Lanthanide ion(III) complexes of deprotonated p-tert-butylcalix[n]arene in acetonitrile

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Abstract: The anionic calixarene derivatives ('calixanions') have been obtained by the reaction of weak bases such as triethylamine, with p-tert-butylcalix[n]arenes in MeCN. To clarify the involvement of the solvent in deprotonation, comparison of media effect (MeCN and DMF) and computational methods (Frontier Molecular Orbital Theory) are employed. The binding of representative lanthanide(III) cations with p-tert-butylcalix[n]arenes (n=4,6, 8) anions form in MeCN monomeric complexes in the case of tetra and hexa calixarenes, and dimeric complexes with the larger calixarene ,calix[8]arene.The conditional stability constants of the lanthanum (La^{3+}), europium (Eu^{3+}), gadolinium ($Gd^{3+)}$ and terbium (Tb^{3+}) complexes were determined. In addition, it was found that deprotonated p-tert-butylcalix[n] arenes (n=4, 8) present an affinity toward europium, while p-tert-butylcalix[6]arene anion shows a significant selectivity for lanthane cation..

Keywords: Calixanions; Lanthanides (III); Complexation; Absorption spectrophotometry; Frontier Molecular Orbital Theory (FMO).

INTRODUCTION

The calixarene skeleton continues to represent one of the most important macrocyclic host molecules in supramolecular chemistry. They are versatile host molecules that efficiently and selectively bind a variety of ionic and neutral guest species [1]. As proposed by Zinck, Ziegler and later by Cornforth [2][3], the condensation of aldehydes and phenols leads to the formation of macrocyclic calix[n] arenes with different sizes by variation of the number of aromatic fragments (n = 4, 6 and 8) as described by Gutsche *et al.* in the 1970s. Calixarenes are basically interesting due to their conformational flexibility, complexing abilities, and reactivity. The calixarenes parent are readily available and can be substantially functionalized both at the phenolic OH groups, at methylene bridged and at the para positions of phenol rings into numerous derivatives, offering selectivities toward a large range of guest ions and small molecules [1b][4]. The structure of calixarenes facilitate hydrogen bonding, both intra molecularly and as a directing force in supramolecular structural motifs[5] which are considered as one of the most important factors in calixarene acidity since the strong hydrogen-bonding stabilize the anion form [6].The hard acid character of the lower rim makes calixarenes parent interesting as potential ligands for metal ion complexation such as: alkali, alkaline earth, transition, lanthanide and actinide metals. In this context, a recent review covering all types of metallo-calixarenes in which the metal is bound directly to the phenolic moiety was described[7]. Early investigations[8] of metal ion complexation by phenolic calixarenes emphasized the need for at least partial deprotonation of the phenolic-OH groups and some pK_a values have been determined in THF[9] and in MeCN for different degrees of deprotonation of terta,penta, hexa and octa-p-*tert*-butylcalixarenes[10].

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Most relevant to the present work studies of lanthanide ion complexation with calix[*n*]arenes in presence of NEt_3, mainly focused on the p-tert-butylcalix[n]arenes (n=4,6,8). For example, europium forms bi-nuclear complexes with anionic p-t-butylcalix[4]arene [13] and p-t-butylcalix[5]arene [11],[12] and with those of both p-t-butylcalix[8] arene [14] and calix[8]arene as well as binuclear and heptanuclear complexes with anionic forms of p-t-butylcalix[9]arene [15], while mononuclear complex is formed with p-t-butylcalix[6]arene dianion [16].

In the present work, we aim to shed new lights on the complexation of lanthanoids (La^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Tb^{3+}) with p-tertbutylcalix[n]arenes-anions in acetonitrile by revealing the values of stability constants of the formed complexes and influence of calixarene size on stoichiometry. The interactions study have been followed by UV-visible spectrophotometric titrations.

Furthermore, solvent effect on deprotonation of calix[4]arene was also studied theoretically using the Frontier Molecular Orbital Theory (FMO) method in order to complement the experimental UV–visible spectrophotometric data. Molecular dynamic study have been also conducted on monoanion p-tert-butylcalix[4]arene complexes with Eu^{3+} and La^{3+} .

EXPERIMENTAL:

1. Materials:

The calixarenes were obtained commercially (Sigma Aldrich, 95%), and were checked for purity by ^1H NMR. Acetonitrile (99.9%, HPLC grade, Sigma-Aldrich) was used without further purification. The lanthanide salts were commercial chlorides (Sigma Aldrich, 99.99 %). Commercial triethylamine (Sigma Aldrich, ≥99%) was used as obtained. The supporting electrolyte used in the stability constant determinations was Et_4NClO_4 (Acros). The spectra were recorded on a Perkin Elmer Lambda 11 using quartz cuvettes (Hellma).

