Tuning the Stoichiometry of Lanthanide Complexes with Calixarenes: Bimetallic Complexes with a Calix[6]arene Bearing Ether-Amide Pendant Arms

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A de-tert-butylated calix[6]arene (A₆L₆) fitted with six ether-amide pendant arms was synthesized and characterized in solution. NMR spectroscopic data point to the six phenoxide units adopting an average D₆h conformation on the NMR time scale. According to MM3 molecular mechanics, and MOPAC quantum mechanical calculations, A₆L₆ is a ditopic ligand featuring two nonadentate coordination sites, each built from three pendant arms, and extending in opposite directions with one above, and the other under the main ring. A₆L₆ reacts with LnIII ions (Ln = La, Eu) in acetonitrile to successively form 1:1 and 2:1 complexes. The isolated EuIII 2:1 complex is luminescent (quantum yield: 2.5% in acetonitrile, upon ligand excitation). In the solid state, the luminescence decay is bi-exponential, with lifetimes equal to 1.66 and 0.46 ms (upon direct metal excitation), pointing to the presence of two differently coordinated metal ions, one with essentially no bound water molecules, and the other one with two ligated water molecules. According to molecular mechanics calculations, the more stable isomer is indeed asymmetric with two nine-coordinated metal ions. Both EuIII ions are bound to three bidentate arms, and one monodentate triflate anion, but one metal ion completes its coordination sphere with two phenoxide oxygen atoms, and the other one with two water molecules, consistent with IR spectroscopic and luminescence data. In acetonitrile solution, the two metal ion sites become equivalent, and the relatively long lifetime (1.35 ms) is indicative of a coordination environment free of water molecules. This work demonstrates, that the stoichiometry of lanthanide complexes with calixarenes can be tuned by a suitable choice of the narrow and/or wide rim substituents.© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Calixarenes act as versatile building blocks in supramolecular and coordination chemistry, since both their lower and upper rims may be derivatized to induce specific functionalities.[1,2] They are currently being used in the design of chemical sensors,[3] catalysts,[4] and selective ligands for the complexation of d[5] and f[6,7] metal ions, as well as for the self-assembly, through π-stacking, H-bonding or coordination interactions, of elaborate supramolecular structures.[8,9] As a consequence, many studies have aimed at using calixarenes for the development of separation processes,[10] and the nuclear industry is particularly interested in these ligands for the separation of highly radioactive actinides from non-radioactive lanthanides before nuclear waste confinement.[11–13]

In recent years, we have been developing model calixarene molecules for the study of energy migration mechanisms in luminescent lanthanide-containing compounds, and of magnetic 4f–4f interactions.[7] We have also been interested in calixarenes having 4f/5f separation capabilities. This leads to the formation of luminescent 4f-species which can be easily analyzed during the extraction process. With this in mind, we have focused on two series of branched calixarenes, one bearing ether-amide pendant arms A, and the other having phosphanylyl groups B (see Scheme 1). The ether-amide substituent was designed so that it can act as a bidentate ligand forming a five-membered cycle upon coordination of its ether and amide functions to trivalent lanthanide ions LnIII. We have shown that A₄bL₄ acts as an inorganic-organic receptor, encapsulating both a lanthanide ion and a solvent molecule. In addition, the crystal structure of the LuIII 1:1 complex shows the coordination cavity predisposed to further accommodate one
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water molecule hydrogen-bonded to the oxygen atoms of the phenol units, which rigidifies the induced cavity, and binds the metal ion.\textsuperscript{[14]} The phosphanylyl-substituted calixarenes $B_n bL_6^m$ ($n = 4, 6$) form complexes with 1:1 and 1:2 Ln$^{III}$ ligand ratios having significant stability in acetonitrile,\textsuperscript{[15,16]} and interesting luminescent\textsuperscript{[15,16]} and 4f–5f separation\textsuperscript{[17]} properties. Several derivatized calix[6]arenes have been tested in extraction studies\textsuperscript{[18–20]} and, in our case, $B_6 bL_6^6$ proved to be a better extracting agent than $B_4 bL_4^4$\textsuperscript{[17]} Despite that calix[6]arene complexes with lanthanide ions have also been proposed as luminescent probes,\textsuperscript{[21,22]} little is known about the interaction between calix[6]arenes and Ln$^{III}$ ions. The reaction of europium nitrate with p-tert-butylcalix[6]arene leads to the formation of a 1:2 (Eu$^{III}$/L) compound in which only one calix[6]arene molecule is bound to the 8-coordinate metal ion through a single phenoxide unit, as shown by its X-ray structure.\textsuperscript{[23]} Replacing nitrate with trifluoromethanesulfonate (triflate) results in oxidation and protonation of the phenoxide groups. The macrocycle is soluble in CH$_2$Cl$_2$, CHCl$_3$, CH$_3$CN, toluene, methanol, and ethanol. Its IR spectrum displays an intense band at 1639 cm$^{-1}$ typical of the carbonyl groups in an $N,N'$-disubstituted amide (1646 cm$^{-1}$ in ABr). The absorption band associated with contributions from the aliphatic ether groups appears at 1126 cm$^{-1}$ (1119 cm$^{-1}$ in ABr), medium bands at 1218 and 1045 cm$^{-1}$ are typical of the phenoxide groups, while the three neighboring aromatic C–H groups generate a characteristic symmetric out-of-plane bending at 765 cm$^{-1}$. In the UV/Vis spectrum, the structured band at 270 nm (37040 cm$^{-1}$) with a shoulder at 278 nm (35970 cm$^{-1}$) indicates complete functionalization of the phenoxide groups. This structured absorption band is associated with $\pi$→$\pi^*$ transitions involving orbitals mainly located on the phenyl rings. A band corresponding to transitions primarily located on the carbonyl groups can be seen at 223 nm (44840 cm$^{-1}$) in the diffuse reflectance spectrum.

