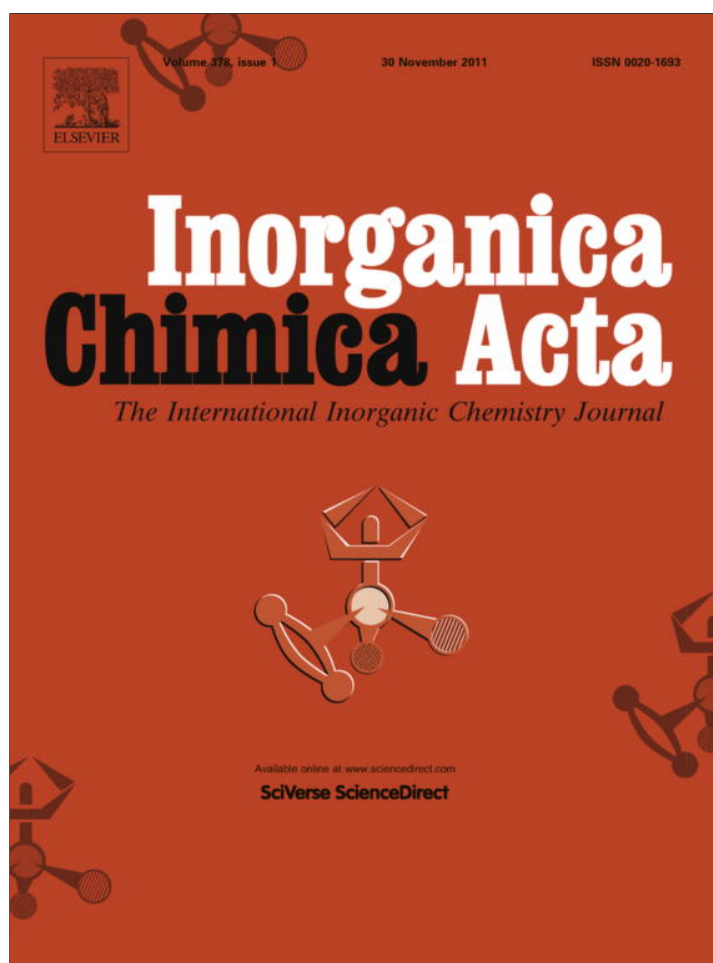


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5f-Element complexes with a *p*-*tert*-butylcalix[4]arene bearing phosphinoyl pendant arms: Separation from rare earths and structural studies

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ABSTRACT

Phosphinoylated calixarenes feature high coordination ability toward *f* elements and a great potentiality toward actinide/rare earth separation. Here, we report three characteristic properties of a tetra-phosphinoylated *p*-*tert*-butylcalix[4]arene, B₄bL⁴ functionalized with phosphinoyl pendant arms: (i) its coordination ability toward Th(IV) complexation in organic medium, (ii) its ability to separate thorium from yttrium, lanthanum, and europium in three different organic media, and (iii) the X-ray crystal structure of the La complex. Thorium(IV) forms 1:1 and 1:2 (M:L) complexes with B₄bL⁴: Th(NO₃)₄(B₄bL⁴)_n·xH₂O (*n* = 1, *x* = 1, **1**; *n* = 2, *x* = 4, **2**). Spectroscopic data point to the inner coordination sphere of **1** and **2** containing nitrate ions and water molecules. Molecular modeling of **1** yielded an 8-coordinate species and its coordination polyhedron can be described as a distorted square antiprism while that for **2**, a 9-coordinate species, as a distorted tricapped trigonal prism. The extraction study of tetravalent thorium and trivalent rare-earth (Y, La, Eu) ions from acidic nitrate media by B₄bL⁴ in chloroform shows thorium being much more extracted than the rare earths, with selectivity close to 100%. The extraction behavior can be easily modulated by changing the initial conditions (pH, nitrate concentration). The X-ray structure of [LaB₄bL⁴(H₂O)₅] CH₃CN·(ClO₄)₃ points to the La^{III} ion lying on a C₄ axis and being 9-coordinated by the four O(P) atoms and five O atoms from water molecules. It is located in the middle of the void formed by the four O-CH₂-PO(Me)₂ pendant arms.

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1. Introduction

Actinide (An) coordination chemistry has been developed in somewhat limited way in consequence of their high radiotoxicity and the very small quantities available for some of the radio-isotopes [1]. Therefore, complexes with weakly α -emitting, long half-life radio-elements such as uranium [2–6] and tetravalent thorium [7] have been the most studied while lanthanide ions (Ln), in an indirect way, have afforded knowledge on the chemical behavior of trivalent actinides [8,9]. Thorium coordination chemistry is also well documented, both with respect to hydration and hydrolysis [10], complexes with oxygen- and nitrogen-donor ligands [7], macrocyclic complexes [11–13], and even quadruple-stranded helicates [14].