2. Deprotonation studies:

A weighed amount of calix[n]arene was dissolved in MeCN (25 cm^3) at 25°C, giving a 4 10^{-5} M solution. Triethylamine (0.00253 g) was dissolved in MeCN (25 cm^3), giving a 1 10^{-3} M solution. p-tert-butylcalix[n]arene solution (2 cm^3) was added by pipette to a cuvette (3.5 cm^3), and a UV spectrum was taken at 25°C on the spectrophotometer between 250 and 400 nm. Successive aliquots of the basic solution were added to the stoppered cuvette using a micropipette, and a UV spectrum was taken after each addition. Additions were repeated until superposition of spectra was observed.

3. Complexation studies and Stability constant measurements:

The apparent overall stability constants β, defined as the concentration ratio $[M_xL_y^{xn+}]/[M^{n+}]^x[L]^y$ referring to the equilibrium: $xM^{3+} + yL \leftrightarrow M_xL_y^{3x+}$ (M^{3+}= cation, L= deprotonated calixarene) were determined in MeCN and DMF by electronic absorption spectrophotometry at 25°C and an ionic strength provided by 0.01 M Et_4NClO_4according to procedures described in literature [17]. Titrations of ligands by metal ion solutions were performed directly in the spectrophotometric cell. The concentration of ligands is ranged between 10^{-5} and 10^{-4} M. The metal to ligand ratios which were reached at the end of the titrations were in the range of 1-10. Spectra were generally recorded between 250 and 350 nm. The spectral changes were interpreted using the program Letagrop [18]. The values of the stability constants given in the tables correspond to the arithmetic means of at least three independent determinations.

4. Computational

Calculations were performed with the GAUSSIAN09 series of programs [19] using the non-local hybrid functional denoted as B3LYP [20] and PBE [21]. Standard pseudo-potentials developped in Toulouse by Durand-Barthelat were used to describe the atomic cores of all other non-hydrogen atoms (C and O) [22]. A double plus polarization valence basis set was employed for each atom (d-type function exponents were 0.80 and 0.85, respectively). For hydrogen, a standard primitive (4s) basis contracted to (2s) was used. A p type polarization function (exponent 0.9) was added for all hydrogen atoms. The geometry of the various critical points on the potential energy surface was fully optimized with the gradient method available in GAUSSIAN 09. Calculations of harmonic vibrational frequencies were performed to determine the nature of each critical point.

RESULTS AND DISCUSSION

Contrary to the modified calixarenes, the complexing properties of parents phenolic calix[n] arene (n=4,6,8) toward lanthanide, have not had as much interest. However, to proceed the exploitation host-guest properties of phenolic calixarenes and lanthanide cations in aprotic solvents, the deprotonation was first investigated.

1. Deprotonation of Calixarenes :

Deprotonation of three p-tertbutylcalix[n]arenes as p-tertbutylcalix[4]arene, p-tertbutylcalix[6]arene and p-tertbutylcalix[8]arene by weak bases such as triethylamine have been conducted in acetonitrile using UV-vis spectrophotometry. In addition, the sensitive spectrophotometric method is the one of choice in such situation, since the solubility of those ligands is very low.

The equilibriums are instantaneous and the spectral changes are consistent with those described by Cunningham[10] for the deprotonation of p-tert-buthylcalix[n]arene in MeCN. Indeed, for the tetramer (Figure 1a) no spectral variation is observed up to 1 equivalent resulting in complete mono deprotonation.

The dissolution of p-tertbutylcalix[6]arene (Figure 1b) and p-tertbutylcalix[8]arene in MeCN at 25°C shows a deformed spectra and already a shoulder above 300 nm similar to that seen for the mono-deprotonated tetramer more marked for the octamere. A similar shoulder was not explained by Gutsche for *p*-allylcalix[4]arene in EtOH or MeCN/water[23]. However Cunningham noted that the titration with triflic acid (a strong acid compared to the calixarenes, in MeCN) of deprotonated calixarene led to loss of this shoulder, and the spectrum regain the form observed for calix[4]arene and for calix[8]arene in chloroform ordioxane [24].The shoulder at λ>300 nm, therefore, was attributed to some preexisting mono-deprotonated calix[4]arene,calix[6]arene and calix[8]arene in the base-free MeCN. They also suggest that this species might be an *endo*-calixarene zwitterion, wherein an H$^+$ has left its hydroxy group to reside within the cavity, stabilized by hydrogen bonding to the remaining hydroxy groups[10].

Titration with triethylamine shows a small further change in the spectrum of octamere that means small further increase in deprotonation, and significant change for hexamer. In both cases, spectral changes indicate the removal of a single proton only. However the pK$_a$ values determined for p-t-butyl-calix[4]arene, -calix[6]arene and –calix[8]arene, in acetonitrile at 298 K are therefore assumed to be 19.1, 15.6 and 17.2, respectively[10].

