**, 1213–1218.
16 A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G. D. Andreetti, G. Calestani and F. Ugozzoli, *J. Incl. Phenom. Mol. Recognit. Chem.*, 1988, **6**, 119.
17 A. Casnati, Y. Ting, D. Berti, M. Fabbi, A. Pochini, R. Ungaro, D. Sciotto and G. G. Lombardo, *Tetrahedron*, 1993, **49**, 9815.
18 N. J. Wolf, E. M. Georgiev, A. T. Yordanov, B. R. Whittlesey, H. F. Koch and D. M. Roundhill, *Polyhedron*, 1999, **18**, 885.
19 G. Calestani, F. Ugozzoli, A. Arduini, E. Ghidini and R. Ungaro, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 344.
20 N. Muzet, G. Wipff, A. Casnati, L. Domiano, R. Ungaro and F. Ugozzoli, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1065.
21 P. D. Beer, M. G. B. Drew, P. B. Leeson and M. I. Ogden, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1273.
22 S. Fanni, F. Arnaud-Neu, M. A. McKervey, M. J. Schwing-Weill and K. Ziat, *Tetrahedron Lett.*, 1996, **37**, 7975.
23 A. Casnati, P. Minari, A. Pochini, R. Ungaro, W. F. Nijenhuis, F. de Jong and D. N. Reinhoudt, *Isr. J. Chem.*, 1992, **32**, 79.
24 A. Casnati, R. Ferdani, A. Pochini and R. Ungaro, *J. Org. Chem.*, 1997, **62**, 6236.
25 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
26 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
27 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
28 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.
29 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
30 D. M. Roundhill, *Prog. Inorg. Chem.*, 1995, **43**, 533.
31 C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93.
32 S. Blanchard, L. LeClainche, M. N. Rager, B. Chansou, J. P. Tuchagues, A. F. Duprat, Y. LeMest and O. Reinaud, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2732.
33 F. J. Parlevliet, A. Olivier, W. G. J. de Lange, P. C. J. Kamer, H. Kooijman, A. L. Spek and P. W. N. M. van Leeuwen, *Chem. Commun.*, 1996, 583.
34 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
35 F. Ugozzoli and G. D. Andreetti, *J. Incl. Phenom. Mol. Recognit. Chem.*, 1992, **13**, 337.
36 M. Perrin and D. Oehler, in *Calixarenes, a Versatile Class of Macrocyclic Compounds*, eds. J. Vicens and V. Böhmer, Kluwer Academic Publishers, Dordrecht, 1991, p. 65.
37 F. Inokuchi, Y. Shiomi, H. Kawabata, T. Sakaki and S. Shinkai, *Chem. Lett.*, 1993, 1595.
38 J. M. Harrowfield, M. I. Ogden and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2625.
39 A. Arduini, A. Pochini and F. Ugozzoli, unpublished results.