FULL PAPER

Alkali and Alkaline-Earth-Metalated Forms of Calix[4]arenes: Synthons in the Synthesis of Transition Metal Complexes

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Abstract: This is the first coherent report on the metalation of calix[4]arene by alkali and alkaline-earth metals, thus providing a high-yield production of appropriate synthons for the synthesis of transition metal calix[4]arenes. In addition, various facets of the coordination chemistry by calix[4]arene anions of alkali and alkaline-earth metal ions have been singled out. Among them: 1) the *exo* and *endo* coordination of metal ions by the calix[4]arene skeleton; 2) the π solvation of the ions by the phenyl rings; 3) the ion-carrier properties of metallacalix[4]arenes; 4) the simulation of the kinetically labile coordination sphere of alkali and alkaline-earth metal ions by a polyoxo rigid skeleton. The peculiarities of the complexation of alkali and alkaline-earth metal ions by calix[4]arenes outlined are deduced from the synthesis and the structural characterization both in solution (¹H NMR) and in the solid state (X-ray structure analysis) of the following classes of compounds: 1) [*p*-*t*Bu-calix[4](OMS$_n$)$_4$]$_2$ (M = Li, Na, K); 2) [*p*-*t*Bu-calix[4](OR)$_2$(O)$_2$ML] (M = Mg, L = THF, R = C$_5$H$_9$; M = Ca, L = TMEDA (tetramethylethylenediamine), R = C$_5$H$_9$; M = Ca, L = DME (dimethoxyethane), R = C$_5$H$_9$; M = Ba, L = TMEDA, R = C$_5$H$_9$; M = Ba, L = none, R = C$_5$H$_9$); 3) [*p*-*t*Bu-calix[4]-(OC$_5$H$_9$)$_2$(O)$_2$Ca$_2$I$_2$(MeCN)$_2$]; 4) [{*p*-*t*Bu-calix[4](OR)$_2$(O)$_2$}$_2$BaNa$_2$].

Keywords: alkali metals · alkaline-earth metals · calixarenes · metalations

Introduction

The entrance of calix[*n*]arenes as ancillary ligands into the organometallic arena[1] is achieved almost exclusively through the reaction of alkali metal calix[*n*]arenes[1, 2] with anhydrous metal halides in a metathesis reaction. This notwithstanding, it is very hard to find a coherent report on the metalation of calix[*n*]arenes by alkali and alkaline-earth metals. This is the purpose of the present report, which is focused on: 1) a synthetic procedure leading to the high-yield synthesis of alkali and alkaline-earth metal derivatives containing the fully deprotonated forms of calix[4]arenes; 2) their structural analysis; 3) the absence of any protic compound in the final material. A number of structural reports, more than on synthetic procedures, are available for partially deprotonated forms of alkali metal calix[4]arenes, mainly containing some additional protic species.[3–6] These are not appropriate for approaching the synthesis of transition metal derivatives designed for studying the reactivity of the metal center in an organometallic environment.[1]

The long-standing proposition on the use of calix[4]arene as ionophores for alkali and alkaline-earth metal ions has very seldom considered the corresponding alkali and alkaline-earth metalated forms. The latter would have both an intrinsic interest per se, and the potential application as carriers for additional metal ions of the same sort.

We report here details on: 1) the high-yield and large-scale synthesis and structural characterization of [*p*-*t*Bu-calix[4]-(OMS$_n$)$_4$] in two different solvated forms; 2) the synthesis of the metalated forms of the bis-alkylated derivatives [*p*-*t*Bu-calix[4](OR)$_2$(OH)$_2$] (R = Me, C$_5$H$_9$) both for alkali metal, [*p*-*t*Bu-calix[4](OR)$_2$(OM)$_2$] (M = Li, Na, K) and alkaline-earth metal ions, [*p*-*t*Bu-calix[4](OR)$_2$(O)$_2$MS$_n$] (M = Mg, Ca, Ba). The latter ones are unique mononuclear complexes of the Group 2 metals in the calix[4]arene series; 3) the ion-carrier properties, which are displayed by calcium derivatives towards CaI$_2$, thus forming an *exo – endo* dicalcium complex; 4) the formation of a sandwich bis-calix[4]arene – barium complex carrying sodium cations in the calix cavities.

Results and Discussion

The reaction of calix[4]arene freed from any protic solvent, which usually derives from its synthesis, has been carried out in THF with a slight excess of the alkali metal (Scheme 1).

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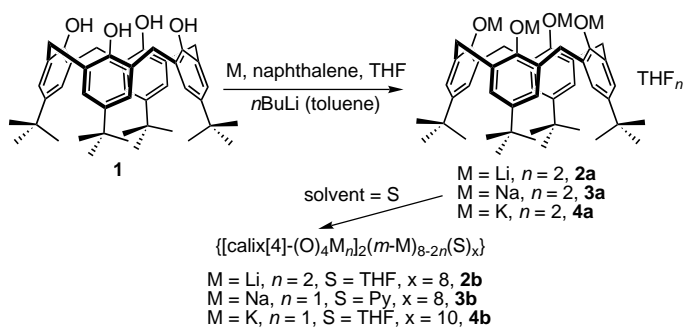
Scheme 1. Synthesis of alkali-metalated forms of calix[4]arene.

Following the procedure reported here, the solvation of the alkali complex remains constant, as shown for **2a**–**4a** (Scheme 1), and can be easily confirmed by ^{1}H NMR and GC-MS data. We refer to those species as synthetic intermediates in the transmetalation reactions. The X-ray analyses have been performed, however, on the recrystallized forms **2b**–**4b**, which have a different degree of solvation (Scheme 1). The NMR analyses were performed on the solvated forms **2a**–**4a**.

Both **3b** (Figure 1) and **4b** (Figure 2) consist of complex molecules in which two [(calix[4]arene)M]$^{3-}$ trianions (M = Na for **3b**; M = K for **4b**) are linked in dimers through
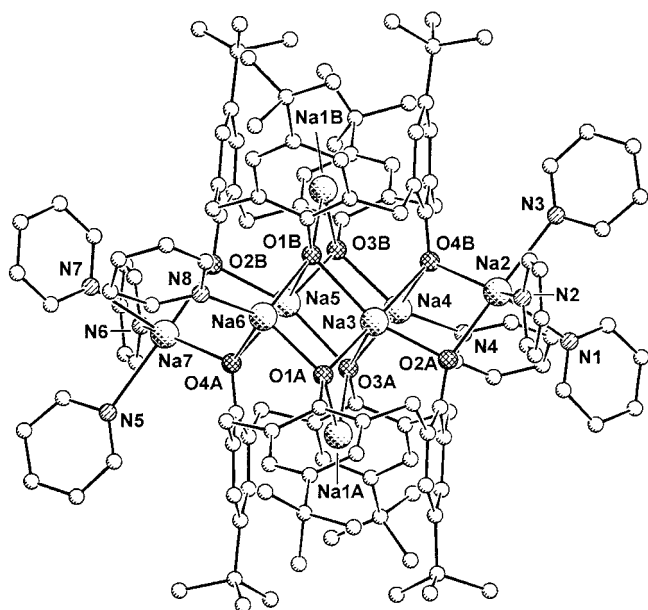
Figure 1. Structure of complex **3b** (SCHAKAL view; disorder affecting one *tert*-butyl group has been omitted for clarity).

interactions of the oxygen atoms with a bridging [M$_6$S$_x$]$^{6+}$ system (S$_x$ = py$_8$ for **3b**; S$_x$ = thf$_{10}$ for **4b**). Complex **4b** possesses crystallographically imposed C_i symmetry, the inversion center lying on the midpoint of the K2···K2′ and K3···K3′ separations (see Figure 2 and Table 1). The numbering scheme adopted for the calix[4]arene skeleton hereafter is given in Scheme 2.