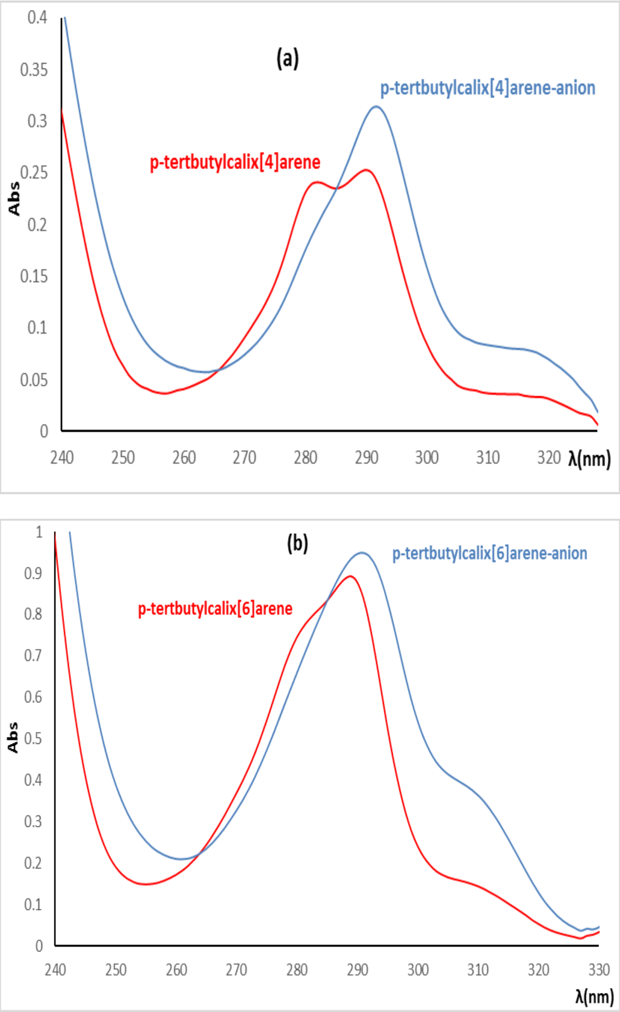


Figure 1. UV spectral change on addition of Et$_3$N to p-tertbutylcalix[4]arene **(a)** and to p-tertbutylcalix[6]arene **(b)**in MeCN.

In protophilic solvent such as .*N*,*N*dimethylformamide which is dipolar aprotic solvents containing oxygen atoms with localized negative charges, the deprotanation of parent calixarenes is less effective than in MeCN. From a previous work, conducted in our group, It was noted that spectral changes could be detected up to NEt$_3$:p-isopropylcalixarene ratios as high as 10 for tetramer, 1000 for the hexamer and 100 for the octamer. Those high ratios were indicative of more complicated equilibria compared to MeCN, so that a full interpretation has not yet been possible. Very similar spectral variations have been shown in DMF to those of MeCN. However it appears that the deprotonation equilibrium is more than 100 times more effective for p-isopropylcalix[4]arene when titrated with triethylamine in DMF (K_{11}= $10^{6.8}$) comparing to p-allylcalix[4]arene when titrated with neopentylamine in MeCN (K_{11} = $10^{4.5}$) [23]. A comparison of DMF and MeCN is useful in that although both are considered as dipolar, aprotic solvents, their acid-base and coordinating properties are very different.

2. Complexation

In the presence of adequate amount of triethylamine, each of the p-tertbutylcalix[n]arenes can be considered to form anion species which can therefore be taken as a solution of a ligand “L”. Although the binding of L to a metal ion such as a Ln(III) species is expected to lead to further deprotonation, again the presence of triethylamine should ensure that a fixed mixture of species “ML” results, so that effective (conditional) equilibrium constants can be evaluated. The complexing properties of deprotonated p-tertbutyllcalix[n]arene (n=4,6,8) with four lanthanide ions La^{3+}, Gd^{3+}, Eu^{3+} and Tb^{3+} were studied in MeCN. Complexation was monitored using spectrophotometric UV-Vis method. Equilibrium appeared to be reached within the time required to begin measurements.

If we consider spectrum variations, it is noted that, the complexation of rare earth cations led to significant spectroscopic changes and in most cases gave rise to one or more isosbestic points. Also, it was noted that equilibrium were always reached within the time scale of the measurements.

Indeed, in case of p-tertbutylcalix[4]arene-anion, addition of increased amounts of lanthanide cation Ln(III), decrease the maximum absorption, with the formation of three isosbestic points correspondding to a formation of one new species.

In case of p-tertbutylcalix[6]arene in NEt_3/MeCN solution, addition of lanthanides cations shows a similar spectral changes for all cations except for lanthanum (Figure 3) where the complex spectra are defined by two maxima contrary to the other complexes which are characterized by a single maximum.