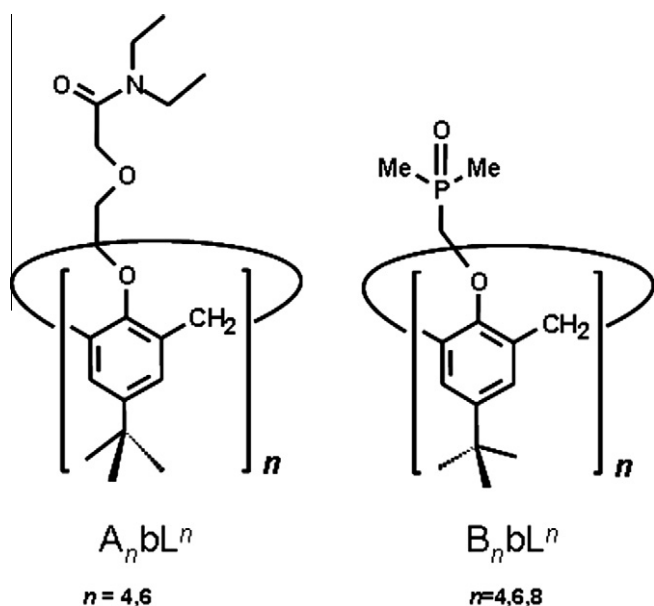
Lately, a large interest has developed for the interaction between *f* elements and properly functionalized calixarenes, in the hope of designing adequate systems for their extraction and for

An/Ln separation. In particular, calixarenes fitted with pendant arms containing groups such as phosphoryl and/or amide have proved to display powerful extraction ability and large selectivity [15–26]. Effectiveness of these macrocycles in the treatment of radioactive wastes containing lanthanides, actinides, alkaline, and alkaline earths has been practically demonstrated [27]. Few calixarene complexes with thorium have been reported [11,21] while phosphorylated calixarenes have been successfully used for thorium extraction [11,13,17,18,25,26].

Taking into account these considerations, we have been involved during the past years in the synthesis of two series of calix[*n*]arenes (*n* = 4, 6, 8, Scheme 1) fitted with ether amide [28,29] and phosphinoyl pendant arms on the narrow rim [11,30–32]. We have reported the structural and photophysical properties of their lanthanide complexes [28–32]. Recently, our work has been expanded to the study of actinide complexes formed with the phosphinoyl-derivatized calix[6]arene B₆bL⁶, as well as to its extraction capability toward uranyl, thorium(IV), and representative trivalent rare earths (Y, La, Eu) [11]. The synergistic effect of the phosphinoyl-derivatized calix[4]arene B₄bL⁴ in the extraction of lanthanides with a pyrazolone derivative has also been shortly reported by one of us [33]. Polystyrene microfibers

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Scheme 1. Calixarenes with ether amide and phosphinoyl pendant arms in the lower rims.

containing this lower-rim substituted calix[4]arene with phosphinoyl pendant arms were easily prepared in one-step procedure by electrospinning [34]. In the continuation of these studies, we report here on the coordination ability of B_4bL^4 toward thorium(IV) cations with a characterization of the resulting 1:1 and 1:2 complexes through several spectroscopic techniques, backed by model calculations as well as the X-ray structure of the 1:1 lanthanum complex. We also present the extraction properties of B_4bL^4 with respect to *f*-elements and Th/Ln separation.

2. Experimental

2.1. Materials and methods

$Th(NO_3)_4 \cdot 5H_2O$, ethanol and di-isopropyl ether were purchased from Merck. Nitric acid (purity 65.1%, specific density 1.3989), formic acid (purity, 90%), sodium formate and nitrate were from Baker. De-ionized water was kindly supplied by the staff of the Nuclear Reactor TRIGA Mark III from the Nuclear Center of Mexico. Anhydrous (<0.005% water) chloroform, acetonitrile, diethyl ether, as well as spectroscopic grade dichloromethane, acetonitrile, and Arsenazo III were purchased from Aldrich and used without further purification or dehydration. The lower-rim substituted *p*-tert-butylcalix[4]arene B_4bL^4 (5, 11, 17, 23-tetra-*tert*-butyl-25, 26, 27, 28-tetrakis (dimethyl-phosphinoylmethoxy)calix[4]arene), was obtained as reported previously [30]. IR spectra were measured on a Perkin–Elmer series 1600 IR spectrometer. UV–Vis and diffuse reflectance spectra were recorded on a Perkin–Elmer Lambda 10 spectrophotometer using 1-cm quartz cells and MgO pellets, respectively. Elemental analyses were performed on a Perkin–Elmer 2400 series II (UAM-I, México) instrument.