The overall structure of **2b**–**4b** can be viewed as that of dimers, where the two monomeric tetraanions are bridged by
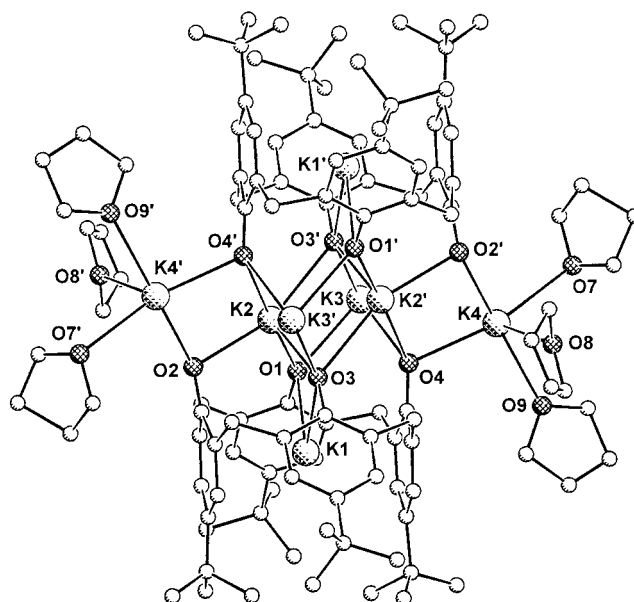

Figure 2. Structure of complex **4b** (SCHAKAL view; the THF molecules bonded to K3 and K3′ and disorder affecting some *tert*-butyl groups and THF molecules have been omitted for clarity). A prime denotes a transformation of $-x, -y, -z$.

Table 1. Selected bond lengths [Å] for complexes **3b** and **4b**.

3b			
Na1−O1A	2.335(8)	Na4−O4B	2.301(9)
Na1−O3A	2.438(8)	Na4−N4	2.473(11)
Na1−O1B	2.447(8)	Na5−O3A	2.407(9)
Na1−O3B	2.319(8)	Na5−O4A	2.527(7)
Na2−O2A	2.266(8)	Na5−O1B	2.384(9)
Na2−O4B	2.355(12)	Na5−O2B	2.245(10)
Na2−N1	2.511(13)	Na5−O3B	2.406(8)
Na2−N2	2.483(14)	Na6−O1A	2.271(9)
Na2−N3	2.552(12)	Na6−O4A	2.297(8)
Na3−O1A	2.438(8)	Na6−O1B	2.356(8)
Na3−O2A	2.227(10)	Na6−N8	2.403(12)
Na3−O3A	2.361(9)	Na7−O4A	2.335(10)
Na3−O1B	2.431(9)	Na7−O2B	2.258(7)
Na3−O4B	2.550(8)	Na7−N5	2.590(12)
Na4−O3A	2.371(8)	Na7−N6	2.507(14)
Na4−O3B	2.289(9)	Na7−N7	2.532(12)
4b			
K1−O1	2.759(8)	K3−O5B	2.784(15)
K1−O3	2.861(5)	K3−O6	2.811(9)
K2−O1	2.572(5)	K4−O4	2.644(8)
K2−O2	2.544(9)	K4−O2′	2.589(7)
K2−O3	2.553(7)	K4−O7	2.747(10)
K2−O3′	2.770(8)	K4−O8	2.744(11)
K2−O4′	2.782(5)	K4−O9	2.749(9)
K3−O1	2.653(9)	O1−C1	1.309(9)
K3−O4	2.704(7)	O2−C13	1.283(14)
K3−O3′	2.700(5)	O3−C20	1.327(13)
K3−O5A	2.688(16)	O4−C27	1.321(13)

eight alkali cations, with a 1:1 metal/solvent molecular ratio in the case of **2b** and **3b** (see Scheme 1). While the M$_8$O$_8$ core in complex **2b** has been recently structurally determined,[5] the unit has a quite different topology in the case of Na and K, even though the latter are very similar. Figures 3 and 4 display
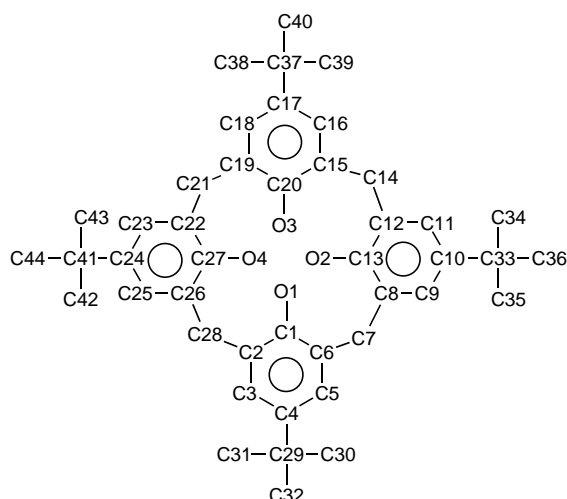
Scheme 2. Numbering scheme for the calix[4]arene skeleton.
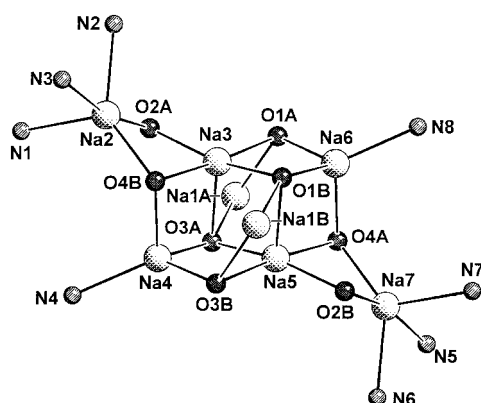
Figure 3. Coordination of the sodium cations in complex **3b** (SCHAKAL view).
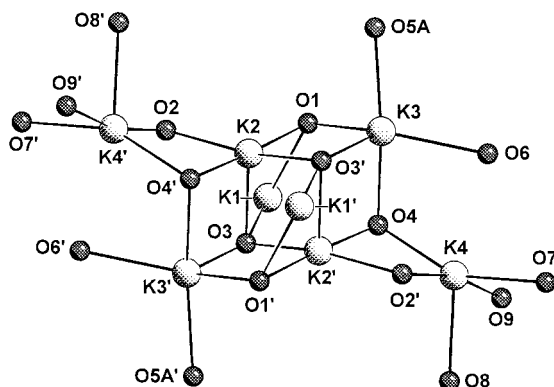
Figure 4. Coordination of the potassium cations in complex **4b** (SCHA-KAL view). Disorder affecting O5 has been omitted. A prime denotes a transformation of $-x, -y, -z$.

the M_8O_8 skeleton in complexes **3b** and **4b**, respectively. The potassium complex core shows the eight cations (four of which are solvent-free, while the remaining have different degrees of solvation by THF), thus forming two fused distorted tetrahedrons and two triangles along the bases of the fused tetrahedrons. Each tetrahedron has one of the faces centered by a single oxygen (O2) (O···faces, 1.208 Å,

complex **4b**), while O4 is shared between two faces (O···faces, 1.411, 1.711 Å, complex **4b**). The basal triangles are centered by a single oxygen atom (O···faces, 1.551 Å, **4b**). Structural details concerning the structure of **3b** and **4b** and their relationship are as follows:

a) Coordination geometry around the Na3 and Na5 cations in **3b** is a square pyramid, with O1A, O2A, O1B, O4B, and O3A, O4A, O2B, O3B defining the base plane for Na3 and Na5, respectively. The metals are displaced from the mean basal plane by 0.226(5) and 0.228(5) Å for Na3 and Na5, respectively. The Na3−O3A and Na5−O1B vectors are perpendicular to the basal plane, the dihedral angle they form with the normal to it being 3.4(2)° and 3.3(2)°, respectively. Analogous coordination is observed for the K2, K2′ cations in **4b**, with the O1, O2, O3′, O4′ and O3, O4, O1′, O2′ defining the basal planes and the O3 and O3′ atoms at the apices of the pyramids. The metals are displaced by 0.206(2) Å from the mean basal plane, the K2−O3 vector forming a dihedral angle of 8.3(1)° with the normal to it.