For the larger ligands such as p-tertbutylcalix [8] arene, spectral changes on titration with the three Ln(III) (Gd^{3+}, Eu^{3+} and Tb^{3+}) were all similar, with important decrease of absorbance around the maximum of absorption and decrease further with well-defined isosbestic points indicating that a single complexation equilibrium was involved. The complexation of lanthane also leads to the formation of one specie however the spectral variations are quite different from other cations since we see the formation of three isobestique points at 302, 287 and 270 nm, testifying once again the particular behavior of anions calixarene toward lanthane cation.

Fitting of the titration results for lanthanides complexation using LETAGROP computational program [17] produced the stability constant values given in Table 1.

The best fit of the experimental data was obtained assuming the formation of ML with tetramer and

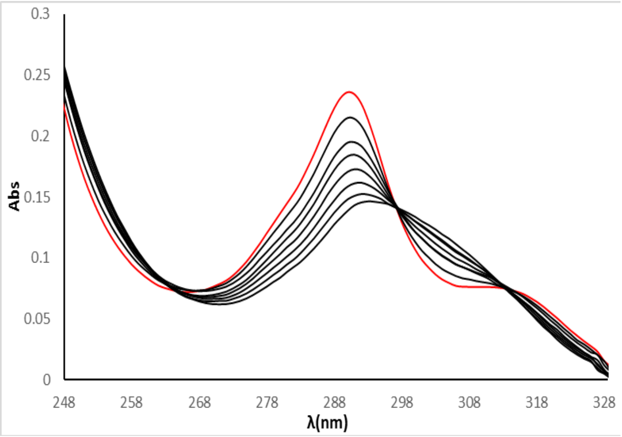


Figure 2. Spectral changes on complexation of terbium with deprotonated p-tertbutylcalix[4]arene in MeCN ($0 \leq R_{M/L} \leq 6$).

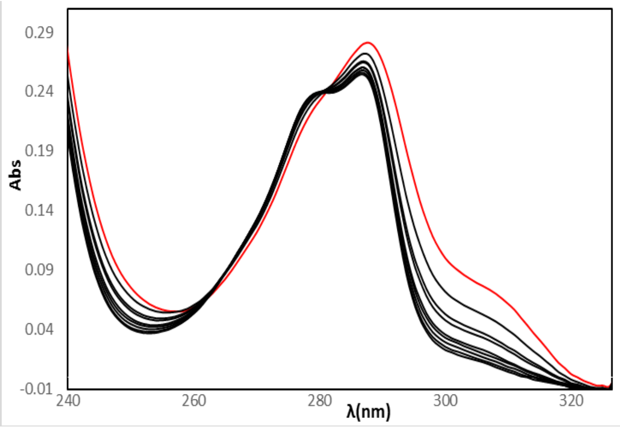


Figure 3. Spectral changes on complexation of lanthanum with deprotonated p-tertbutylcalix[6]arene in MeCN($0 \leq R_{M/L} \leq 1.6$).

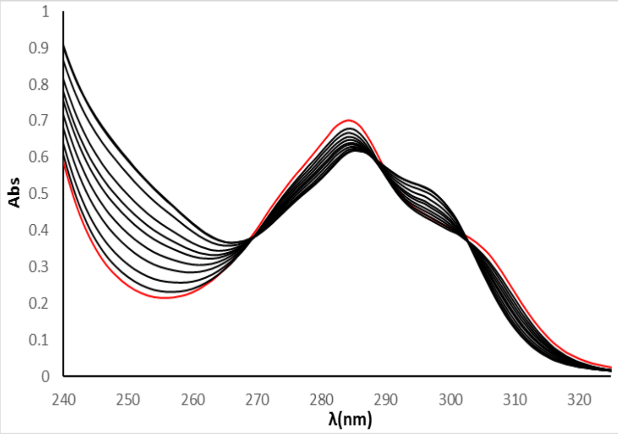


Figure 4. Spectral changes on complexation of lanthanum with deprotonated p-tertbutylcalix[8]arene in MeCN ($0 \leq R_{M/L} \leq 2.1$).