2.2. Syntheses and characterization of the thorium complexes

The hygroscopic 1:1 and 1:2 complexes were prepared according to the procedure reported recently for B_6bL^6 [11]. Yield: 65%. *Anal. Calc.* for $Th(B_4bL^4)(NO_3)_4 \cdot H_2O$, $C_{56}H_{86}N_4O_{21}P_4Th$ (**1**): C, 44.63; H, 5.75; N, 3.72. Found: C, 44.70; H, 5.72; N, 3.58%. After heating the KBr disk at 95 °C for 25 h, IR (cm^{-1}): B_4bL^4 : $\nu(P-CH_3)$, 1297; $\nu(P=O)$, 1196, 1172; $\nu(=C-O-CH_2-)$, 1018; $\nu H_2O_{lattice}$, 555,

522, 494, 356; (**1**): $\nu(P-CH_3)$, 1298; $\nu(P=O)$, 1187; $\nu(=C-O-CH_2-)$, 1012; νNO_{3ionic} , 1384, $\nu NO_{3coord.}$, 1547, 1518, 1490, 761 (monocoordinated), 1566, 1286 (bicoordinated); $\nu H_2O_{lattice}$, 550, $\nu H_2O_{coord.}$, 508_{strong}, 365_{m-strong}. Diffuse reflectance in MgO without drying the pellets ($\pi \rightarrow \pi^*$ transitions, cm^{-1}): B_4bL^4 : P=O, 42020 (238 nm); $-C=C_{phenyl}$, 35335 (283 nm); (**1**) P=O, 45045 (222 nm); $-C=C_{phenyl}$, 33225 (301 nm). UV–Vis spectra in CH_3CN : λ_{max} 275 nm; ϵ ($M^{-1} cm^{-1}$): B_4bL^4 , 3780; (**1**), 4408. Yield: 67%. *Anal. Calc.* for $Th(B_4bL^4)_2(NO_3)_4 \cdot 4H_2O$, $C_{112}H_{176}N_4O_{32}P_8Th$ (**2**): C, 52.33; H, 6.90; N, 2.18. Found: C, 52.92; H, 7.17; N, 2.34%. After heating the KBr disk at 95 °C for 25 h, IR (cm^{-1}): $\nu(P-CH_3)$, 1299; $\nu(P=O)$, 1195, 1173; $\nu(=C-OCH_2-)$, 1021; νNO_{3ionic} , 1384, $\nu NO_{3coord.}$, 1515, 768; $\nu H_2O_{lattice}$, 550, 493, 359; $\nu H_2O_{coord.}$, 509, 387. Diffuse reflectance in MgO without drying the pellets ($\pi \rightarrow \pi^*$ transitions, cm^{-1}), 35715 cm^{-1} (280 nm). UV–Vis spectra in CH_3CN : λ_{max} 275 nm; ϵ ($M^{-1} cm^{-1}$) 6215.

2.3. Extraction procedure

The aqueous phases 1, 2 and 3 of Th^{4+} and/or trivalent rare-earth nitrates (RE = Y, La, Eu) were prepared as reported previously [11]. Organic phases of the calixarene were prepared in anhydrous chloroform. Organic phase 4: B_4bL^4 1.24×10^{-4} M; organic phase 5: B_4bL^4 3.27×10^{-4} M in order to maintain 1:1 and 1:2 metal-to-ligand ratio, respectively during the extraction process. The aqueous phase (5 cm^3) containing the metal salt(s) was poured into a high-quality glass vial fitted with a hermetic top; the corresponding organic B_4bL^4 phase (5 cm^3) was then added. The vial was capped and shaken at a speed of 300 rpm during 7 h at 291 ± 2 K. The vial was then kept still for 2 h to ensure optimum separation. When an emulsified phase formed between the organic and aqueous phases, the organic phase was slowly separated using a funnel; the combined aqueous and emulsified phases were filtered on a glass frit funnel (4–5.5 μm) under vacuum (1.33 Pa). The added metal content of the aqueous and emulsified phases after filtration was always identical to that found in a portion of the aqueous phase before filtration. In general, the metal concentration was analyzed in each aqueous and organic phases before and after extraction by spectroscopic techniques, as described previously [11].

2.4. Molecular modeling

The structures were built and their minimum energies calculated using the CAChe WorkSystem Pro 5.02 program package for Windows® (Fujitsu Ltd., 2000–2001). Sequential application of Augmented MM3/CONFLEX procedures yielded the most stable conformers for compounds **1** and **2** and the free calixarene. The calixarene structure has also been calculated by MOPAC/PM5 and MOPAC/PM5/COSMO procedures. COSMO evaluates the solvent effect in the stabilization of a structure and therefore the resulting calixarene structure was the base for the simulation of the thorium complexes. The MOPAC procedure could not be applied to the thorium complex molecules because it lacks parameters for *f*-elements.