b) Na2 and Na7 in **3b** show a slightly distorted trigonal bipyramidal coordination, with the O4B, N1, N2 and O4A, N6, N7 defining the equatorial planes and the O2A, N3 and O2B, N5 atoms in the axial positions. The metals are displaced by 0.072(5) and 0.079(5) Å from the equatorial planes toward N3 and N5, respectively. The K4 (and the symmetry-related K4′) cation in **4b** displays a similar, even if distorted to a greater extent, coordination environment, with the O4, O7, O8 atoms defining the equatorial plane and the O9, O2′ in the axial positions. The metal atom lies on the equatorial plane within experimental error.

c) The coordination polyhedra around Na6 and Na4 in **3b** should be described as distorted tetrahedra, O1A, O4A, O1B, N8 and O3A, O3B, O4B, N4 defining the tetrahedron around Na6 and Na4, respectively. The corresponding K3 (and the symmetry-related K3′) cation in **4b** is five-coordinate, residing in a distorted trigonal bipyramid environment. The equatorial plane is defined by the O1, O6, O3′ atoms, the apices by the O4 and the disordered O5 oxygen atoms. The metal atom is displaced by 0.369(3) Å from the equatorial plane toward O5.

d) Both the Na1A and Na1B cations in **3b** are hosted inside the cavity of a calixarene macrocycle bonded to O1A, O3A and O1B, O3B, respectively, and displaying a η^6 interaction with the aromatic rings associated to O2A, O4A and O2B, O4B. The latter interactions are consistent with the narrow ranges of the Na···C$_{aromatic ring}$ separations (Na1A···C8A−C13A 2.869(17)−3.432(16), Na1A···C22A−C27A 2.828(16)−3.522(13), Na1B···C8B−C13B 2.865(15)−3.346(16), Na1B···C22B−C27B 2.807(16)−3.617(13) Å). Similarly, the K1 (and the symmetry-related K1′) cation in **4b** is bonded to O1 and O3 and through η^6 interactions with the aromatic rings[7] associated to O2 and O4 (K1···C8−C13 3.026(12)−3.244(14), K1···C22−C27 3.001(12)−3.342(11) Å).

In both complexes, the calixarene macrocycles show an elliptical conformation, the presence of alkali cation−C$_{aromatic}$ η^6 interactions forcing the opposite C8−C13 and C22−C27 aromatic rings to be nearly parallel.

All three metalated forms **2a–4a** are synthetically important, since the reaction with transition metal halides produces alkali halides displaying very different solubility in organic solvents, and various degrees of complexation of the alkali metal cation inside the calix[4]arene cavity or at the O_4 periphery.[3–6, 8] The complexation of alkali metal cations inside the calix[4]arene cavity is strongly dependent on the shape of the cavity, which is in turn determined by the coordination number of the transition metal ion fixed on the O_4 core. Significant selectivity has been observed for Li, Na, and K as a function of the size of the transition metal ion and its coordination geometry. The possible choice of producing LiX, NaX, or KX allows one to make salt-free transition metal calix[4]arene complexes.[8, 9]

A synthetically versatile calix[4]arene derivative is the dialkylated form,[10] which has been used for tuning the charge of the macrocycle and the degree of functionalization of the metal. Such an O_4 ligand has, in addition, a number of other significant characteristics, like the difference in binding strength between the two anionic and the two neutral oxygen atoms, as well as the possibility of creating, thanks to the steric hindrance of the alkyl groups, a protecting cavity for the transition metal. We chose two different R substituents, namely R = Me and cyclopentyl (see **5** and **6** in Scheme 3), as limiting cases. The preferential use of the cyclopentyl[11] substituent has been dictated by its good solubility. Owing to the limited structural information on this class of O_4 dianionic ligands, it would be interesting to report here the X-ray structural information on the protic form **6**.

Scheme 3. Synthesis of mononuclear alkaline-earth-metalated forms of calix[4]arene.

Two independent molecules of **6** are present (A and B) in the solid state, each one possessing a crystallographic imposed C_i symmetry. In Figure 5 a side view of molecule A is given. The main feature of **6** is the *chair* conformation assumed by the calixarene macrocycles, the opposite aromatic rings being oriented opposite with respect to the "reference" plane
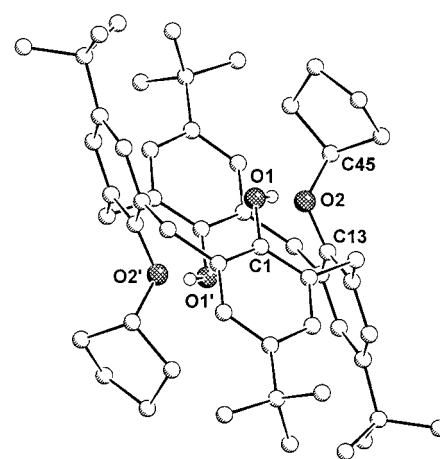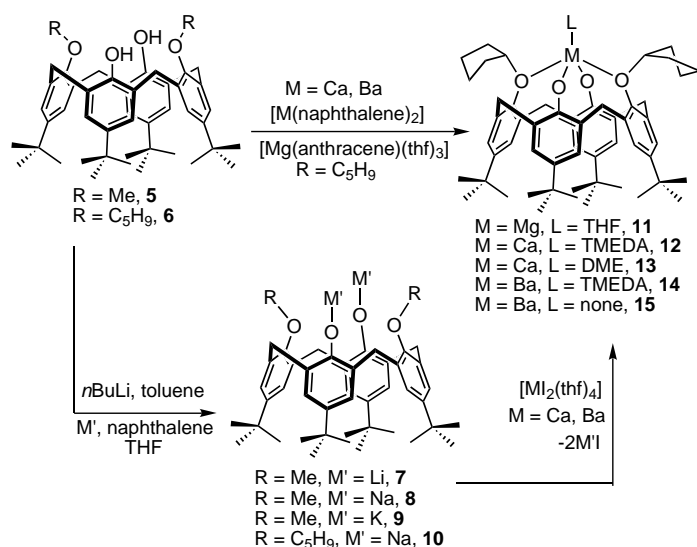

Figure 5. Molecule A in compound **6** (SCHAKAL view). A prime denotes a transformation of $1-x$, $-y$, $1-z$.

through the bridging methylene carbon atoms. This conformation is favored by the presence of intramolecular hydrogen bonds occurring between the proton associated to the O1, O1′ oxygen atoms and the adjacent O2, O2′ atoms: O1A−H1A 0.96 Å; O1A···O2A 2.751(2) Å; H1A···O2A 1.80 Å; O1A-H1A···O2A 173°; O1B−H1B 0.88 Å; O1B···O2B 2.742(2) Å; H1B···O2B 1.88 Å; O1B−H1B···O2B 165°.

The metalation of **5** and **6** has been carried out both using alkali and alkaline-earth metals. A structural report has appeared for the sodium derivative,[12] while the synthesis of the lithium and potassium derivatives has been carried out analogously to the conditions specified in Scheme 1. Details on the large scale synthesis of **7–10**, which are key intermediates in the synthesis of metalla-calix[4]arenes, are in the Experimental Section. Following our synthetic methods, such compounds can be used in situ in metathesis reactions, with inorganic salts.

