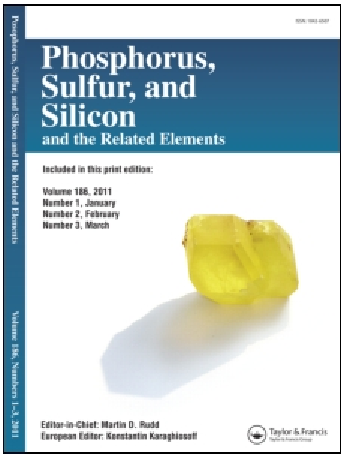

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LOWER-RIM POLYPHOSPHORYLATED CALIX[4]ARENES. THEIR USE AS EXTRACTING AGENTS FOR THORIUM (IV) AND EUROPIUM (III) IONS

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The extraction of thorium (IV) and europium (III) ions from aqueous nitrate media (1 M nitric acid and sodium nitrate) using six p-tert-*butylcalix[4]arene derivatives bearing phosphine oxide units (—$CH_2P(O)Ph_2$) anchored at the lower rim has been investigated at 25°C. All ligands display higher extracting properties toward thorium than europium ions. The number and position on the lower rim of the ligating groups play a crucial role in the extraction process, the highest extraction percentages being in each case achieved with the tetraphosphorylated calixarene. In the presence of sodium nitrate the extraction percentages are considerably higher than those obtained in the presence of nitric acid.*

Keywords: Calix[4]arene; europium; phosphine oxide; solvent extraction; thorium

A number of molecules containing phosphoryl groups exhibit remarkable extraction and complexation properties towards actinides and lanthanides.[1] Particular interest has been devoted recently to the use of macrocyclic compounds bearing bundles of converging phosphine oxide substituents that create a cage-type receptor suitable for metal ion complexation. Preorganized ligand systems of this type recently were shown to enhance extraction of metal ions in comparison to their individual components.[2] A logical way to construct such multitopic ligands consists in tethering phosphine oxide units onto a circular platform containing several exo-oriented anchoring points.[3–5] Thus, we described

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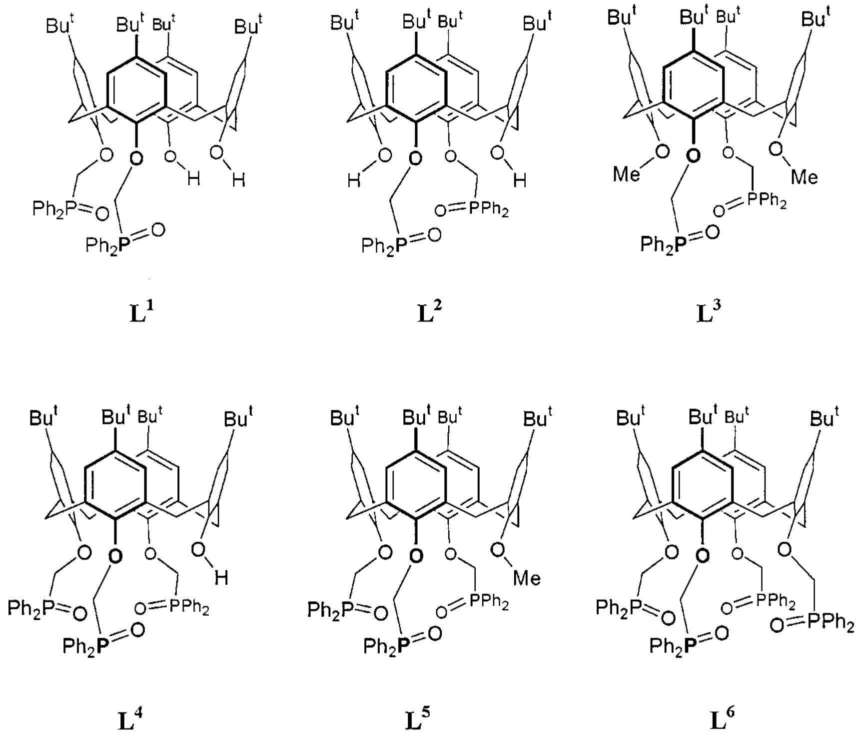