2.5. X-ray crystal structure of $\{[LaB_4bL^4(H_2O)_5] CH_3CN\} \cdot (ClO_4)_3$

The crystal data and structure refinement parameters are presented in Table 1. Crystals were mounted in glass capillaries. Diffraction data were collected on a mar345 Imaging Plate Detector System. The cell was determined using 232 spots from the first image. Refinement of cell parameters, integration and scaling of data were performed with the program marHKL, release 1.9.1 [35]. No absorption correction was applied. The solution and refinement were performed by SHELX [36]. The structure was refined using full-matrix least-squares based on F^2 with all nonhydrogen atoms

Table 1
Crystal data and structure refinement.

Compound	[LaB ₄ BL ⁴ (H ₂ O) ₅] CH ₃ CN·(ClO ₄) ₃
Formula unit	C ₅₈ H ₉₇ Cl ₃ LaNO ₂₅ P ₄
Molecular weight	1577.51
Crystal system	tetragonal
Space group	P4/n (ITC no. 85)
a (Å)	14.080(2)
b (Å)	14.080(2)
c (Å)	23.794(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å ³)	4717.1(13)
Z	2
ρ _{calc} (g cm ⁻³)	1.111
T (K)	140(2)
μ (mm ⁻¹)	0.663
λ (Å)	0.71073
F(000)	1640
Total reflections	5436
Observed reflections [I > 2σ(I)]	4452
Parameters refined	288
R ₁ [I > 2σ(I)]	0.0745
wR ₂ [I > 2σ(I)]	0.2076

anisotropically defined (except the CH₃CN within the calixarene). Hydrogen atoms were placed in calculated positions by means of the “riding” model. Rotational disorder was evident in the case of the *t*-butyl group and ClO₄⁻; it was modeled by means of the split model and by the application of some reasonable restraints (SIMU, SADI, DFIX cards). The additional electronic density found outside the calixarene, representing highly disordered solvent (CH₃CN or H₂O), was treated by the SQUEEZE algorithm found in PLATON [37].

3. Results and discussion

3.1. Isolation and characterization of the thorium complexes

Reaction of B₄BL⁴ with thorium nitrate in stoichiometric ratios 1:1 in ethanol and 1:2 in acetonitrile yielded the following white complexes: Th(NO₃)₄(B₄BL⁴)_n·xH₂O (*n* = 1, *x* = 1, **1**; *n* = 2, *x* = 4, **2**). The reaction yields for both thorium calixarene complexes were similar, pointing to the formation of species being essentially governed by the affinity of the phosphinoyl arms toward the metal ions. The Th(B₄BL⁴)₂ complex is more hydrated than the 1:1 compound, a fact which can be traced back to the large affinity of the phosphinoyl groups for water [11,30–32].

The vibrational spectra of the complexes reveal that one component of the P=O vibrations of free B₄BL⁴, at 1172 cm⁻¹, disappears

completely upon formation of the 1:1 complex (**1**) while the other component is slightly red shifted (Table 2). Bands attributable to coordinated (bidentate, monodentate) nitrate and water molecules are present in the spectrum as well as un-coordinated nitrate [38]. After drying, the spectrum does not change and two bands are seen at 508 and 365 cm⁻¹ assigned to vibrations from coordinated water molecules; this implies that the water molecule is directly coordinated to the metal ion (Fig. S1, Supplementary data). As for the 1:1 complex, vibrations corresponding to coordinated nitrate and water molecules appear in the spectrum of the thorium 1:2 complex (**2**).

In the diffuse reflectance spectrum of the 1:1 complex the π → π* (P=O) transition is blue shifted by 3010 cm⁻¹ with respect to the free ligand, while the π → π* (C=C-phenyl) transition is red shifted by 2115 cm⁻¹. Once more the P=O-metal cation interaction is demonstrated and the involvement of the calixarene scaffold to the stability of this complex. The spectrum of the 1:2 complex was less informative.

3.2. Solution study

The UV-Vis spectra of B₄BL⁴ and its complexes in acetonitrile display the main phenyl π → π* ligand band in the range 275–279 nm. It is slightly red shifted (1–4 nm) in the complexes which additionally display a shoulder on the low-energy side (≈284 nm). The molar absorption coefficient of the 1:1 complex is about 14% larger compared to the free ligand. In the corresponding complex with B₆BL⁶ the increase in the molar absorption coefficient was about 20%, indicating more influence of the metal center on the electronic structure of the larger calixarene, in line with its better suited conformation for interacting with actinides [11]. The molar absorption coefficient of the 1:2 complex is substantially smaller than two times the value for the free ligand, displaying 63% increase over the latter only. The increase is smaller than the one reported for the 1:2 complex with B₆BL⁶ and Th⁴⁺ (+90%). Here again a similar explanation as above can be given. Contributions to the differences observed between the two complexes with B₄BL⁴ on one hand, and between B₄BL⁴ and B₆BL⁶ complexes on the other hand, may come from differences in hydration and/or nitrate interaction.

