Extraction and Complexation of Alkali, Alkaline Earth, and F-Element Cations by Calixaryl Phosphine Oxides

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Abstract: A series of new calixarene derivatives with phosphine oxide groups on the lower rim and, for comparison, a series of noncalixarene phosphine oxides have been synthesised. Their extraction power for alkali and alkaline earth cations from aqueous metal picrate solution into dichloromethane have been determined as well as the stability constants in methanol of the 1:1 complexes of several members of the calixarene series. Important selectivity trends are revealed by both methods. The extraction power from aqueous nitrate solutions (1M in HNO_3) towards europium(III), as a model for trivalent actinides, and thorium(IV), as a model for tetravalent actinides, has been studied in detail for eight symmetrical calixarene derivatives, which differ in either calixarene size (4, 5, 6 or 8), the substituent at the upper rim (*tert*-butyl or hydrogen) or the number of methylene groups separating the phenolic oxygen atoms from the phosphorus atoms (1 or 2). The stoichiometry of the extracted species was characterised by a classical log–log plot analysis. All the calixarenes tested are far better extractants than typical noncalixarene extractants, for example, TOPO and CMPO, currently in use in the treatment of radioactive waste; they extract thorium better than europium. The influence of the nitric acid concentration and of the sodium nitrate concentration in the aqueous phase on the extraction efficiency was also examined in order to assess the possible application of these compounds for the decategorisation of liquid nuclear waste. Several thorium complexes have been characterised by their stability constants in methanol.

Keywords: calixarenes · cations · nuclear waste · phosphorus · thermodynamics

Introduction

Calixarenes are very amenable to chemical modification at the upper or lower rim, or both.[1, 2] Lower rim modifications through the phenolic oxygen atoms have been widely explored in the design and synthesis of receptors for metal cations.[1b] Much of our earlier work in this area has concentrated on calix[4], calix[5]- and calix[6]arenes with lower rim carbonyl-containing substituents in the form of esters, ketones, amides, thioamides and carboxylic acids.[3] Extraction, transport, stability constant and calorimetric measurements, augmented by NMR, X-ray and computer simulation studies, provide evidence that many of these lower rim derivatives have very significant ionophoric properties for cations, several with good selectivity within groups of metals.[3] Thus esters and ketones show selectivity within the alkali cation series, and amides within the alkaline earth cation series. Thioamides show selectivity for silver and lead. Other research groups have successfully pursued similar objectives with lower and upper rim bridged calixarenes, including calixcrowns and calixspherands.[2, 4]

The use of phosphine and phosphine oxide containing calixarenes as ligands is a relatively recent extension of cation complexation to the synthesis of transition metal complexes with catalytic activity.[5] Our work has now established that phosphine oxides can be employed very successfully for the separation of selected lanthanides and actinides.[6, 7, 8] Inter- and intra-group separations of lanthanides and actinides are important strategies in the management and declassification of nuclear waste.[9] Of particular importance in separation processes is liquid–liquid extraction, in which a charged metal ion is transferred as a complex from a polar aqueous phase to another immiscible phase. In the case of nuclear waste, the aqueous phase is frequently highly acidic and rich in sodium nitrate, both of which place severe limitations on the type of extractants that may be employed. Of the various extractants used in actinide process chemistry, neutral organophosphorus compounds are among the most useful. For example, the extracting ability of tributylphosphate forms the

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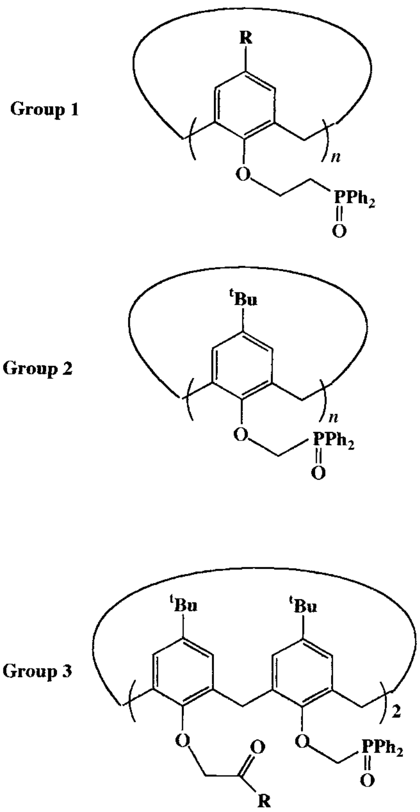
basis of the PUREX process for separating plutonium and uranium.[10] Bifunctional organophosphorus extractants include carbamoylphosphonates (CMPs) and carbamoylmethylphosphine oxides (CMPOs).[9]

We have recently reported in a preliminary paper on the high efficiency in the extraction of Eu^{III}, Th^{IV}, Pu^{IV} and Am^{III} from inactive and simulated radioactive wastes of tetra-, hexa- and octaphosphine oxides with or without *tert*-butyl groups at the *para* positions of the phenolic rings[6] (Scheme 1: compounds **1a–f**). Another approach to the use of the calixarenic platform for the treatment of radioactive waste employs calix[4]arenes bearing both P=O and C=O groups on the upper rim to simulate the carbamoylmethylphosphine oxides as the classical extractant CMPO used in the TRUEX process.[8] Both classes of compounds have been shown to be excellent extractants, more efficient than TOPO (trioctylphosphine oxide) and the CMPO octylphenyldiisobutylcarbamoylmethylphosphine oxide, and to extract Th^{IV} better than Eu^{III}.