A greater interest was focused on the alkaline-earth metals with the intent, thanks to the charge of the macrocycle, of making mononuclear complexes. Macrocyclic complexes of alkaline-earth metal ions are a quite rare species. In the case of Mg, the reaction has been carried out using a Mg–anthracene (complex **11**), while in the case of Ca and Ba, the active form of the metal has been employed (complexes **12–15** in Scheme 3). They have been isolated in different solvated forms, namely **12** and **13** in the case of Ca, **14** and **15** in the case of Ba. All of them display a C_2 symmetry in the ^{1}H NMR spectra. The C_2 symmetry is revealed by the existence of two singlets for the *t*Bu groups with the same integration and two singlets for the aromatic protons, while only one set of doublets is observed for the methylene groups. In addition, they show a quite analogous structure in the solid state. The structure of **11** is displayed in Figure 6. The complex possesses a crystallographically imposed C_2 symmetry, the twofold axis being coincident with the Mg1–O5 direction. Magnesium shows a trigonal-bipyramidal coordination, the O1, O1′, O5 oxygen atoms defining the equatorial plane and the O2, O2′ oxygen atoms in the axial positions. The metal center lies perfectly onto the equatorial plane for symmetry requirements. The O_4 core shows remarkable tetrahedral distortion,
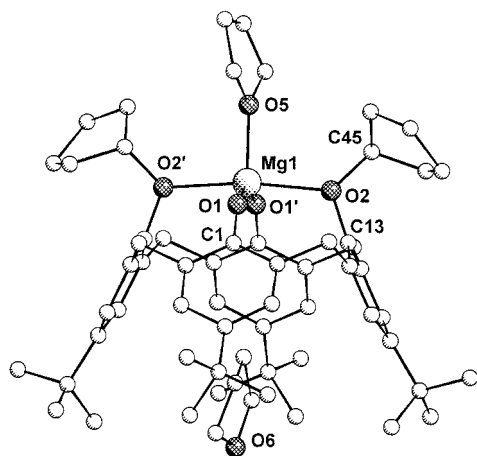
Figure 6. Structure of complex **11** (SCHAKAL view). Disorder affecting the THF molecules has been omitted for clarity. A prime denotes a transformation of $1 - x, -y, z$.

Figure 7. Structure of complex **12** (SCHAKAL view). Disorder affecting one *tert*-butyl group has been omitted for clarity.

the metal being displaced by 0.361(2) Å from the mean plane through it. The Mg distances to the anionic O1, O1′ oxygen atoms are remarkably shorter than those to the neutral O2, O2′, and O5 oxygen atoms, as expected (Table 2). The calixarene macrocycle displays a slightly elliptical conformation, this conformation allowing a THF molecule to be hosted into the calix cavity.

Table 2. Selected bond lengths [Å] for complexes **11** and **12**.

11			
Mg1−O1	1.849(4)	O1−C1	1.317(8)
Mg1−O2	2.232(4)	O2−C13	1.423(8)
Mg1−O5	2.033(4)	O2−C45	1.488(8)
12			
Ca1−O1	2.127(2)	O1−C1	1.318(4)
Ca1−O2	2.809(2)	O2−C13	1.412(4)
Ca1−O3	2.120(2)	O2−C45	1.462(4)
Ca1−O4	2.547(3)	O3−C20	1.318(4)
Ca1−N1	2.600(4)	O4−C27	1.416(4)
Ca1−N2	2.580(4)	O4−C50	1.459(3)

Complex **12** (Figure 7) contains naphthalene and *n*-pentane of crystallization.

The calix[4]arene skeleton displays an elliptic conformation, with Ca ion being −0.834(1) Å out of the O₄ average plane. The calcium cation, which is essentially pentacoordinate, interacts with only three of the oxygen atoms of the calix[4]arene ligand at short distances (Table 2), the Ca1−O2 distance being particularly long (2.809(2) Å). An alternative synthetic access to **12 – 15** is the metathesis reaction between **10** and calcium and barium iodides (see the Experimental Section). Complexes **11 – 15**, besides their interest as synthetic intermediates in the reaction with anhydrous transition metal salts, are rather unique complexes in the context of coordination chemistry of Group 2 metals.

The coordination number of the metal sitting on the O₄ surface is crucial in shaping the calix[4]arene cavity. The
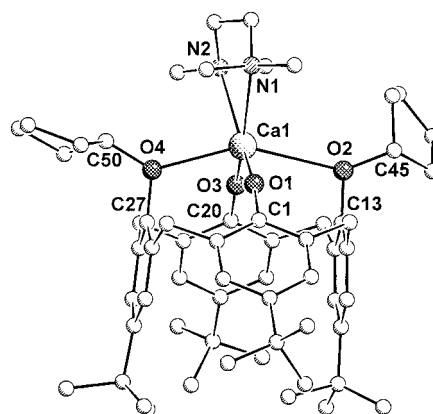
pentacoordination, for example, is diagnostic for a cylindrical calix[4]arene cavity, like in complex **11**, while, in the case of a hexacoordinate metal, like in complexes **12 – 14**, the calix[4]-arene skeleton displays an elliptical conformation. Such a conformation opens the cavity, which is able to host alkali metal cations. As a matter of fact, an interesting property of complexes **12** and **13**, which may be extended to other metalla-calix[4]arenes, is the ability to bind an additional metal ion inside the calix cavity. The reaction of **12** and **13** with CaI₂ dissolved in acetonitrile led to the formation of the dicalcium complex **16** (Scheme 4). Complex **16** emphasizes the metalla-calix[4]arenes ability in alkali and alkaline-earth metal ion carrying properties. Its solid state structure is shown in Figure 8. The Ca1 metal achieves a distorted octahedral
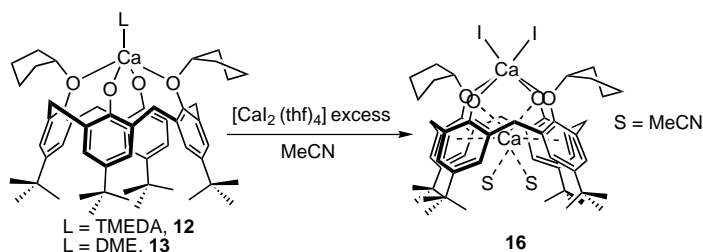
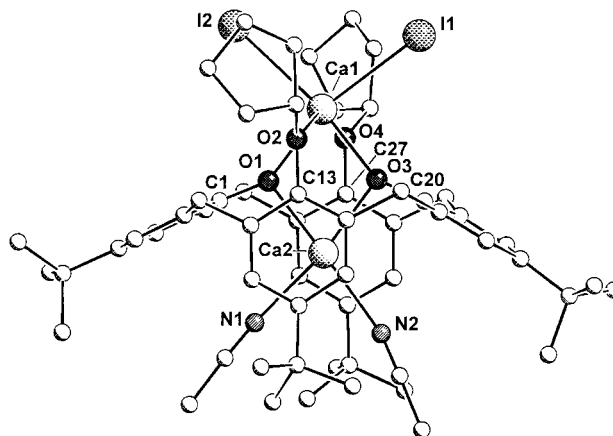Scheme 4. The ion-carrier properties of calcium-calix[4]arene.

Figure 8. Structure of complex **16** (SCHAKAL view).

coordination. The best equatorial plane is defined by the O1, O2, O4, I1 atoms, with the metal displaced by 0.424(1) Å toward I2 from the mean plane through them. The six-coordination to the metal removes the planarity of the O_4 core, thus producing an elongated elliptical conformation of the macrocycle. The Ca2 ion inside the cavity is bonded to O1 and O3, while it displays an η^6 interaction with two opposite aromatic rings (Ca2···$C_{aromatic\ rings}$ separations: Ca2···C8–C13 3.072(3)–3.515(3) Å; Ca2···C22–C27 3.014(4)–3.403(4) Å). Ca2 completes its coordination sphere with two acetonitrile molecules. The Ca–O bond lengths related to the neutral O2 and O4 (mean value 2.564(3) Å) are significantly longer than those involving the anionic O1 and O3 oxygen atoms (Table 3) for both the Ca ions. The π solvation of alkali
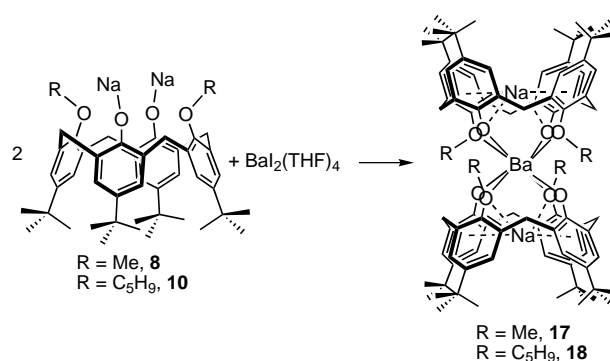
Scheme 5. The bis-calix[4]arene complex of barium complexing sodium cations.