3.3. Molecular modeling

In order to substantiate the experimental results described above, model calculations have been performed both in vacuum and in a polar solvent on the free calixarene and on the thorium complexes. Surprisingly, the predominant low-energy isomer calculated for B₄BL⁴ was a 1,3 alternate conformer, even in water, while in less polar solvents such as CHCl₃ and CH₃CN, NMR data

Table 2
Calculated structures for the free calixarene and their thorium complexes, and the most important spectroscopic data.

Compound	E (kcal mol ⁻¹) ^a	Proposed formula and geometry ^b	Vibrational frequencies (cm ⁻¹)				ε (M ⁻¹ cm ⁻¹)
			P=O	NO ₃ ⁻		Coordinated H ₂ O	
				Monocoordinated	Bicoordinated		
B ₄ BL ⁴	37, 37, -492, -516	1,3 alternate cone conformer, C ₄	1196, 1172				3780
1	435, 435	[Th(B ₄ BL ⁴)(NO ₃) ₂ (H ₂ O)] ²⁺ CN = 8; distorted square antiprism Mean Th ← O=P: 2.50(2) Å	1187	1518, 1490, 1547, 761	1286, 1566	508 _s , 365 _{vw}	4408
2	639, 625	[Th(B ₄ BL ⁴) ₂ (NO ₃)(H ₂ O) ₂] ³⁺ CN = 9; distorted tricapped trigonal prism Mean Th ← O=P: 2.52(2) Å	1195 1173	1515, 768		509 _m , 387 _m	6215

^a In sequence: MM3, CONFLEX, MOPAC/PM5, and MOPAC/PM5/COSMO.

^b From the optimum geometries found by MM3 and CONFLEX (CACHeworkSystem Pro 5.02).

are consistent with a cone conformation. Such conformation was also found for the acetonitrile adduct of this calixarene in the solid state by X-ray crystallography [30].

The structural versatility of actinide complexes in solution and solid arises from the lack of strong crystal field effects for the 5*f* electronic configurations as well as from their large ionic radii. The predominant ionic character of the bonding leads to a wide variety of coordination numbers (CN) and symmetries. For thorium(IV) complexes, CN = 8 and 9 in square antiprismatic and trigonal prismatic geometries are the most common, although CN ranging from 6 to 12 have been found [1,7,25]. Thorium complexes with calixarenes are known, the most related with this work are complexes with CMPO-[18] and phosphine oxide-derivatized [11,17] calixarenes, whose stoichiometries suggest usually CN = 8–9.

3.3.1. Th(IV) complexes

The calculated coordination polyhedron of the most stable modeled structure of $[\text{Th}(\text{NO}_3)_2(\text{B}_4\text{bL}^4)(\text{H}_2\text{O})]^{2+}$ (**1**) is a distorted square antiprism (CN = 8; effective ionic radius = 1.19 Å (Fig. 1) and a distorted tricapped trigonal prism (CN = 9; effective ionic radius = 1.23 Å) for $[\text{Th}(\text{NO}_3)(\text{B}_4\text{bL}^4)_2(\text{H}_2\text{O})_2]^{3+}$ (**2**). The 1,3 alternate conformation of the calculated calixarene is maintained in the complexes. In fact, electrostatic repulsion and van der Waals interaction energy terms from the ligands are detrimental to the calculated energy of the optimized molecular geometry (Table 1). However, bond lengths and angles are in the usual range for Th–O coordination [7,11]. The Th ← OP average bond lengths are 2.505 ± 0.025 and 2.521 ± 0.085 Å for **1** and **2**, respectively (Supplementary data, Table S1). A model of **2** with two calixarenes completely coordinated to Th(IV) does not yield the most stable structure (CN = 8); however, three OP arms per calixarene, one monodentate nitrate and two water molecules coordinated to Th(IV), yield the most stable structure given above. This is in agreement with the experimental results. For instance, the infrared spectrum of **2** reveals that not all the OP arms of the calixarenes are coordinated to the cation and bands corresponding to coordi-

nated water molecule and monocoordinate-nitrate were observed (see Section 2). The overall shape of the OP bands was very similar to that of $\text{Th}(\text{B}_6\text{bL}^6)_2$ [11], for which we proposed the two calixarenes to be partially coordinated to thorium. However, the minimum energies resulting from the semiempirical calculations of the thorium B_4bL^4 complexes suggest their lower stability with respect to those formed with B_6bL^6 probably due to the smaller size of B_4bL^4 , an effect which is not compensated by its rigidity.