**Results and Discussion**

**Synthesis and Characterization of the Substituted Calixarene $A_n L_6$**

The branched calix[6]arene $A_6 L_6$ (Scheme 1) was obtained in two steps via a Williamson reaction (Scheme 2) from the brominated pendant arm AB$_r$, synthesized as described previously,\textsuperscript{[14]} and the calix[6]arene $H_6 L_6^6$. The hexa-sodium derivative of calix[6]arene was prepared in toluene, demonstrating that this salt can be formed in a non-polar solvent despite the high fluxionality of calix[6]arene, provided adequate experimental conditions are used i.e. heating, vigorous stirring, and a nitrogen atmosphere to avoid oxidation and protonation of the phenoxide groups. The macrocycle is soluble in CH$_2$Cl$_2$, CHCl$_3$, CH$_3$CN, toluene, methanol, and ethanol. Its IR spectrum displays an intense band at 1639 cm$^{-1}$ typical of the carbonyl groups in an $N,N'$-disubstituted amide (1646 cm$^{-1}$ in ABr). The absorption band associated with contributions from the aliphatic ether groups appears at 1126 cm$^{-1}$ (1119 cm$^{-1}$ in ABr), medium bands at 1218 and 1045 cm$^{-1}$ are typical of the phenoxide groups, while the three neighboring aromatic C–H groups generate a characteristic symmetric out-of-plane bending at 765 cm$^{-1}$. In the UV/Vis spectrum, the structured band at 270 nm (37040 cm$^{-1}$) with a shoulder at 278 nm (35970 cm$^{-1}$) indicates complete functionalization of the phenoxide groups. This structured absorption band is associated with $\pi$→$\pi^*$ transitions involving orbitals mainly located on the phenyl rings. A band corresponding to transitions primarily located on the carbonyl groups can be seen at 223 nm (44840 cm$^{-1}$) in the diffuse reflectance spectrum.

**Scheme 1**

In this paper, we discuss how the removal of the p-tert-butyl groups influences the conformation of the calix[6]arene derivatized with pendant arms A and, consequently, the stoichiometry of the Ln$^{III}$ complexes. Removal of the tert-butyl groups should result in easier conformational interconversion, and a relief in steric hindrance is expected to favor the formation of the 2:1 complexes, contrary to what has been observed for $B_6 bL_6^0$, which forms 1:2 complexes. The calixarene $A_6 L_6^6$, with tert-butyl groups removed, was therefore synthesized, and characterized both in the solid state and in solution, as well as its 2:1 complex with Eu$^{III}$. Molecular mechanics and quantum mechanical calculations were performed to help understand the structures of both the free ligand and the complex.