Table 3. Selected bond lengths [Å] for complexes **16** and **18**.

16			
Ca1–I1	3.113(1)	Ca2–N1	2.445(3)
Ca1–I2	3.103(1)	Ca2–N2	2.479(4)
Ca1–O1	2.219(3)	O1–C1	1.339(4)
Ca1–O2	2.572(3)	O2–C13	1.401(5)
Ca1–O3	2.206(3)	O2–C45	1.479(4)
Ca1–O4	2.557(2)	O3–C20	1.336(4)
Ca2–O1	2.274(3)	O4–C27	1.400(5)
Ca2–O3	2.281(3)	O4–C50	1.479(4)
18			
Ba1–O1A	2.573(2)	Ba1–O1B	2.602(2)
Ba1–O2A	2.967(3)	Ba1–O2B	3.129(2)
Ba1–O3A	2.569(2)	Ba1–O3B	2.583(3)
Ba1–O4A	3.083(2)	Ba1–O4B	3.084(2)
Molecule A		*Molecule B*	
Na1–O1	2.329(3)	Na1–O1	2.241(3)
Na1–O3	2.266(3)	Na1–O3	2.300(2)
Na1–N1	2.370(3)		

and alkaline-earth metal ions has, very probably, a greater, than expected, contribution to their carrier processes both in chemical and biochemical systems. In addition, such a kind of bonding mode of aromatic rings to Ca has some significant precedents in the organometallic derivatives, though is much more rare to single out this interaction for neutral alkaline-earth metal ion derivatives.

In the case of large alkaline-earth metal ions, such as Ba^{II}, the dialkyl-calix[4]arene dianion, when a 2:1 ligand:metal molar ratio is used, can produce complexes where the metal ion is sandwiched between two anions, as exemplified by compounds **17** and **18** in Scheme 5. The structure of **18** has been clarified with an X-ray analysis and is shown in Figure 9. The two different calix[4]arene moieties are named A and B. Complex **18** crystallizes with pyridine solvent molecules in a complex/solvent stoichiometric molar ratio of 1/3. Electroneutrality of the complex is achieved by the presence of a [Na(py)]$^+$ ion hosted in the cavity of calixarene A and a Na$^+$ ion hosted in the cavity of calixarene B. The different nature of the included fragment and its different bonding mode is responsible of the distinct conformation displayed by the calixarene macrocycles. In particular:

Figure 9. Structure of complex **18** (SCHAKAL view). Disorder has been omitted for clarity.

1) The Na1A cation is bonded to calixarene unit A interacting with O1A and O3A and it completes its coordination binding to the opposite aromatic rings associated to O2A and O4A. The narrow range of values observed for the following contact distances involving C8A, C12A, C13A (Na1A···C8A 3.072(3); Na1A···C12A 3.167(3); Na1A···C13A, 2.934(3) Å; the contact distances with C9A, C10A, C11A are greater than 3.6 Å) and C22A, C26A, C27A (Na1A···C22A, 3.127(4); Na1A···C26A 3.097(3); Na1A···C27A 2.906(3) Å; the contact distances with C23A, C24A, C25A are greater than 3.6 Å) are consistent with a η^3 interaction of the aromatic ring with sodium cation. The elliptical conformation makes the appropriate room for pyridine entering the cavity and binding to the alkali metal.

2) The Na1B cation similarly binds to O1B and O3B and completes its coordination by interacting with the opposite aromatic rings associated to O2B and O4B. In the present case, however, the narrow range of the contact distances ((Na1B···C8B–C13B: 2.831(2)–3.438(4) Å; Na1B···C22B–C27B: 2.916(3)–3.159(2) Å)) are consistent with

η^6 interactions. The Ba–O bond lengths involving the anionic O1 and O3 (mean value 2.582(8) Å) are remarkably shorter than those involving the neutral O2 and O4 oxygen atoms (mean value 3.08(3) Å) (Table 3), as reported in this series of complexes.

3) These complexes maintain their structural features in solution since the ^{1}H NMR spectrum of **17** shows two distinct calixarene moieties A and B, displaying both a twofold symmetry.

The syntheses of **11 – 15** illustrate we can both produce some new calix[4]arene intermediates devoted to the synthesis of transition metal derivatives, and establish the coordination chemistry of Group 2 metal ions with calix[4]arenes. A major issue of this research was also to establish the solvation sphere of kinetically labile ions by the use of a rigid skeleton bearing both anionic and neutral oxygen donor atoms.

Experimental Section

Synthesis of 2a

Method A: nBuLi (39 mL, 1.73 N, 67.47 mmol) was added dropwise to a suspension of [p-tBu-calix[4]-(OH)$_4$]·(C$_7$H$_8$) (12.5 g, 16.87 mmol) in toluene (180 mL) at room temperature. The reaction mixture was heated overnight at 110 °C to give a white suspension. DME (40 mL) was added and volatiles were evaporated to dryness. The white residue was washed with n-hexane (90 mL) and dried in vacuo to yield [(p-tBu-calix[4]-(OLi)$_4$]·DME·(C$_6$H$_{14}$)$_{0.5}$ (12.7 g; 93%). ^{1}H NMR (400 MHz, [D$_6$]benzene and [D$_8$]THF, 25 °C, TMS): $\delta = 7.30$ (m, 2H; ArH), 7.24 (m, 2H; ArH), 6.94 (m, 2H; ArH), 6.91 (m, 2H; ArH), 4.75 – 4.50 (br, 2H; $endo$-CH$_2$) overlapping with 4.52 (d, $J = 13.2$ Hz, 2H; $endo$-CH$_2$), 3.32 – 3.18 (m, 4H; exo-CH$_2$) overlapping with 3.31 (s, 4H; DME), 3.11 (s, 6H; DME), 1.44 (s, 18H; tBu), 1.20 (m, 4H; C$_6$H$_{14}$) overlapping with 1.16 (s, 9H; tBu), 1.06 (s, 9H; tBu), 0.83 (m, 3H; C$_6$H$_{14}$); ^{1}H NMR (400 MHz, [D$_6$]benzene and [D$_8$]THF, 52 °C, TMS): $\delta = 7.28$ (m, 2H; ArH), 7.20 (m, 2H; ArH), 6.91 (m, 2H; ArH), 6.88 (m, 2H; ArH), 4.65 (d, $J = 12.4$ Hz, 2H; $endo$-CH$_2$), 4.45 (d, $J = 13.6$ Hz, 2H; $endo$-CH$_2$), 3.34 (s, 4H; DME), 3.27 (d, $J = 13.6$ Hz, 2H; exo-CH$_2$), 3.19 (d, $J = 12.8$ Hz, 2H; exo-CH$_2$), 3.14 (s, 6H; DME), 1.43 (s, 18H; tBu), 1.23 – 1.10 (m, C$_6$H$_{14}$) overlapping with 1.12 (s, 9H; tBu), 1.03 (s, 9H; tBu), 0.84 (m, 3H; C$_6$H$_{14}$); elemental analysis calcd (%) for **2**· DME·(C$_6$H$_{14}$)$_{0.5}$, C$_{51}$H$_{69}$Li$_4$O$_6$ (805.8): C 76.01, H 8.63; found: C 76.01, H 8.61. Crystals suitable for X-ray structure analysis were grown in a THF/ diglyme solution at 3 °C, leading to the solvated form **2b**.