hexamer and M_2L species for the larger ligand, the octamer. These results are consistent with what has been observed by isolation of solid Ln(III) complexes of p-t-butylcalix[n]arene in DMF [24]. As far as comparable stoichiometries have been observed in a previous study conducted in DMF, It is highlighted that size effect is mainly the most important determination factor for stoichiometry compared to solvent effect. Furthermore the higher conformational flexibility and the difference in oxygen atoms donor number should also influence the nature of the complexes. Concerning the stability of mononuclear complexes, calix[6]arene seems to be a stronger binder than calix[4]arene in MeCN ($4.4<\text{Log } \beta_{ML}<6.13$ and $3.2<\text{Log } \beta_{ML}<4.2$ respectively), with relatively high stability constants toward the majority of considered lanthanide cations. Indeed, calix[6]arene show remarkable selectivity for the biggest lanthanide cation La^{3+} (ionic radius of 1.06 Å)[25]with a good selectivity factor $S = \beta_{11}(La^{3+})/\beta_{11}(Eu^{3+}) \geq 53$. It should be noted that despite their very close ionic radius sizes Gd^{3+} (0.94 Å) and Eu^{3+} (0.95 Å) [25] can be distinguished by tetramer and haxamer ligands ($S = \beta_{11}(Gd^{3+})/\beta_{11}(Eu^{3+}) \approx 10$). Concerning the binuclear complexes formed with calix[8]arene there is a change in stability of about 1log unit between the weakest complex of La^{3+}($\log\beta_{21}$=8.66) and the strongest three lanthanide complexes, and ($\log\beta_{21}(Eu^{3+})$=9.8, $\log\beta_{21}(Gd^{3+})$ =9.48 and $\log\beta_{21}$ (Tb^{3+}) =9.62). The behavior of anion calix[8]arene during complexation seems to be similar to that of anion calix[4]arene, as deduced from selectivity profile, and since the lanthane complex represents the lowest stability and europium complex represents the highest stability contrary to calix[6] arene. This may suggest a better fit of europium cation with a tetramer cavity or similar cavity, considering size and oxygen atom number of the coordination site; and better recognition of larger cavity of calix[6]arene for larger cation such as lanthane. Besides the effect of size and number of heteroatoms, the binding properties of p-tertbutylcalix[n]arene anions can be affected also on para substitution and on the medium where the complexation process takes place. Dipolar aprotic solvents containing oxygen atoms with localized negative charges such as .*N,N*dimethylformamide is protophilic solvents and therefore are expected to solvate cations better than acetonitrile (protophobic dipolaraprotic solvent) [26,27]. Indeed, according to a previous study conducted in our group with analogous p-isopropylcalix[n]arene anions toward lanthanide cations Ln (III) carried out in MeCN and DMF, it was noted that (i) stoichiometry and stabilities are comparable to those of p-tertbutylcalix[n]arenes anions in MeCN ($3.2<\log\beta_{11}<5.6$ for ML and $9.5<\log\beta_{21}<10.3$ for M_2L) (ii) in DMF, stoichio-metries are generally comparable to those obtained in MeCN, except for

Table I. Stability constants ($\text{Log}\beta_{ML}$) of lanthanide complexes with p-tertbutylcalix[n]arenes, n = 4, 6, 8, in MeCN/ NEt_3 (25°C, I=10^{-2} M Et_4NClO_4).

Ligand	**Complex M:L**	**Log β_{ML}**			
		La^{3+}	**Eu^{3+}**	**Gd^{3+}**	**Tb^{3+}**
Tetramer	**1:1**	3.2±0.1	4.2±0.2	3.34±0.1	3.8±0.1
Hexamer	**1:1**	6.13±0.1	4.4±0.1	5.41±0.2	5.1±0.2
Octamer	**2:1**	8.66±0.1	9.8±0.1	9.48±0.2	9.62±0.1

Table II. HOMO and LUMO energies of p-t-butylcalix [4]arene.

	Gaz phase	DMF	MeCN
E_{HOMO}(u.a)	-0,18319	-0,20066	-0,28568
E_{LUMO}(u.a)	-0,05056	-0,0144	-0,00576
ΔE_1 (eV)	4.59		
ΔE_2 (eV)	4.08		
$\Delta E'_1$ (eV)	4.83		
$\Delta E'_2$ (eV)	6.40		

$\Delta E_1 = E_{LUMO}$(DMF) - E_{HOMO}(p-t-butylcalix[4]arene)
$\Delta E_2 = E_{LUMO}$(p-t-butylcalix[4]arene) - E_{HOMO}(DMF)
and
$\Delta E'_1 = E_{LUMO}$(MeCN) - E_{HOMO}(p-t-butylcalix[4]arene)
$\Delta E'_2 = E_{LUMO}$(p-t-butylcalix[4]arene) - E_{HOMO}(MeCN)

p-isopropyllcalix[8]arenes wherein a second species ML accompanies M_2L species. Concerning stabilities of the formed complexes in DMF, they appear to be lower than those obtained in MeCN with major equilibrium time (up to 50 h) for the same conditions.