**Scheme 2**

The $^1$H NMR spectrum of $A_6 L_6^6$ in CD$_3$CN at room temperature is shown in Figure 1 together with its complete assignment (see Scheme 1 for atomic numbering). The limited number of signals points to a high average symmetry on the NMR time scale. This may be interpreted as a consequence either of fast interconversion processes between the different conformers on the NMR timescale, or of the presence of a single species of high symmetry, such as the 1,3,5 alternate conformation belonging to the $S_6$ point group. While the introduction of long complexing arms on the p-tert-butylcalix[6]arene moiety may be expected to freeze the oxygen-through-the-annulus rotation,\textsuperscript{[25,26]} removal of the
bulky tert-butyl groups favors the aromatic-through-the-annulus rotation. Since the latter mechanism has been observed with O-substituted p-tert-butylcalix[6]arenes, it is reasonable to assume that the lack of rotation on the phenol groups allows for rapid aromatic-through-the-annulus rotation and, hence, the apparent high symmetry observed is the result of fast interconversion between the different conformers.

A detailed comparison of the chemical shifts of the proton atoms of the complexing arms in A6L6 and A4bL4 further enlightens an unusual point. While the ethyl groups of the amide functions are found essentially at the same chemical shifts in both ligands, signals corresponding to the H1 and H2 protons are shifted significantly upfield (more than 0.4 ppm) in A6L6 compared with A4bL4.[14] 1H NMR spectroscopic data of A4bL4 indeed showed the compound to be isomerized to the cone conformation in solution, in which the four ethylene bridges are held together in closed proximity, thereby providing a suitable octadentate coordination site for lanthanide cations.[14] The X-ray crystal structure of the lutetium complex further showed that a water molecule was encapsulated in the cavity formed by the four dioxoethylene bridges (O–C1–C2–O), with H-bonding interactions between this water molecule and the oxygen atoms. Interestingly, an elemental analysis of free A4bL4 revealed the presence of one water molecule, even after the drying process. It was suspected that the H-bonding interactions with the water molecule are also present in the free ligand in solution, leading to a decrease of the electronic density on the pendant arms, and a concomitant upfield shift of the corresponding signals in the 1H NMR spectrum. For the larger and more flexible calix[6]arene, NMR spectroscopic data indicate that the cone conformation is not the most favorable conformation, leading to chemical shifts similar to those found in the brominated ABr macrocycle or its hydroxy precursor. The same reasoning can be applied to the corresponding carbon atoms (C1 and C2), one of which is shifted upfield by 1.1 ppm in A4bL4 compared with A6L6.

13C{1H} NMR spectra in both CDCl3 and CD3CN confirm the fast exchange hypothesis (see Figure S1 in the Supporting Information; see also the footnote on the first page of this article) since \( \delta(C^{13}) = 30.95 \) ppm points to a syn orientation of adjacent phenol rings,[27] thus excluding the hypothetical 1,3,5-alternate conformation in which adjacent rings are in an anti conformation. Only four signals are observed for the aromatic carbon atoms, indicating the equivalence of the six aromatic rings on the NMR time scale, and an average hexagonal \((D_{6h})\) symmetry for the calixarene core. All the carbon atoms of the pendant arms also give rise to one signal, except those of the ethyl groups which are split into two components pointing to a somewhat restricted rotation around the amide function.

To substantiate the interpretation of the NMR spectra, we turned to molecular mechanics calculations, and evaluated the A6L6 structure using a MOPAC PM3 procedure, taking into account solvent effects (water). The conformer with the lowest energy is shown in Figure 2. It displays a pinched “chair” conformation of the 1,2,3-alternate type. Three consecutive phenol groups are positioned in such a way that the pendant arms form two cavities predisposed towards metal ion coordination, each built up of three pendant arms, and extending on opposite sides of the macrocycle.

**Interaction of A6L6 with LaIII and EuIII in Acetonitrile**

To gain information on the interaction between lanthanide ions and the calixarene A6L6, solutions of the latter (typically 10⁻³ M) were titrated with solutions of lanthanide triflates Ln(OTf)3·6H2O (typically 10⁻² M, Ln = La, Eu) for ratios \( R = [La^{3+}]/[A_6L_6] \), varying from 0 to 3. The spectra are shown in Figure 3 (S2, and S3, see Supporting Information). In all cases, the spectra display broad overlapping signals, probably as a result of fast exchange reactions of the complexed species. This prevented a quantitative treatment. For \( R < 1 \), the free ligand and a complex species coexist in solution. For \( R = 1 \), a distinct AB spin system can be observed (Ln = La) with two doublets at 4.45 and...
3.60 ppm for the methylene proton atoms bridging two phenolic units. This strongly suggests an average cone-like conformation for the 1:1 LnA₆L⁶ complex. The broadness of the peaks corresponding to the protons of the arms may be attributed to exchange processes, possibly between forms in which these arms are complexed or not complexed to the metal cation. For R > 1, the peaks of the non-coordinated ligand disappear, and signals corresponding to at least two species with different LnA₆L⁶ stoichiometries can be identified. Since the spectra do not change further when R is increased from 2 to 3, we conclude that two species form successively in solution, with 1:1 and 2:1 metal-to-ligand ratios. This is in line with the calculated structure of A₆L⁶ which shows two sets of three pendant arms extending on opposite sides of the calixarene (cf. Figure 2). Attempts to establish a more quantitative speciation by ES-MS failed due to hydrolysis at high dilution in the capillary during the analysis (T = 200 °C). As a result, only monometallic species were detected for R values in the range 1–3, in addition to free A₆L⁶ (Table 1).