Method B: Li (128 mg, 18.44 mmol) and naphthalene (2.38 g, 18.57 mmol) were added to a suspension of [p-tBu-calix[4]-(OH)$_4$]·(C$_7$H$_8$) (3.43 g, 4.63 mmol) in THF (120 mL) under an argon atmosphere. The reaction mixture was stirred overnight at room temperature to give a colorless solution. Volatiles were evaporated to dryness, and the white residue was washed with n-hexane (50 mL) and dried in vacuo to yield [(p-tBu-calix[4]-(OLi)$_4$]·(C$_4$H$_8$O)$_2$ (3.22 g, 85.5%). ^{1}H NMR (400 MHz, [D$_6$]benzene and [D$_8$]THF, 51 °C, TMS): $\delta = 7.39$ (m, 2H; ArH), 7.31 (m, 2H; ArH), 7.02 (m, 2H; ArH), 6.93 (m, 2H; ArH), 4.62 (d, $J = 12.5$ Hz, 2H; $endo$-CH$_2$), 4.49 (d, $J = 13.6$ Hz, 2H; $endo$-CH$_2$), 3.56 (m, 8H; THF), 3.33 (d, $J = 13.6$ Hz, 2H; exo-CH$_2$), 3.29 (d, $J = 12.5$ Hz, 2H; exo-CH$_2$), 1.52 (s, 18H; tBu), 1.45 (m, 8H; THF), 1.18 (s, 9H; tBu), 1.02 (s, 9H; tBu); elemental analysis calcd (%) for **2a**, C$_{52}$H$_{68}$Li$_4$O$_6$ (816.8): C 76.46, H 8.39; found: C 76.06, H 8.35.

Synthesis of 3a: Sodium (3.77 g, 164 mmol) and naphthalene (21.07 g, 164.4 mmol) were added to a suspension of [p-tBu-calix[4]-(OH)$_4$]·(C$_7$H$_8$) (29.7 g, 40.1 mmol) in THF (300 mL) at room temperature. The reaction mixture was refluxed overnight yielding a white solid in a slightly red solution. The solid was collected, washed with THF (3 × 50 mL), and dried in vacuo to yield [(p-tBu-calix[4]-(ONa)$_4$]·(C$_4$H$_8$O)$_2$ (33.9 g; 96%). ^{1}H NMR (400 MHz, [D$_5$]pyridine, 60 °C, TMS): $\delta = 7.00$ (s, 8H; ArH), 5.02 (d, $J = 13.4$ Hz, 4H; $endo$-CH$_2$), 3.63 (m, 8H; THF), 3.21 (d, $J = 13.4$ Hz, 4H; exo-CH$_2$), 1.59 (m, 8H; THF), 1.25 (s, 36H; tBu); elemental analysis calcd (%) for **3a**, C$_{52}$H$_{68}$Na$_4$O$_6$ (881.0): C 70.89, H 7.78; found: C

70.87, H 7.90. Crystals suitable for an X-ray structure analysis were grown in a pyridine solution, leading to the solvated form **3b**.

Synthesis of 4a: Potassium (1.47 g, 37.6 mmol) and naphthalene (4.83 g, 37.68 mmol) were added to a suspension of [p-tBu-calix[4]-(OH)$_4$]·C$_7$H$_8$ (6.98 g, 9.42 mmol) in THF (140 mL) at room temperature. The reaction mixture was stirred for 10 h and then refluxed overnight to give a white suspension. The solid was collected, washed with THF (50 mL), and dried in vacuo to yield [(p-tBu-calix[4]-(OK)$_4$]·(C$_4$H$_8$O)$_2$ (7.85 g; 88%). ^{1}H NMR (400 MHz, [D$_5$]Py, 25 °C, TMS): $\delta = 7.14$ (br, ArH), 4.94 (d, $J = 12.8$ Hz, 4H; $endo$-CH$_2$), 3.19 (d, $J = 12.8$ Hz, 4H; exo-CH$_2$), 1.39 (br, tBu); ^{1}H NMR (400 MHz, [D$_5$]Py, 72 °C, TMS): $\delta = 7.20$ (s, 8H; ArH), 4.95 (d, $J = 12.4$ Hz, 4H; $endo$-CH$_2$), 3.69 (m, 8H; THF), 3.20 (d, $J = 12.4$ Hz, 4H; exo-CH$_2$), 1.68 (m, 8H; THF), 1.44 (s, 36H; tBu); elemental analysis calcd (%) for **4a**, C$_{52}$H$_{68}$K$_4$O$_6$ (945.5): C 66.06, H 7.25; found: C 66.28, H 7.32. Crystals suitable for an X-ray structure analysis were obtained in a THF/TMEDA solution at 3 °C, leading to the solvated form **4b**.

Synthesis of 7: The synthesis of **7** has been carried out analogously to that of **2a**, either in THF or in toluene, to give in both case a colorless solution. Compound **7** was usually used in situ in the transmetalation reactions with the alkaline-earth metal salts. ^{1}H NMR of **7**, [p-tBu-calix[4]-(OMe)$_2$-(OLi)$_2$] (400 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 7.47$ (s, 4H; ArH), 6.93 (s, 4H; ArH), 4.69 (d, $J = 11.6$ Hz, 4H; $endo$-CH$_2$), 3.49 (s, 6H; OCH$_3$), 3.42 (d, $J = 11.6$ Hz, 4H; exo-CH$_2$), 1.53 (s, 18H; tBu), 0.76 (s, 18H; tBu).

Synthesis of 8: Na (1.41 g, 61.33 mmol) and naphthalene (7.88 g, 61.48 mmol) were added to a solution of **5**, [p-tBu-calix[4]-(OMe)$_2$-(OH)$_2$], (20.82 g, 30.75 mmol) in THF (350 mL) at room temperature. The reaction mixture was stirred overnight to give a white suspension. Volatiles were evaporated to dryness and n-hexane (80 mL) was added to the white residue. The solid was collected, washed again with n-hexane (2 × 30 mL), and dried in vacuo to yield [(p-tBu-calix[4]-(OMe)$_2$-(ONa)$_2$] (**8**) (19.1 g, 86%). ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 7.49$ (s, 4H; ArH), 7.07 (s, 4H; ArH), 4.81 (d, $J = 11.6$ Hz, 4H; $endo$-CH$_2$), 3.43 (s, 6H, OCH$_3$ overlapping with d, 4H; exo-CH$_2$), 1.54 (s, 18H; tBu), 0.76 (s, 18H; tBu); elemental analysis calcd (%) for **8**, C$_{46}$H$_{58}$Na$_2$O$_4$ (720.9): C 76.63, H 8.11; found: C 76.33, H 8.27.

Synthesis of 9: Potassium (2.32 g, 59.34 mmol) and naphthalene (7.61 g, 59.37 mmol) were added to a solution of **5**, [p-tBu-calix[4]-(OMe)$_2$-(OH)$_2$], (20.1 g, 29.69 mmol) in THF (300 mL) at room temperature. The reaction mixture was stirred overnight to give a white suspension. The solid was collected, washed with n-hexane (3 × 30 mL), and dried in vacuo to yield [(p-tBu-calix[4]-(OMe)$_2$-(OK)$_2$] (**9**) (18.8 g, 84%). ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 7.44$ (s, 4H; ArH), 7.29 (s, 4H; ArH), 4.39 (br, 4H; CH$_2$), 3.62 (br, 4H; CH$_2$), 3.50 (s, 6H; OCH$_3$), 1.51 (s, 18H; tBu), 1.07 (s, 18H; tBu). ^{1}H NMR (400 MHz, [D$_5$]pyridine, 67 °C, TMS): $\delta = 7.43$ (s, 4H; ArH), 7.28 (s, 4H; ArH), 4.45 (d, $J = 12.8$ Hz, 4H; $endo$-CH$_2$), 3.57 (s, 6H; OCH$_3$), 3.54 (d, $J = 12.8$ Hz, 4H; exo-CH$_2$), 1.54 (s, 18H; tBu), 1.12 (s, 18H; tBu); elemental analysis calcd (%) for C$_{46}$H$_{58}$K$_2$O$_4$ (753.1): C 73.36, H 7.76; found: C 73.63, H 7.95.