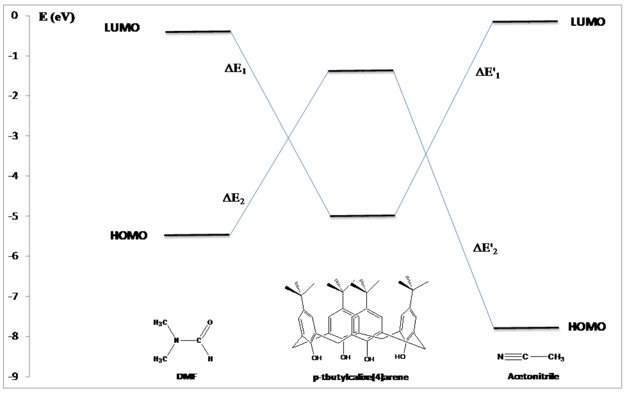


Figure 5. Correlation diagram of frontier molecular orbitals of DMF, MeCN and p-t-butylcalix[4]arene

Interaction of p-t-butylcalix[4]arene with solvent molecules. Frontier orbital theory:

Frontier orbital theory can be applied to predict the reactivity of p-t-butylcalix[4]arene in different solvents (DMF and MeCN).Geometry optimization at the DFT/PBE level of theory calculation and use of double-zeta Durand-Barthelat basis sets with polarization functions and pseudo-potentials of the

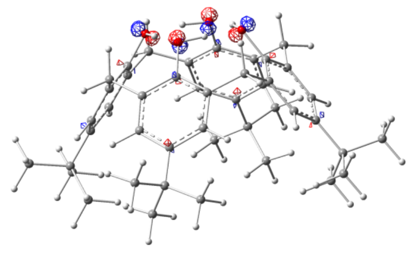
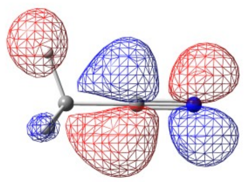
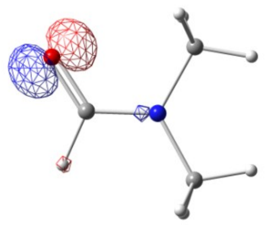
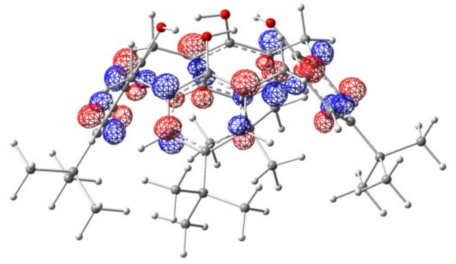
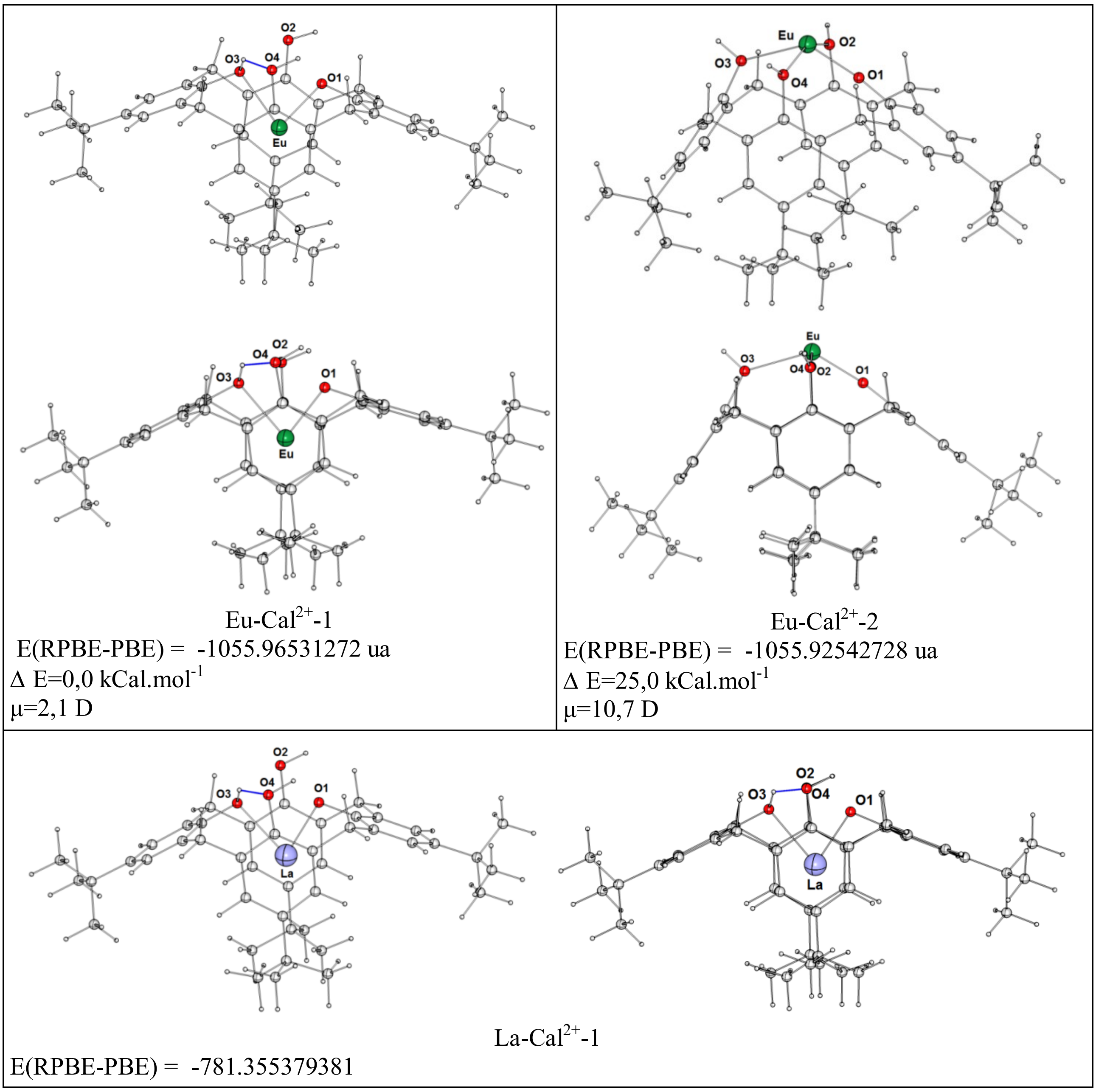
Donor	acceptor
	