Isolation and Characterization of the 2:1 Eu²⁺ Complex

The complex can be isolated in good yield from stoichiometric mixtures of A₆L⁶ and europium triflate in acetonitrile. The elemental analysis is consistent with the formula [Eu₂(OTf)₆(A₆L⁶)₉H₂O]. Coordination of the carbonyl groups of the pendant arms can be ascertained from the IR data (obtained after drying the pellet at 118 °C), the νC=O vibration being red-shifted by 25 cm⁻¹ compared with the ligand, pointing to a strong metal-to-ligand interaction. Moreover, the intensity of the band arising from the aliphatic ether functions of the arm is strongly reduced, in line with the coordination of these moieties to the metal ion. The vibration involving contribution from the aromatic ether could not be identified, probably being masked by another band, contrary to what we reported for the [Lu(A₄bL₄)(H₂O)](OTf)₃ complex, for which (i) this band is little affected by the complexation, and (ii) the crystal structure of [Lu(A₄bL₄)(H₂O)](OTf)₃·2Et₂O does not show evidence of any coordination of aromatic ethers. In our case, this suggests some change in the ligand conformation upon complexation and, possibly, coordination of these groups to the metal ion. Other ligand vibrations, for instance the bending CH₂ mode (1450 cm⁻¹), and the out-of-plane ring bending mode (760 cm⁻¹), experience small, but characteristic changes upon complexation. In addition, two strong bands at 1030 and 638 cm⁻¹ can be assigned to the νₗ(SO₃) and νₜ(SO₃) modes of coordinated triflate, while the band at 1321 cm⁻¹ is evidence for ionic triflate. Finally, water coordination can be deduced from a sharp band near 520 cm⁻¹.[29] Attempts to grow single-crystals by slow vapor diffusion of diethyl ether or diisopropyl ether in acetone, THF, or MeOH, were unsuccessful.

¹H NMR spectra obtained during the titration of A₆L⁶ with europium triflate (Figure S3, see Supporting Information) revealed that complexation induces freezing of the ligand conformation, resulting in a very complex pattern, which is difficult to interpret. Variable temperature NMR spectra of a Eu₂(OTf)₆(A₆L⁶)·9H₂O solution in CD₃CN were recorded up to 75 °C. Although the overall pattern becomes somewhat simplified, the spectrum remains complex. Higher temperatures could not be reached, because the complex experiences de-metallation in DMSO, a solvent in which, for instance, B₈bL₆ undergoes complete interconversion of its isomers on the NMR time scale at 132 °C.[16]

Photophysical Properties of A₆L⁶ and Its 2:1 Eu²⁺ Complex

The photophysical properties of A₆L⁶, and of the 2:1 Eu²⁺ complex have been determined both for solid state samples (295 and 77 K), and for frozen acetone solutions (77 K). The excitation spectrum of the ligand is similar to the absorption and reflectance spectra discussed above. Excitation of a solid sample of A₆L⁶ at 275 nm

Table 1. Main species observed in the ES-MS spectra of solutions containing A₆L⁶ and Eu(OTf)₆·6H₂O in various proportions (see text)