Synthesis of 10: The reaction of **6** with sodium and naphthalene in a 1:2:2 molar ratio in THF at room temperature led to a colorless solution of [p-tBu-calix[4]-(OCyp)$_2$-(ONa)$_2$] (**10**). It was usually used in situ in the following transmetalation reaction with the alkaline-earth metal salts (see synthesis of **12** and **14**). ^{1}H NMR of **10** (400 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 7.48$ (s, 4H; ArH), 7.07 (s, 4H; ArH), 4.78 (d, $J = 11.8$ Hz, 4H; $endo$-CH$_2$), 4.36 (m, 2H; OCyp), 3.36 (d, $J = 11.8$ Hz, 4H; exo-CH$_2$), 1.88 (m, 4H; OCyp), 1.59 (m, 4H; OCyp) overlapping with 1.54 (s, 18H; tBu), 1.44 (m, 4H; OCyp), 1.26 (m, 4H; OCyp), 0.89 (s, 18H; tBu).

Synthesis of 11: [p-tBu-calix[4]-(OCyp)$_2$-(OH)$_2$] (4.03 g, 5.13 mmol) and [Mg(anthracene)(thf)$_3$] (2.14 g, 5.11 mmol) were suspended in THF (140 mL) at room temperature. The reaction mixture was stirred overnight to yield a yellowish solution. A small amount of solid was filtered off and volatiles were evaporated to dryness. The resulting residue was washed with n-hexane (40 mL) and dried in vacuo to give [(p-tBu-calix[4]-(OCyp)$_2$-(O)$_2$Mg(thf)] as a white powder (2.22 g, 61.4%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 7.46$ (s, 4H; ArH), 7.08 (s, 4H; ArH), 4.61 (d, $J = 12.2$ Hz, 4H; $endo$-CH$_2$), 4.47 (m, 2H; OCyp), 3.85 (m, 4H; THF), 3.40 (d, $J = 12.2$ Hz, 4H; exo-CH$_2$), 1.88 (m, 4H; OCyp), 1.64 (s, 18H; tBu), 1.48 (m, 16H; THF overlapping with OCyp), 1.13 (s, 18H; tBu); elemental analysis calcd (%) for **11**, C$_{58}$H$_{78}$MgO$_5$ (879.5): C 79.20, H 8.94; found: C

79.41, H 8.93. Crystals suitable for X-ray structure analysis were grown in a THF solution at 3°C.

Synthesis of 12: Sodium (0.22 g, 9.57 mmol) and naphthalene (1.24 g, 9.67 mmol) were added to a solution of [*p-t*Bu-calix[4]-(OCyp)$_2$-(OH)$_2$] (3.79 g, 4.83 mmol) in THF (120 mL). The reaction mixture was stirred overnight at room temperature to give a colorless solution. [CaI$_2$(thf)$_4$] (2.81 g, 4.83 mmol) was added and the mixture was refluxed for one day. Volatiles of the resulting solution were evaporated, and toluene (120 mL) was added to give a white suspension. The solid was filtered off and TMEDA (ca. 1 mL) was added. Volatiles were evaporated to dryness to give a white residue which was washed with pentane (40 mL) and dried in vacuo to yield [(*p-t*Bu-calix[4]-(OCyp)$_2$-(O)$_2$)Ca(tmeda)] (3.86 g; 85%). ^{1}H NMR (400 MHz, [D$_5$]Py, 25°C, TMS): δ = 7.49 (s, 4H; ArH), 7.06 (s, 4H; ArH), 4.78 (d, *J* = 11.6 Hz, 4H; *endo*-CH$_2$), 4.37 (m, 2H; OCyp), 3.42 (d, *J* = 11.6 Hz, 4H; *exo*-CH$_2$), 2.36 (s, 4H; TMEDA), 2.14 (s, 12H; TMEDA), 1.67 (m, 8H; OCyp), 1.57 (s, 18H; *t*Bu), 1.32 (m, 4H; OCyp), 1.10 (m, 4H; OCyp), 0.92 (s, 18H; *t*Bu); elemental analysis calcd (%) for **12**, C$_{60}$H$_{86}$CaN$_2$O$_4$ (939.4): C 76.71, H 9.23, N 2.98; found: C 76.81, H 8.88, N 2.52. Crystals suitable for X-ray structure analysis were grown in a THF/pentane solution at 3°C.

Synthesis of 13: [*p-t*Bu-calix[4]-(OCyp)$_2$-(OH)$_2$] (5.04 g, 6.42 mmol) was added to a black suspension of active calcium (6.42 mmol) in THF (150 mL) at room temperature. This rapidly led to a colorless solution which was stirred overnight. Volatiles were evaporated to dryness, and toluene (150 mL) was added to give a white suspension which was stirred for a few minutes. The solid was filtered off and DME (5 mL) was added. Volatiles were evaporated to dryness to give a white residue which was washed with pentane (40 mL) and dried in vacuo to yield [(*p-t*Bu-calix[4]-(OCyp)$_2$-(O)$_2$)Ca]·DME (4.98 g, 84.9%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C, TMS): δ = 7.43 (s, 4H; ArH), 7.10 (s, 4H; ArH), 4.55 (d, *J* = 11.6 Hz, 4H; *endo*-CH$_2$), 4.45 (m, 2H; OCyp), 3.34 (d, *J* = 11.6 Hz, 4H; *exo*-CH$_2$), 3.27 (br. s, 6H; DME), 2.88 (br. s, 4H; DME), 1.85 (m, 4H; OCyp), 1.67 (m, 4H; OCyp), 1.59 (s, 18H; *t*Bu) overlapping with (m, 4H; OCyp), 1.35 (m, 4H; OCyp), 1.14 (s, 18H; *t*Bu); elemental analysis calcd (%) for **13**, C$_{58}$H$_{80}$CaO$_6$ (913.3): C 76.27, H 8.83; found: C 76.09, H 8.74.

Synthesis of 14: Sodium (0.29 g, 12.61 mmol) and naphthalene (1.63 g, 12.72 mmol) were added to a solution of [*p-t*Bu-calix[4]-(OCyp)$_2$-(OH)$_2$] (5 g, 6.37 mmol) in THF (150 mL). The reaction mixture was stirred overnight at room temperature to give a colorless solution. [BaI$_2$(thf)$_4$] (4.34 g, 6.39 mmol) was added and the mixture was refluxed overnight. Volatiles were evaporated and toluene (150 mL) was added to give a white suspension. The solid was filtered off and TMEDA (ca. 1 mL) was added. Volatiles were evaporated to dryness to give a white residue which was washed with *n*-hexane (40 mL) and dried in vacuo to yield [(*p-t*Bu-calix[4]-(OCyp)$_2$-(O)$_2$)Ba(tmeda)] (4.64 g; 71%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C, TMS): δ = 7.33 (s, 4H; ArH), 6.94 (s, 4H; ArH), 4.74 (d, *J* = 12.4 Hz, 4H; *endo*-CH$_2$), 4.49 (m, 2H; OCyp), 3.21 (d, *J* = 12.4 Hz, 4H; *exo*-CH$_2$), 2.34 (brs, 4H; TMEDA), 2.13 (br. s, 12H; TMEDA), 1.84 (m, 4H; OCyp), 1.77 (m, 4H; OCyp), 1.55 (s, 18H; *t*Bu), 1.26 (m, 4H; OCyp), 1.07 (m, 4H; OCyp), 0.98 (s, 18H; *t*Bu); elemental analysis calcd (%) for **14**, C$_{60}$H$_{86}$BaN$_2$O$_4$ (1036.6): C 69.52, H 8.36, N 2.70; found: C 69.44, H 7.96, N 2.30.

Synthesis of 15: [*p-t*Bu-calix[4]-(OCyp)$_2$-(OH)$_2$] (4.07 g, 5.18 mmol) was added to a black suspension of active barium (5.19 mmol) in THF (150 mL) at room temperature. This rapidly led to a white suspension which was stirred overnight. Volatiles were evaporated to dryness, and toluene (150 mL) was added again giving a white suspension. The solid was filtered off. Volatiles were evaporated to dryness and the white residue was dried in vacuo (10^{-6} Torr) to give [(*p-t*Bu-calix[4]-(OCyp)$_2$-(O)$_2$)Ba] (4.20 g, 89%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C, TMS): δ = 7.32 (s, 4H; ArH), 6.94 (s, 4H; ArH), 4.74 (d, *J* = 12.4 Hz, 4H; *endo*-CH$_2$), 4.49 (m, 2H; OCyp), 3.20 (d, *J* = 12.4 Hz, 4H; *exo*-CH$_2$), 1.84 (m, 4H; OCyp), 1.77 (m, 4H; OCyp), 1.55 (s, 18H; *t*Bu), 1.25 (m, 4H; OCyp), 1.07 (m, 4H; OCyp), 0.98 (s, 18H; *t*Bu); elemental analysis calcd (%) for **15**, C$_{54}$H$_{70}$BaO$_4$ (920.4): C 70.46, H 7.66; found: C 70.23, H 7.78.