FIGURE 1 Calix[4]arenes used in this work.

the preparation of conical calix[4]arenes, multiply substituted at the phenolic oxygen atoms by —$CH_2P(O)Ph_2$ groups,[3,4] and also investigated their binding properties toward a variety of metal ions, notably of rare earth metal ions.[6–10] Following our previous studies we now report on the extraction of thorium (IV) and europium (III) ions in the presence of sodium nitrate and nitric acid by the six lower-rim phosphorylated calix[4]arenes **L^1–L^6** (Figure 1). Thorium and europium ions may be regarded as fair models for tetravalent and trivalent actinides respectively.[11,12]

RESULTS AND DISCUSSION

Table I shows the extraction percentages of thorium and europium ions from aqueous 1 M sodium nitrate solutions (25°C) into a dichloromethane. It is well known that aqueous phases arising from nuclear fuel reprocessing are usually highly acidic. Management of

TABLE I Extraction Percentages of Th (IV) and Eu (III) Ions (1×10^{-4} M) from 1 M Nitrate Medium ($NaNO_3$ or HNO_3) by Calixarenes $\mathbf{L^1}$–$\mathbf{L^6}$ (1×10^{-2} M) in Dichloromethane at 25°C[a]

	$NaNO_3$		HNO_3	
Ligand	Th	Eu	Th	Eu
$\mathbf{L^1}$	20.9	<1	<1	<1
$\mathbf{L^2}$	36.5	3	6.8	2.8
$\mathbf{L^3}$	19.3	<1	<1	<1
$\mathbf{L^4}$	28.8	5.3	<1	<1
$\mathbf{L^5}$	26.7	4.1	<1	<1
$\mathbf{L^6}$	78.9	14.8	27.6	4.6

[a] Mean of three independent experiments.

nuclear waste therefore requires the use of ligands that are not only selective but also remain effective in high concentrated acid media.[1] Therefore, we also investigated the extractive properties of ligands $\mathbf{L^1}$–$\mathbf{L^6}$ toward Th (IV) and Eu (III) ions from 1 M nitric acid solutions. These results are also presented in Table I.

From Table I it can be deduced that, for all the ligands used in this study, the extraction of thorium is better than that of europium ions. This observation holds for both media, sodium nitrate or nitric acid. Similar observations already have been made for other phosphorylated calixarenes.[11–13]

In both media the tetra-phosphorylated calix[4]arene $\mathbf{L^6}$ shows the best extracting properties toward thorium and europium ions. The extraction percentages observed for the di- and tri-phosphorylated ligands $\mathbf{L^1}$–$\mathbf{L^5}$ are lower than that obtained with the tetraphosphorylated compound $\mathbf{L^6}$. The higher binding properties of the latter ligand are likely to reflect the ability of the four pendant arms of $\mathbf{L^6}$ to form a highly symmetrical cavity suitable for encapsulation of the studied metal ions. Note, this cavity contains eight oxygen binding sites, four from the phosphoryl units and four from the lower rim, but of course we have no proof that all eight oxygen atoms are involved in complexation. The stoichiometry of the lanthanide complex formed with $\mathbf{L^6}$ was previously determined by a classical log-log method and found to be 1:1.[6]

The two tri-phosphorylated calixarenes, $\mathbf{L^4}$ and $\mathbf{L^5}$, which are structurally very similar, were found to lead to comparable extraction percentages toward thorium (28.8 and 26.7% respectively) and europium (5.3 and 4.1% respectively) ions, and as expected are weaker extractants than $\mathbf{L^6}$.