<table>
<thead>
<tr>
<th>Species</th>
<th>Obsd. m/z</th>
<th>Rel. Int.</th>
<th>Calcd. m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Eu(OH)₃(A₆L⁶)(H₂O)₉ + H]⁺</td>
<td>1873.4</td>
<td>&lt; 15%</td>
<td>1873.9</td>
</tr>
<tr>
<td>[Eu(OH)(CF₃SO₃)₆(A₆L⁶)(CH₃CN)]⁺</td>
<td>1940.3</td>
<td>&lt; 15%</td>
<td>1939.1</td>
</tr>
<tr>
<td>[Eu(OH)(CF₃SO₃)₆(A₆L⁶)(H₂O)(CH₃CN)]⁺</td>
<td>1958.4</td>
<td>15–20%</td>
<td>1957.1</td>
</tr>
<tr>
<td>[Eu(OH)(CF₃SO₃)₆(A₆L⁶)(H₂O)₃(CH₃CN)]⁺</td>
<td>1993.8</td>
<td>25–50%</td>
<td>1993.2</td>
</tr>
<tr>
<td>[A₆L⁶ + H]⁺</td>
<td>1580.8</td>
<td>100%</td>
<td>1581.0</td>
</tr>
</tbody>
</table>
and 77 K yields two emission bands centered at 305 nm (32790 cm−1), which can be assigned as arising from the 5ππ* state, and at 446 nm (22420 cm−1), attributed to the ππ* state, as ascertained by the lifetime, which amounts to 104 ± 8 ms in frozen acetonitrile solution (2 × 10⁻³ m). This can be compared with 83 ± 4 ms for B₆l₆ under the same experimental conditions.[16]

The absorption spectrum of the 2:1 complex in acetonitrile (4.74 × 10⁻³ m) displays three bands at 268 nm (37310 cm⁻¹, ε = 9490 mol⁻¹·cm⁻¹), 276 nm (36230 cm⁻¹, ε = 8650 mol⁻¹·cm⁻¹), and 293 nm (34130 cm⁻¹, ε = 3380 mol⁻¹·cm⁻¹). The first two bands are blue-shifted 265 cm⁻¹ compared with those in the uncomplexed ligand. The third band is only present in the complex. The excitation spectrum of the complex, obtained at 10 K with concomitant monitoring of the 5D₀→7F₂ transition, reveals the usual f–f transitions as well as a broad band in the range of 320–450 nm with a maximum at 372 nm (26880 cm⁻¹), which could possibly be associated with a ligand-to-metal charge transfer (LMCT) band. Excitation in the ligand levels yields a luminescence spectrum displaying both ligand-centered and metal-centered 5D₀→7F₁ emission bands, pointing to incomplete ligand-to-metal energy transfer. The high-resolution laser-excited excitation spectrum in the range of the 5D₀→7F₂ transition, monitored via the 5D₀→7F₁ transition, results in a single, broad component at 17267 cm⁻¹ at 10 K (full width at half height fwhh = 37 cm⁻¹), and 17280 cm⁻¹ at 295 K (fwhh = 24 cm⁻¹), indicative of a sample with several slightly different chemical environments for the EuIII ion, possibly arising from different conformations of the macrocycle and associated pendant arms.[30] Excitation in either the 5D₀→7F₀ or 5L₆→5D₀ transitions yields relatively broad emission spectra dominated by the hypersensitive 5D₀→7F₂ transition, which are characteristic of a chemical environment with low symmetry (Figure S4, Supp. Inf.). The relative and corrected intensities of the 5D₀→7F₂ transitions are 1.0, 7.4, 0.1, and 1.9 (10 K) and 1.0, 7.2, 0.2, and 2.0 (295 K) for J = 1, 2, 3, and 4, respectively.

The lifetimes of the excited 5D₀ level were measured at 10, 77, and 295 K both upon ligand and direct metal excitation (Table 2). The luminescence decays of the solid state sample are bi-exponential and temperature dependent, decreasing roughly by a factor of two between 10 K and room temperature. This is indicative of vibrational and/or electronic radiationless de-activation mechanisms. Here, both processes are probably operating in view of the fluxional nature of the calixarene, and of the LMCT band apparent in the excitation spectrum. Lifetimes measured upon ligand excitation are longer than those obtained through direct excitation of the 5D₀ level, pointing to a feeding level with a long lifetime, namely the triplet state. High energy vibrations such as those generated by O–H groups are known to efficiently de-excite LnIII excited levels[31] and phenomenological equations have been proposed to relate Δτobsd = 1/τobsd − 1/τref where τref is the lifetime measured on the corresponding deuterated sample or in deuterated water, and the number of water molecules q directly bound to the LnIII ion, either in the solid state[32] or in solution.[33] Interpreting our lifetime data along these lines, we note that one lifetime, τ₁, is long. It decreases, under direct excitation, from 1.66 ms (10 K) to 0.86 ms (295 K). Such a lifetime, at least at low temperature, is consistent with the inner coordination sphere containing no water molecules. The other lifetime, τ₂, is much shorter, decreasing from 0.46 ms (10 K) to 0.28 ms (295 K), under direct excitation of the EuIII ion. Taking τ₁ = τref as a first approximation, and q = 1.05 Δτobsd,[32] we calculate, that the number of bound water molecules lies between 1.6 (10 K) and 2.5 (77 and 295 K). The apparent increase in q with increasing temperature could be simply due to outer sphere water molecules hydrogen-bonded to the complex, which become more labile when the temperature increases, or to other vibrational temperature-dependent deactivation processes affecting the de-excitation of the two metal ions differently.