Synthesis of 16: [CaI$_2$(thf)$_4$] (4.58 g, 7.86 mmol) was added to a solution of [(*p-t*Bu-calix[4]-(OCyp)$_2$-(O)$_2$)Ca]·DME (2.02 g, 2.21 mmol) in acetonitrile (130 mL) and the reaction mixture was refluxed overnight. The resulting colorless solution was concentrated to about 30 mL and the resulting white crystalline precipitate was collected and dried in vacuo. ^{1}H NMR (400 MHz, [D$_3$]acetonitrile, 25°C, TMS): δ = 7.26 (s, 4H; ArH), 7.12 (s, 4H; ArH), 4.61 (m, 2H; OCyp), 4.16 (d, *J* = 13.6 Hz, 4H; *endo*-CH$_2$), 3.41 (d, *J* = 13.6 Hz, 4H; *exo*-CH$_2$), 2.06 (m, 4H; OCyp), 1.95 (m, 8H; OCyp overlapping with CH$_3$CN), 1.61 (m, 4H; OCyp), 1.33 (s, 18H; *t*Bu), 1.09 (s, 18H; *t*Bu). Crystals suitable for an X-ray structure analysis were obtained by recrystallization in acetonitrile at 3°C, and the compound

Table 4. Experimental data for the X-ray diffraction studies on crystalline compounds **3b**, **4b**, **6**, **11**, **12**, **16**, and **18**.

Compound	3b	4b	6	11	12	16	18
formula	C$_{128}$H$_{144}$N$_8$Na$_8$O$_8$	C$_{128}$H$_{184}$K$_8$O$_{18}$· 4C$_4$H$_8$O	C$_{54}$H$_{72}$O$_4$· C$_6$H$_{14}$	C$_{58}$H$_{78}$MgO$_5$· C$_4$H$_8$O	C$_{60}$H$_{86}$CaN$_2$O$_4$· C$_{10}$H$_8$·C$_5$H$_{12}$	C$_{58}$H$_{76}$Ca$_2$I$_2$N$_2$O$_4$· 5C$_2$H$_3$N	C$_{113}$H$_{145}$BaNNa$_2$O$_8$· 3C$_5$H$_5$N
a [Å]	25.350(5)	15.127(3)	13.480(3)	12.664(2)	18.394(3)	12.650(3)	24.359(2)
b [Å]	14.563(3)	15.124(3)	14.148(3)	12.664(2)	16.264(5)	12.233(2)	19.082(2)
c [Å]	34.227(7)	19.722(4)	16.552(3)	33.669(7)	23.841(4)	24.057(3)	26.643(3)
α [°]	90	110.69(3)	110.21(3)	90	90	75.47(1)	90
β [°]	110.71(3)	93.62(3)	107.21(3)	90	104.36(2)	75.52(1)	112.97(1)
γ [°]	90	111.67(3)	102.79(3)	90	90	80.56(1)	90
V [Å^3]	11819(5)	3824.2(20)	2638.9(15)	5399.7(16)	6909(3)	3468.7(9)	11402(2)
Z	4	1	2	4	4	2	4
formula weight	2106.5	2612.1	871.3	951.7	1139.8	1404.5	2066.0
space group	*P*2$_1$/*n* (no. 14)	*P*1̄ (no 2)	*P*1̄ (no. 2)	*P*4̄2$_1$*c* (no. 114)	*P*2$_1$/*n* (no. 14)	*P*1̄ (no. 2)	*P*2$_1$/*n* (no. 14)
T [°C]	143	143	143	143	143	143	143
λ [Å]	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
ρ_{calcd} [g cm^{-3}]	1.184	1.134	1.097	1.171	1.096	1.345	1.204
μ [cm^{-1}]	0.98	2.85	0.62	0.78	1.38	10.88	4.14
transmission coeff	0.999–1.000	0.997–1.000	0.999–1.000	0.998–1.000	0.998–1.000	0.905–1.000	0.994–1.000
R [a,b]	0.087	0.101	0.079	0.059 [0.060]	0.077	0.042	0.050
wR$_2$	0.211	0.284	0.229	0.148 [0.150]	0.232	0.099	0.137
GOF	0.990	0.970	0.976	1.012	1.063	1.016	1.038
N observed [c]	3573	3903	6801	1755	7837	9910	14707
N independent [d]	12178	8561	10777	3303	11330	14435	18095
N refinement [e]	9588	7418	9850	2925	10543	13800	17360
variables	1363	759	578	311	736	748	1288

[a] Calculated on the observed reflections having *I* > 2σ(*I*). [b] Values in square brackets refer to the "inverted" structure. [c] *N* observed is the total number of the independent reflections having *I* > 2σ(*I*). [d] *N* independent is the number of independent reflections. [e] *N* refinement is the number of reflection used in the refinement having *I* > 0 and corrected for absorption.

was analyzed as a CaI$_2$ adduct, [{(*endo*-Ca(CH$_3$CN)$_2$)({*p-t*Bu-calix[4]-(OCyp)$_2$-(O)$_2$CaI$_2$}] · 5 CH$_3$CN.

Synthesis of 17 and 18: The reaction of **8** or **10** with [BaI$_2$(thf)$_4$] in a 2:1 molar ratio and in refluxing THF led to the bis-calix[4]arene-barium species **17** and **18**, respectively. A THF/pyridine solution of **18** gave crystals suitable for an X-ray structure analysis: {bis(*p-t*Bu-calix[4]arene-(OCyp)$_2$-(O)$_2$)Ba}{Na$_2$}. Compounds **17** and **18** display the expected C_2 symmetry in the ^{1}H NMR spectra. ^{1}H NMR of {bis(*p-t*Bu-calix[4]arene-(OMe)$_2$-(O)$_2$)Ba}{Na$_2$} (**17**) (400 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 7.49$ (s, 4H, ArH); 7.46 (s, 4H, ArH); 7.08 (s, 4H, ArH); 7.04 (s, 4H, ArH); 4.91 (d, $J = 11.7$ Hz, 4H, *endo*-CH$_2$); 4.70 (d, $J = 12$ Hz, 4H, *endo*-CH$_2$); 3.93 (s, 6H, OCH_3); 3.90 (s, 6H, OCH_3); 3.50 (d, $J = 11.7$ Hz, 4H, *exo*-CH$_2$); 3.34 (d, $J = 12$ Hz, 4H, *exo*-CH$_2$); 1.55 (s, 18H, *t*Bu); 1.52 (s, 18H, *t*Bu); 0.91 (s, 18H, *t*Bu); 0.89 (s, 18H, *t*Bu).

X-ray crystallography for compounds 3b, 4b, 6, 11, 12, 16, and 18: Single crystals suitable for X-ray diffraction were grown from common organic solvents (Table 4). Data for **3b**, **4b**, **6**, **11**, **12**, and **18** were collected on a MAR345 IPDS image plate at 143 K using Mo$_{K\alpha}$ radiation, while those for **16** were collected on a Rigaku AFC7S diffractometer equipped with a Mercury CCD detector at 143 K using Mo$_{K\alpha}$ radiation. The solutions and refinements were carried out using the programs SHELX76[13] and SHELX93.[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-173769 (**3b**), CCDC-173770 (**4b**), CCDC-173771 (**6**), CCDC-173772 (**11**), CCDC-173773 (**12**), CCDC-173774 (**16**), CCDC-173775 (**18**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223 – 336 – 033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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