3.4. Liquid–liquid extraction of *f*-elements

The extraction ability of B_4bL^4 toward Th(IV), Y(III), La(III), and Eu(III) ions was tested. The study was performed using three different aqueous nitric phases (aqueous phases 1, 2 and 3) and two different calixarene concentrations in chloroform corresponding to metal:ligand ratios of ≈ 1 (organic phase 4) and ≈ 2.5 (phase 5). Results are collected in Table 3.

Generally speaking, actinide cations are much better extracted than rare earths, which is encouraging in the perspective of An/Ln separation since in some cases theoretical separation factors are very large. Increasing the concentration of the calixarene by a factor 2.5 in going from organic phase 4 to phase 5 leads to a concomitant increase in the extraction of the thorium cations (average increase is 2.3-fold), in line with the formation of 1:2 complex demonstrated in the above description. However, the extraction efficiency of Th^{4+} also depends on the aqueous phase. Increasing the concentration of nitric acid in the aqueous phase from 1 to 3 M is quite detrimental to thorium extraction about 25–30%. However, boosting sodium nitrate concentration from 0.5 to 3.5 M results in a much better extraction of thorium by a factor ≈ 2 . It has been recently demonstrated that the salting-out effect plays an important role in $\text{Th}^{4+}/\text{La}^{3+}$ separation with calix[6]arene B_6bL^6 [11]. We find a similar behavior with B_4bL^4 since the increase in nitrate concentration gives rise to a remarkable improvement in La^{3+} extraction, by a factor ≈ 10 . Consequently, the extraction selectivity (Th/La) for the more concentrated organic phase 5 goes down

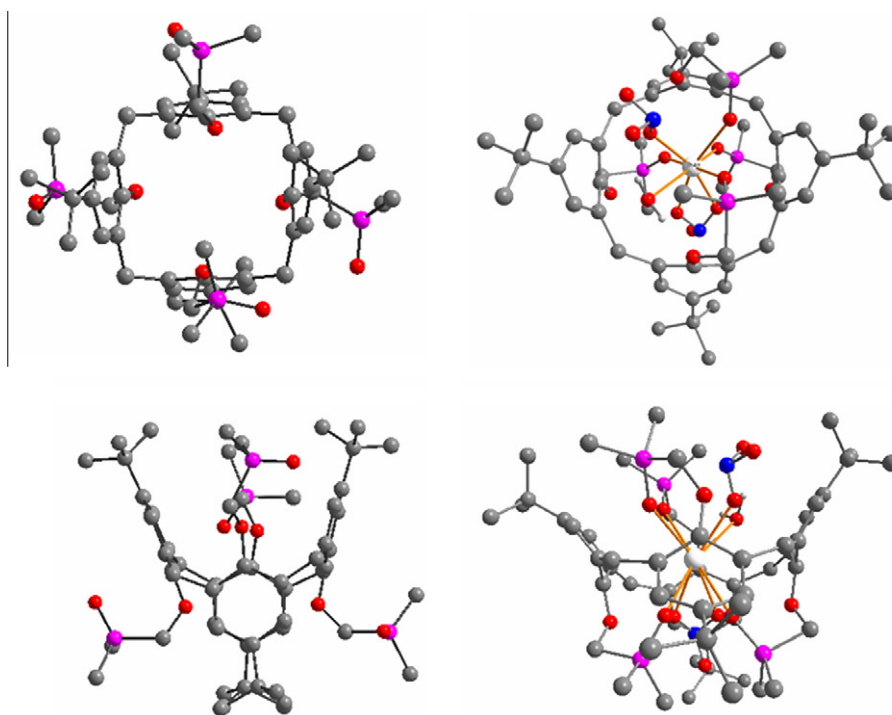


Fig. 1. On the right side, two views of the modeled $[\text{Th}(\text{NO}_3)_2\text{B}_4\text{bL}^4(\text{H}_2\text{O})]^{2+}$ by Augmented MM3/CONFLEX calculations, and on the left side those of the free calixarene B_4bL^4 by MOPAC/PM5/COSMO calculations. Hydrogen atoms have been removed for clarity.

Table 3
Percentages of recovered cations after liquid–liquid extraction of thorium and rare earth nitrates at 18 ± 2 °C by B_4bL^4 in chloroform (7 h shaking).