Table 2. Lifetimes (ms) of the 5D₀(Eu) level in a solid state sample of Eu₂(OTf)₆(A₆L₆)·H₂O under various experimental conditions

<table>
<thead>
<tr>
<th>T (K)</th>
<th>vₑₐ (cm⁻¹)</th>
<th>τ₁ (ms)</th>
<th>τ₂ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>32468</td>
<td>2.01 ± 0.05</td>
<td>0.97 ± 0.04</td>
</tr>
<tr>
<td>77</td>
<td>32468</td>
<td>1.71 ± 0.03</td>
<td>0.48 ± 0.01</td>
</tr>
<tr>
<td>295</td>
<td>32468</td>
<td>1.09 ± 0.02</td>
<td>0.36 ± 0.01</td>
</tr>
<tr>
<td>10</td>
<td>17268</td>
<td>1.66 ± 0.01</td>
<td>0.46 ± 0.02</td>
</tr>
<tr>
<td>77</td>
<td>17268</td>
<td>1.19 ± 0.04</td>
<td>0.31 ± 0.01</td>
</tr>
<tr>
<td>295</td>
<td>17280</td>
<td>0.86 ± 0.02</td>
<td>0.28 ± 0.01</td>
</tr>
<tr>
<td>295[^4]</td>
<td>25445</td>
<td>—</td>
<td>1.38 ± 0.02</td>
</tr>
</tbody>
</table>


In solution, the 5D₀ luminescence decay becomes a single exponential, with a value (1.38 ms) compatible with the absence of OH oscillators directly bound to EuIII. Dissolution of the complex results, therefore, in a change in the coordination environment of the EuIII ions, since the lifetime is now larger than those observed for the two different sites in the solid state. The quantum yield measured in acetonitrile upon ligand excitation Qₑₐ amounts to 2.5%, a value similar to that found for [Eu(B₆l₆)₃]³⁺.

**Optimized Structure of the EuIII 2:1 Complex**

In order to confirm the feasibility of our interpretation, we resorted to molecular mechanics calculations to evaluate a potential structure for the 2:1 complex. Several systems were tested, taking into account the experimental data, which suggested that the isolated compound has coordinated triflate anions and water molecules (1R), and two different metal ion sites with q ≈ 0 and 2 (luminescence lifetimes). It turned out, that the conformer with the lowest energy, as calculated by the MM3 and Conflex procedures, and shown in Figure 4 (see also Table S1 in the Supporting Information), has indeed an asymmetric structure with two 9-coordinate EuIII ions. One ion (site I) is bound to two phenolic oxygen atoms, three bidentate arms, and one monodentate triflate anion. The coordination environment of

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the second ion (site II) is somewhat different, with two water molecules replacing the bonding to the phenolic ether atoms. Therefore, the suggested formulation of the 2:1 complex is \( \text{[Eu}_2(\text{OTf})_2(A_{6b}L^6)(\text{H}_2\text{O})_2]^{4+} \). Generally speaking, the Ln–O distances are too long compared with the expected ones for 9-coordinate Eu\(^{III}\), which lie in the range 2.45–2.60 Å\(^{[34]}\) [averages: 2.72(17) A for site I and 2.83(18) A for site II]. Relative distances, however, can be discussed. The coordination in site I is comprised of six short bonds (three carbonyl groups, one ether function, and the two phenoxo moieties), and three longer bonds (13%) involving two ether functions and the triflate anion. The situation for site II is somewhat different in that it features only three short bonds (carbonyl groups) identical to those of Site I, all the other distances being 13% longer. It is noteworthy, that site I builds a more protective cavity around the metal ion than site II does. Moreover, contrary to what was inferred from the ligand design, the phenoxide groups participate more than expected in the bonding (Site I), with Ln–O distances similar to those with carbonyl functions.