HOMO calix isoval=0.09 (oxygen lone pair)	LUMO MeCN isoval=0.55 (C-N π* bond)
	
HOMO DMF isoval=0.15 (oxygen lone pair)	LUMO calix isoval=0.055 (C=C π* ring bonds)

Figure 6. Frontier molecular orbital of p-t-buthylcalix[4]arene and the HOMO of the DMF and the LUMO MeCN calculated by DFT/PBE level of theory with Durand-Barthelat effective core potential (ECP) and double zeta basis set with polarization function in all atoms.

p-t-butylcalix[4]arene molecule and the two solvents molecules, DMF and MeCN, provided the energy of the HOMO and LUMO frontier orbitals (Figure 5).

Comparison of ΔE_1 to ΔE_2 ($\Delta E_2<\Delta E_1$) indicate that the most favorable interaction is between the HOMO molecular orbital of the DMF and the LUMO molecular orbital of the p-t-butylcalix[4] arene (Table 2). Therefore DMF is the donor and p -t-butylcalix[4]arene is the acceptor.

DMF can donate its electron from the lone pair of oxygen and p-t-butylcalix[4]arene accept with the phenolic ring C=C π* antibonding orbital. (Figure 6). $\Delta E'_1< \Delta E'_2$ indicates that the most favorable interaction is between the molecular orbital HOMO of the calix and the LUMO orbital of the MeCN. Therefore the p-t-butylcalix[4]arene molecule is the donor and MeCN is the acceptor of the electron.p-t-Butylcalix[4]arenecan donate its electron from the lone pair of oxygen and MeCN



Eu-Cal^{2+}-1
E(RPBE-PBE) = -1055.96531272 ua
Δ E=0,0 kCal.mol^{-1}
μ=2,1 D

Eu-Cal^{2+}-2
E(RPBE-PBE) = -1055.92542728 ua
Δ E=25,0 kCal.mol^{-1}
μ=10,7 D

La-Cal^{2+}-1
E(RPBE-PBE) = -781.355379381

Figures7*:* Geometry of the two solvent free complexes [Eu p-tert-butylcalix[4]arene]$^{2+}$ and [La p-tert-butylcalix[4] arene]$^{2+}$ optimized at DFT / PBE.

Table III: Some optimized complex geometric parameters of [Eu p-tert-butylcalix[4]arene] $^{2+}$ and [La p -tert-butylcalix[4]arene]$^{2+}$ complexes, using functional PBE with bases and potential pseudo-SDD on Eu and La atomes and bases and potential pseudo-DZP of Durand-Barthelat on C, O and H atomes.

	Eu-Cal^{2+}-2	Eu-Cal^{2+}-1	La-Cal^{2+}-1
Distances en Å			
O2-H	0.983	0.983	0.983
O3-H	0.984	0.994	0.994
O4-H	0.983	0.983	0.985
O4 …. H3	-	1.993	2.011
M-O1	2.013	2.131	2.185
M-O2	2.426	3.837	3.861
M-O3	2.373	2.400	2.491
M-O4	2.426	3.601	3.659
M-C moy	-	2.938	3.020
O1-C	1.338	1.350	1.373
O2-C	1.448	1.350	1.349
O3-C	1.448	1.419	1.419
O4-C	1.448	1.372	1.371
Angles en °			
O1-M-O3	133.2	78.4	73.8
O2-M-O4	155.5	94.4	90.4
M-O1-C	173	109.3	100.8
M-O3-C	132.2	102.3	102.5

accepts with the C≡N π* anti-bonding orbital (Figure 6). It seems that MeCN which is an acceptor of the oxygen lone pair, polarizes the OH bond of p-t-butylcalix[4]arene and therefore increases its acidity.