Interestingly, the relative position of the phosphine oxide arms in the diphosphorylated compounds, adjacent or distal, significantly affects the extraction level of the thorium and europium ions. Thus, as can be inferred from Table I, the thorium and europium extraction percentages of di-(phosphine oxide) are significantly higher for $\mathbf{L^2}$ than for $\mathbf{L^1}$, suggesting that the complexation process favors the formation of a species with the highest possible symmetry, namely C_{2v}. We have no rational explanation for the lower extraction efficiency of $\mathbf{L^3}$ with respect to $\mathbf{L^2}$ toward Th and Eu. A possible explanation for this finding is that each phosphoryl substituent of $\mathbf{L^2}$ is hydrogen bonded to a neighboring phenolic group, hence rigidifying the cavity and thus allowing better complexation. Steric effects due to the larger methyl groups could also account for the observed results.

Considering that $\mathbf{L^4}$ and $\mathbf{L^5}$ contains one phosphoryl group less than $\mathbf{L^6}$, the lower extraction percentages observed with these two ligands versus $\mathbf{L^6}$ appear to be normal. Obviously, the presence of a single hydroxy group in $\mathbf{L^4}$ does not induce a significant rigidification of the receptor unit (as generated in $\mathbf{L^2}$ through P=O···HO bonds) with respect to that formed in calixarene $\mathbf{L^5}$.

A drastic decrease in extraction was observed when the experiments were carried out in the presence of nitric acid instead of sodium nitrate. This simply reflects the propensity of phosphoryl groups to bind protons which, when present, compete with the Th (IV) and Eu (III) ions. In other terms the presence of H^+ ions breaks the cage structure of the receptor. Note, the tetra-phosphorylated calix[4]arene $\mathbf{L^6}$ remains the most efficient ligand in this medium. Being lower than 1%, the extraction percentages in nitric acid for $\mathbf{L^1}$, $\mathbf{L^3}$, $\mathbf{L^4}$, and $\mathbf{L^5}$ were not determined with accuracy.

EXPERIMENTAL

The calixarenes used in this study ($\mathbf{L^1}$–$\mathbf{L^6}$) were synthesized according to the procedure described previously.[14,15] The dichloromethane (Merck) used for the extraction experiments was washed three times with distilled water in order to remove the solvent stabilizers. The europium solutions were prepared from a weighed amount of the corresponding oxide (Fluka) in hot concentrated nitric acid and diluted to a known volume. $Th(NO_3)_4,6H_2O$ (Fluka) was used for the preparation of thorium solutions. The stock solutions were standardized by complexometric titration with EDTA. All other chemicals were laboratory reagent grade. The solvent extraction experiments were carried out in a stoppered glass tube immersed in a thermostated water bath

(25 ± 0.1°C) using equal volumes (5 mL) of the organic (1×10^{-2} M of ligand in dichloromethane) and the aqueous (1×10^{-4} M metal ion in the presence of 1 M sodium nitrate or nitric acid) phases. The extraction equilibrium was reached after 30 min under continuous magnetic stirring. After separation of the two phases, the concentration of the cation remaining in the aqueous phase was measured spectrophotometrically using Arsenazo III.[16] A volume of 5 mL of Arsenazo III solution (6×10^{-4} M) was added to a 1 mL aliquot of the aqueous phase and the volume was finally adjusted to 25 mL with either a 4 M nitric acid solution for the determination of thorium or with a sodium formate/formic acid buffer (pH = 2.80) for the determination of europium. The absorbance was then measured at 660 nm for thorium and 655 nm for europium determinations.

CONCLUSION

cone-Calix[4]arenes in which the lower rim is equipped with $-CH_2P(O)Ph_2$ substituents exhibit good extracting properties toward thorium (IV) ions, the highest extraction percentages being observed with the tetraphosphorylated derivative $\mathbf{L^6}$, a ligand with eight potential oxygen binding sites. The particular results observed with the dihydroxycalixarene $\mathbf{L^2}$ suggest that through rigidification the receptor properties of the phosphorylated ligand may considerably have been increased. A logical extension of this work is to structurally modify $\mathbf{L^6}$ in order to obtain a more rigid O_8-cage, for instance by linking the phosphorus arms, so as to enhance the extraction efficiency.

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