Cation	Aqueous phase [M(NO ₃) _n]/10 ⁻⁴ M	Organic phase, [B ₄ bL ⁴]/10 ⁻⁴ M 1.27 (4) 3.17 (5)		Extraction selectivity ^a					
				Th/La		Th/Eu		Th/Y	
				(4)	(5)	(4)	(5)	(4)	(5)
1 M HNO ₃ –0.5 M NaNO ₃ (1)				7	11	2	3	3	6
Th ⁴⁺	1.30	21.2 ± 0.4	53.8 ± 0.8						
La ³⁺	1.29	3.0 ± 1.0	5.0 ± 1.0						
Eu ³⁺	1.08	14.0 ± 1.1	16.0 ± 1.2						
Y ³⁺	1.15	7.0 ± 0.1	9.0 ± 0.2						
1 M HNO ₃ –3.5 M NaNO ₃ (2)				1	2			10	3
Th ⁴⁺	1.17	55.8 ± 1.0	79.0 ± 1.0						
La ³⁺	1.11	38.7 ± 1.1	43.8 ± 1.1						
Eu ³⁺	1.19	no extraction	no extraction						
Y ³⁺	1.19	5.60 ± 0.03	23.5 ± 1.1						
3 M HNO ₃ –0.5 M NaNO ₃ (3)						80	3		
Th ⁴⁺	1.09	16.0 ± 0.4	38.3 ± 0.8						
La ³⁺	1.16	no extraction	no extraction						
Eu ³⁺	1.28	0.20 ± 0.03	13.0 ± 1.0						
Y ³⁺	1.24	no extraction	no extraction						

^a Extraction selectivity is not given when the rare earth is not extracted.

9-fold for thorium under these experimental conditions, although Th(IV) is 80% extracted. For rare-earth ions, the extraction percentages are usually small or even in several cases no extraction is detectable. In particular, the behavior of B_4bL^4 as extractant for rare earths is similar to that found for the *p*-*tert*-butylcalix[4]arene derivative containing diphenyl-phosphinoyl [15] or other phosphoryl groups [17,26].

3.5. Stoichiometric correlation of extraction–complexation data

It has been reported that extraction of thorium in dichloromethane containing *p*-*tert*-butylcalix[4–8]arene diphenylphosphine oxides attached to the lower rim results in the co-extraction of complexes with different stoichiometries; indeed, the slopes of the logD versus log[L] graphs are between 1.8 and 2.6 and co-extraction of nitric acid or activity coefficients could not be ruled out [17]. For europium, the slopes are between 2.0 and 2.5. Ln complexation studies with these ligands revealed 1:1 species for Pr³⁺, Eu³⁺ and Er³⁺ [17]. Recently, a 1:1 stoichiometry was reported for the europium species extracted from acidic media into *m*-nitrobenzotrifluoride with *p*-*tert*-butylcalix[5]arene di-butylphosphine oxide [26]. Complexation studies with this ligand in acetonitrile revealed 1:1 stoichiometry for europium while with the *p*-*tert*-butylcalix[4]arene di-butylphosphine oxide ligand 1:1 and 1:2 Eu:ligand ratios were found in methanol. The stoichiometry of thorium and europium species extracted from acidic-salty media with B_6bL^6 into chloroform was 1:1 [11]. In the present work with B_4bL^4 , no stoichiometry could be established for the Th(IV) and Eu(III) species: distribution ratios could not be estimated for calixarene concentrations larger than 4×10^{-4} M, the emulsified phase between the aqueous and organic phases starting to be problematic (Table 3, aqueous phase 2).

Complexation studies of lanthanides with B_4bL^4 [30] and B_6bL^6 [11,31] in acetonitrile revealed two predominant species with 1:1 and 1:2 stoichiometries. The corresponding isolated complexes with thorium and europium were obtained with reaction yields between 50% and 65% [11,30,31] very close to those found for the thorium complexes reported in the present work (65–67%). We note that lanthanum is better extracted than europium with aqueous phase 2 (Section 3.6) and the reaction yields of its complexes with B_4bL^4 was 80 (1:1) and 66 (1:2)%, respectively [30]. This encouraged us to try to isolate single crystals suitable for X-ray analysis. Out of all experiments carried out, only the 1:1 complex

of B_4bL^4 with lanthanum could be crystallized, the structure of which is described in the following section.