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Conclusion

The calix[6]arene \( A_{6b}L^6 \) exhibits a 1,2,3-alternate conformation in which two sets of three arms extend on opposite sides of the phenoxide framework, henceforth leading to a ditopic ligand able to bind to two metal ions. Complexes with a 2:1 (Ln\(A_{6b}L^6\)) stoichiometry could effectively be observed in solution by \(^1\)H and \(^{13}\)C NMR spectroscopy, and the Eu\(^{III}\) complex was isolated. The calculated structure of this complex confirms the results of the luminescence study, and resembles those found experimentally for the 2:1 complexes with \( p\)-tert-butylcalix[6]arene \( H_{6b}L^6 \) (Ln = Sm, Yb).\(^{[24]}\) The absence of substituents on the narrower rim of \( H_{6b}L^6 \) allows easy interconversion between different conformers, through either one of the “\( p\)-tert-butyl through the annulus” or “narrower rim through the annulus” pathways\(^{[35]}\) facilitating the formation of the 2:1 complexes. On the other hand, \( p\)-tert-butyl-substituted \( B_{6b}L^6 \) displays a less labile alternate \( in\)-\( out \) conformation in which the six phosphanyl pendant arms are located on the same side of the molecule, and no 2:1 complexes are obtained with this receptor but, instead, compounds with 1:1 and 1:2 stoichiometries can be isolated.\(^{[16]}\) This demonstrates once again the versatility of the calixarene frameworks, since a conformation favoring a given stoichiometry of the Ln\(^{III}\) complexes can be induced by modifying either the wider or the narrower rim of the ligand, a property which should prove useful in the development of convenient extraction systems.

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Experimental Section

Solvents and Starting Materials: Tetrahydrofuran and toluene were distilled from Na, and acetonitrile was distilled from CaH\(_2\).\(^{[36]}\) Diglycolic anhydride, \( \text{BH}_3\cdot\text{Me}_2\text{S} \) (2 m solution in THF), \( \text{Et}_3\text{NH} \), \( \text{Et}_3\text{N} \), formalin (36% solution), butylphenol, KOH, \( \text{AlCl}_3 \) phenol, chloroform, acetone, and SO\(_{2}\)Br\(_2\) were purchased from Fluka AG (Buchs, Switzerland) or Merck, and used without further purification.

Preparation of the Pendant Arm: The brominated ether-amide arm \( A\text{Br} \) was synthesized as described previously (see Scheme 1).\(^{[34]}\) It was dried for 3 h over 4Å molecular sieves, which had been previously dried at 240 °C under high vacuum (24 h, \( 10^{-5} \) Torr).

Calix[6]arene \( H_{6b}L^6 \): \( p\)-tert-Butylcalix[6]arene \( H_{6b}L^6 \) was synthesized according to the procedure reported by Gutsche et al.\(^{[37]}\) and its purity checked by TLC analysis: \( R_d = 0.65 \) in \( \text{CH}_2\text{Cl}_2/\text{petroleum ether} \) (1:1, \( \text{v/v} \)), \( R_d = 0.36 \) in acetone/petroleum ether (1:9, \( \text{v/v} \)). The compound was further characterized by IR, \(^1\)H, and \(^{13}\)C NMR spectroscopy, and EI mass spectrometry. The tert-butyl groups were then removed following an \( \text{AlCl}_3 \) catalyzed retro-Friedel–Crafts reaction in the presence of phenol.\(^{[38]}\) TLC analysis yielded \( R_d = 0.61 \) in \( \text{CH}_2\text{Cl}_2/\text{petroleum ether} \) (1:1, \( \text{v/v} \)), and \( R_d = 0.31 \) in acetone/petroleum ether (1:9, \( \text{v/v} \)). It was further characterized by IR, \(^1\)H, and \(^{13}\)C NMR and EI mass spectrometry.