The DMF is a donor by its oxygen lone pair, and increases the density of the ring. This affects the OH bond of p-t-butylcalix[4]arene by decreasing the polarization and then its acidity decrease.

The results of our calculations are in good agreement with the scales of donor[28] and acceptor[29] established for the two solvents.

Since the donor number: DN (DMF) = 26.6, DN (MeCN) = 14.1 and the acceptor number: AN (DMF) = 16 and AN (MeCN) = 18.9, DMF must be the best donor and MeCN must be the best acceptor.

Molecular dynamic study of monoanion p-tert-butylcalix[4]arene complexes with Eu^{3+} and La^{3+}

The gaz phase structures of [Eu p-tert-butylcalix [4]arene]$^{2+}$ and [La p-tert-butylcalix[4]arene]$^{2+}$ complexes have been optimised. The calculations were done with program Gaussian09W [21] using the PBE functional [30]. The SDD basis [31] has been used to describe the atoms of lanthanum and europium. Standard Pseudo potentials developed in Toulouse by Durand-Barthelat [22a] were used to describe the cores of carbon and oxygen atoms [22b]. Double zeta valence basis set with polarization (DZP) were used for each atom (the exponents of the polarization functions of type d are respectively 0.80 and 0.85). For the description of the hydrogen atoms, a standard primitive basis (4s) contracted [2s] was used and a polarization function of type p was added (exponent 0.9).

The geometries of different critical points on the potential energy surface have been completely optimized with the gradient method as implemented in Gaussian09w. The calculation of vibration frequencies was performed in order to determine the nature of the critical points.

Geometry optimizations which are performed on monoanion calix[4]arene europium complex allowed us to detect two stationary points on the potential energy surface corresponding to two isomers noted Eu-Cal^{2+}-1 and Eu-Cal^{2+}-2 (figure7). In the case of Eu-Cal^{2+}-1 isomer, the Eu^{3+} ion is intercalated inside the cone cavity of calixanion and is found encapsulated between two parallel phenol rings with an average distance Eu-C 2,938Å (Table3). The shortest distance Eu-O is 2,131Å and is found between the metal ion and the deprotonated oxygen O1 (Fig 7). An additional bond is observed between the europium ion and OH with a distance Eu-O3 equal to 2.400Å and an angle O1-O3-Eu equal to 78.0° (Table3). The relative energy DE calculated between the two isomers shows that the Eu-isomer Cal^{2+}-1 is more stable than the isomer Eu-Cal^{2+}-2 by 25kCal mol^{-1}. In the case of the complex with lanthanum, the geometry optimization gives a single stable isomer noted Cal^{2+}-1 which is the analog to the most stable isomer obtained with Eu^{3+} ion. La^{3+} is found to be housed inside the cone between two parallel phenol rings with an average distance La-C of 3,020Å. The shortest distance between the O-negative oxygen and La^{3+} ion is 2.185Å (figure7).

CONCLUSION

From different data collected from experimental and theoretical studies of deprotonation of p-tert-butylcalix[n]arenes and complexation properties of anion calixarenes toward lanthanide cations (La^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Tb^{3+}) the following main points emerge:

(i) Acidity of p-tert-butylcalix[n]arenes seems more important in MeCN than in DMF since DMF interact toward its oxygen lone pair with calixarene OH, decreasing their polarization and their acidity. Furthermore from theoretical study we deduce that DMF must be the best donor and MeCN must be the best acceptor.

(ii) Cavity size, higher conformational flexibility and the difference in oxygen atoms donor number, are mainly the most important determination factor for stoichiometry compared to solvent effect.

(iii) Complexation of trivalent lanthanide cations showed a formation of ML species with calix[4] arene and calix[6]arene anion while calix[8]arene anion form M_2L complexes.

(iv) Significant selectivities have been revealed for monoanion p-tert-butylcalix[6]arenes toward lanthane, followed by Gd^{3+} toward Eu^{3+} and for monoanion calix[8]arene toward europium cation.

(v) Geometry of monoanion calix[4]arene europium and lanthane complexes were optimized solvent free. According to the obtained results, two isomers have been detected in the case of europium complex and only one isomer in the case of lanthane. For the first europium isomer end lanthane complexes, Eu^{3+} and La^{3+} ions are encap-sulated into the upper rim cavity of calixanion between two parallel phenol rings. The second isomer of europium complex indicate that Eu^{3+} is bound into the lower rim cavity defined by three phenoxy oxygens and one deprotonated oxygen. From energy DE calculated between the two isomers, the first one seems more stable than the second one by 25kCal mol^{-1}.

This work furthers our understanding of the best conditions of deprotonation, as well as the complexation performances and selectivities of p-tert-butylcalix[n]arenes anion toward lanthanide trivalent cations. The results highlight also the importance of the contribution of DFT study in our understanding, therefore a second geometry optimi-zation study is under investigation, taking into account the presence of solvent - the subject of our further studies.

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