3.6. Crystal structure of $\{[LaB_4bL^4(H_2O)_5]CH_3CN\} \cdot (ClO_4)_3$

Single tetragonal crystals with composition $[LaB_4bL^4(H_2O)_5]CH_3CN \cdot (ClO_4)_3$ and suitable for X-ray crystallography could be obtained by slow diffusion of diisopropyl ether into a 1:2 (La: B_4bL^4) solution in non-anhydrous acetonitrile. The crystals belong to the $P4/n$ crystallographic space group and the corresponding molecular structure is displayed on Fig. 2 while distances and angles relevant to the coordination polyhedron are listed in Table 4. The La^{III} cation lies on the C₄ axis and is 9-coordinated by the four O(P) atoms and five O atoms from water molecules. It sits on top of the macrocycle and therefore is not encapsulated into its cavity. Four water molecules are bound on the upper side while the fifth one (lying on the crystallographic 4-fold axis) is located in the middle of the void formed by the four O–CH₂–PO(Me)₂ pendant arms. It is most probably held in this position by a remarkable network of symmetrical hydrogen bonds since O(1)···O(3) contacts are 2.886(3) Å (H atoms could not be located). The coordination polyhedron is a monocapped square antiprism with C_{4v} symmetry, the four O(4) and O(2) atoms defining the upper and lower planes, respectively while their centroid, the La and the O(3) atoms are perfectly aligned. The average La–O bond length is equal to 2.549(3) Å, with significant differences among them. The La–O(2) distance [2.464(3) Å] is standard for 9-coordinated La^{III}, but La–O(4) is 0.177 Å longer. This may be traced back to weak interactions with perchlorates: four anions (each having occupancy 0.75) are located on top of and in between the four H₂O(4) molecules with one oxygen atom of each at 2.86(1) Å contact distance from O(4). The La–O(3) distance is 0.057 Å longer than La–O(2) again in line with the water molecule implied in H-bonding. The calixarene adopts its classical cone conformation and an acetonitrile molecule, lying on the 4-fold axis, is inserted into the lower rim. This structure corresponds to one of the two structures evidenced in acetonitrile solution by NMR spectroscopy [35]. The structure of a 1:2 lanthanum complex with diethoxyphosphoryl-*p*-*tert*-calix[4]arene has been reported [39]. The two calixarenes adopt a cone conformation and a pseudo C₄ axis goes through the lanthanum atom and the centers of the two cones. The La–O distances lie in a narrow range (2.42–2.55 Å) with a mean value of 2.49 Å, quite comparable the La–O(2) bond length reported in Table 4.

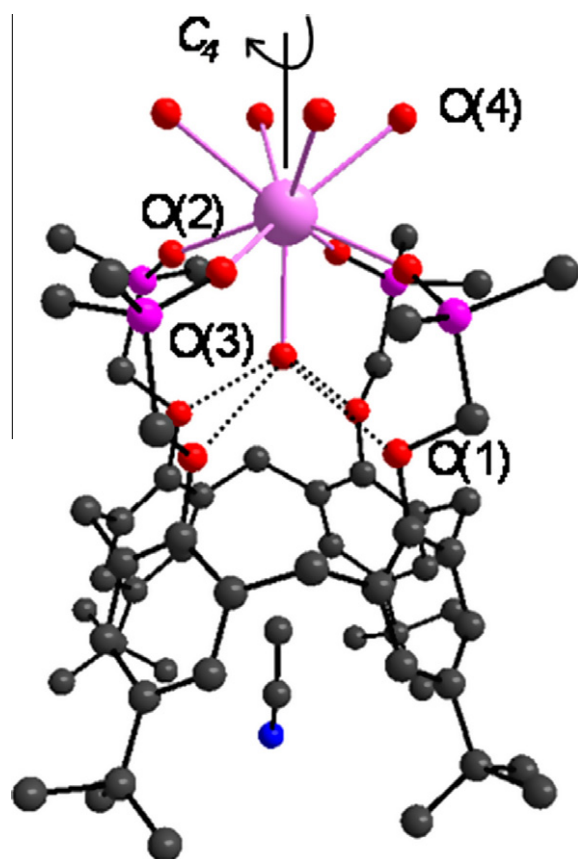


Fig. 2. Molecular structure of tetragonal $\{[LaB_4bL_4(H_2O)_5]^{3+} \cdot CH_3CN\}$ cation with O-atom numbering scheme; for the sake of clarity hydrogen atoms have been removed.

Table 4

Distances and angles pertaining to the coordination polyhedron in $[LaB_4bL_4(H_2O)_5]^{3+}$; refer to Fig. 2 for atom labeling.

Distances (Å)		Angles (°)			
La–O(2)	2.464(3)	O(2)–La–O(2)	83.33(4)	O(3)–La–O(4)	127.62(7)
La–O(3)	2.521(5)	O(2)–La–O(3)	70.07(6)	O(4)–La–O(2)	68.66(9)
La–O(4)	2.641(3)	O(2)–La–O(4)	74.41(9)	O(4)–La–O(4)	68.12(8)

4. Conclusions

The tetra-phosphinoylated *p-tert*-butylcalix[4]arene forms stable thorium complexes with 1:1 and 1:2 stoichiometries in organic media. A combination of several experimental analytical techniques and theoretical modeling leads to the conclusion that coordination numbers are most probably 8–9 in these edifices. The B_4bL_4 calixarene is a reasonably good extractant for thorium but a poor one for rare earths. The extraction behavior and separation ability is much dependent on the initial conditions, pH and nitrate concentration, so that modulation of the extraction process is easy. Further study on these systems will be focused on more lipophilic macrocyclic receptors in which the wider rim of the calixarene is decorated with octyl substituents.

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Appendix A. Supplementary material

CCDC 812313 contains the supplementary crystallographic data for $\{[LaB_4bL_4(H_2O)_5] \cdot CH_3CN\} \cdot (ClO_4)_3$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.08.049.

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