Functionalization of Calix[6]arene: All operations were performed under strictly anhydrous conditions under nitrogen. Dried calix[6]arene \( A_{6b}L^6 \) (135 mg, 0.21 mmol) and NaH (60% in mineral oil, 149 mg, 3.73 mmol) were placed into a 100-mL round-bottomed flask fitted with a nitrogen inlet and a condenser, and dried toluene (60 mL) was added. The turbid mixture was heated with stirring, becoming almost transparent at 70 °C. The temperature increased spontaneously to 76 °C, hydrogen evolved, and a white emulsion formed. The temperature was slowly increased to 90 °C, and the mixture maintained at this temperature until no fluorescent UV spot corresponding to \( H_{6b}L^6 \) was observed on the TLC plate (approximately 1 h). The hot emulsion was quickly poured into a 100-mL three-necked round-bottomed flask fitted with a nitrogen inlet and a condenser, and dried toluene (5 mL), which had been previously heated with stirring at 115 °C for 2 h. More toluene was added (10 mL), and the temperature was increased to 130 °C. As the reaction progressed the solution became
turbid and its color changed from brownish-orange to reddish-orange. The reaction was stopped after 6 days. The solid was separated at room temp. by vacuum filtration, and washed with warm toluene until the filtrate became colorless. The filtered organic solution was washed several times with doubly distilled water until the pH of the latter remained unchanged, and no AgBr formed upon addition of 2% AgNO3 to the aqueous phase. During the washing, a white emulsified intermediate phase formed, which disappeared quickly. The organic phase was dried with anhydrous magnesium sulfate, filtered, concentrated at 40 °C, and finally evaporated under vacuum (10⁻² Torr) at 60—70 °C. A deep orange glassy-solid was obtained (ca. 150 mg) which was ground up. n-Hexane (20 mL) was added, the mixture was stirred and heated to 45 °C for 30 min, and the yellow solution was separated. This step was repeated until the solution became colorless. The bulk of the solvent was separated, the remaining solvent removed under vacuum (10⁻² Torr), and the orange waxy solid dried at 70 °C under high vacuum (10⁻³ Torr) for 1 day. It was then re-dissolved in a minimum amount of methanol, and disopropyl ether was added until cloudiness was observed. This mixture was left in the refrigerator overnight to induce precipitation. Small and slightly yellow, glassy crystals formed after 2 days, which were collected and dried at 100 °C under high vacuum (10⁻⁵ Torr) for 48 h. The final deliquescence compound (66 mg, 0.042 mmol, 20% yield) was then characterized, C₉H₁₂N₂O₃S (Mol wt. 1580.02). IR (KBr, cm⁻¹): ν = 1639 (νC=O), 1249 (νC–O–C), 1126 (νυ(C–O–C)), 1218 and 1045 (νυ(O–C)). UV/Vis (dried and degassed spectroscopic grade CH₃CN): λ = 270, 278 nm. Diffuse reflectance (5% in MgO): 44840 (C=O), 36630 (phenyl) cm⁻¹. 36630 (phenyl) cm⁻¹.

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**Spectroscopic and Analytical Measurements:** IR spectra were recorded with a Bruker AM-360 (360 MHz) or DRX Advance 400 (400 MHz) spectrometers; chemical shifts δ are given with respect to TMS or CD₃CN. Low resolution luminescence spectra of solid state samples (295 and 77 K) were recorded with a Perkin—Elmer LS-50B spectrofluorimeter. Lifetimes of solutions (data reported are averages of at least five determinations), and quantum yields were measured with the same instrument. The quantum yield of the metal-centered luminescence was determined in degassed and anhydrous CH₃CN at room temperature with respect to [Eu(L)₃]⁺ + 3 × 10⁻³ M in acetonitrile (Qₑ(calc) = 23% [49]) where L is a cyclen derivative {1,3,7,10-tetraakis[N-(4-phenylacyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane} using the following formula:

\[
Q/\tau = \frac{\lambda(\lambda)/\lambda(\lambda)\cdot \tau(\tau)/\tau(\tau)}{\tau(\tau)/\tau(\tau)}
\]

where the subscript \( r \) stands for the reference, and \( \lambda \) for the sample. \( A \) is the absorbance at the excitation wavelength \( \lambda \), \( n \) the refractive index (1.344 for solution in CH₃CN and 1.333 for the solution in water), and \( D \) the integrated luminescence intensity. The same excitation wavelength (279 nm) and absorbance (0.27) were used for the sample and the reference, and a bandpass filter (350 nm or 390 nm) was used to eliminate both the Rayleigh diffusion band and second order spectra. High resolution laser excited luminescence spectra were recorded using published procedures. [90] Lifetime data for solid samples were measured at different temperatures under pulsed excitation provided by a FL-3001 dye laser from Lambda Physik coupled to an excimer XeCl laser EMG-101-MSC from Lambda Physik. Elemental analyses were performed by Dr H. Eder (Microchemical Laboratory, University of Geneva).

**Semi-Empirical Calculations:** The optimized structures and energy minima of the free ligand, and of the 2:1 complex were calculated by using MM3 augmented and CONFLEX procedures, respectively, from the CAChe Pro 5.02 or 5.04 program package for Windows® (Fujitsu Ltd., 2000—2002). The structure of A₄L₆ was further optimized with respect to its enthalpy of formation by MOPAC PM3 molecular orbital calculations using the same program package. The effect of solvent (water) was taken into account using the COSMO procedure built into CAChe Pro. Experimental data for both the free ligand and the EuIII complex (IR, NMR, luminescence) were taken into account for optimizing the calculations.

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