We now present a more complete report on the complexing properties of calixarenes bearing phosphine oxide groups on their lower rim, by extending our preliminary report to include new homo- and hetero-substituted calix[4]- and calix[5]arene derivatives. We have also extended the metal ions to include alkali and alkaline earth series.

Abstract in French: *Une série de nouveaux calixarènes porteurs de groupements oxyde de phosphine sur le bord inférieur a été synthétisée ainsi que, à titre de comparaison, une série d'oxydes de phosphine non calixaréniques. Leur pouvoir extractant vis-à-vis des cations alcalins et alcalino-terreux à partir d'une solution aqueuse de picrate métallique vers le dichlorométhane a été déterminé ainsi que, pour plusieurs composés de la série des calixarènes, les constantes de stabilité dans le méthanol de leurs complexes 1:1. Des sélectivités importantes ont été mises en évidence par les deux méthodes. Le pouvoir extractant à partir de solutions aqueuses de nitrates métalliques (1 M en HNO_3) vis-à-vis de l'europium(III), pris comme modèle d'actinides trivalents, et du thorium(IV), pris comme modèle d'actinides tétravalents, a été étudié en détail pour huit dérivés symétriques des calixarènes, différant l'un de l'autre soit par la taille du calixarène (4, 6 ou 8), soit par le substituant sur le bord supérieur (tert-butyle ou hydrogène) soit encore par le nombre de groupements méthyléniques séparant les atomes d'oxygène phénolique des atomes de phosphore (1 ou 2). La stoiechiométrie des espèces extraites a été caractérisée par la méthode des pentes. Tous les calixarènes testés se sont révélés être de bien meilleurs extractants que les extractants non calixaréniques classiques, tels que le TOPO ou le CMPO, utilisés couramment dans le traitement des déchets radioactifs: ils extraient mieux le thorium que l'europium. L'influence sur l'efficacité de l'extraction des concentrations initiales en acide nitrique ou en nitrate de sodium dans la phase aqueuse a également été étudiée, en vue d'une possible application de ces composés à la décatégorisation des déchets nucléaires. Plusieurs complexes du thorium ont été caractérisés par leurs constantes de stabilité dans le méthanol.*



Scheme 1. The calixarene phosphine oxides studied. Group 1: **1a**: R = *t*Bu, *n* = 4; **1b**: R = *t*Bu, *n* = 6; **1c**: R = *t*Bu, *n* = 8; **1d**: R = H, *n* = 4; **1e**: R = H, *n* = 6; **1f**: R = H, *n* = 8; Group 2: **2a**: *n* = 4; **2b**: *n* = 5; Group 3: **3a**: R = NEt_2; **3b**: R = O-*t*Bu.

The complete series now consists of: group **1**, the tetra-, hexa- and octaphosphine oxide with two methylene groups between the phenolic oxygen and the phosphorus atom (Scheme 1); a new group **2** with the tetramer **2a** and the pentamer **2b**, in which there is a single methylene group between the phenolic oxygen atom and the phosphorus atom; and group **3** with two mixed functionality tetramers **3a** and **3b** also with a single methylene spacer, but in which two distal phosphine oxides have been replaced by two diethyl amide groups and two *tert*-butyl ester groups, respectively. For comparison purposes, several noncalixarene polyphosphine oxides were tested (Scheme 2) for their extracting power towards Eu^{III} and Th^{IV}.

All the phosphine oxides with two methylene spacers between the phenolic oxygen and the phosphorus atom on the lower rim were synthesised from the parent calixarenes **5** via the known ethyl acetates **6** (Scheme 3). The sequence involved reduction of **6** to primary alcohols **7** by use of DIBAL in toluene, followed by conversion of the alcohols into tosylates **8** with *p*-toluenesulfonyl choride in pyridine. Introduction of diphenylphosphine residues through exposure of the tosylates to sodium diphenylphosphide in dioxane/tetrahydrofuran and, finally, oxidation of the resulting phosphines **9** to phosphine oxides **1** by use of either dimethyldioxirane or hydrogen peroxide in acetone. All the phosphine oxides were fully characterised spectroscopically and analytically. ^1H NMR analysis revealed that both tetramers **1a** and **1d** exist in stable cone conformations in solution. The X-ray

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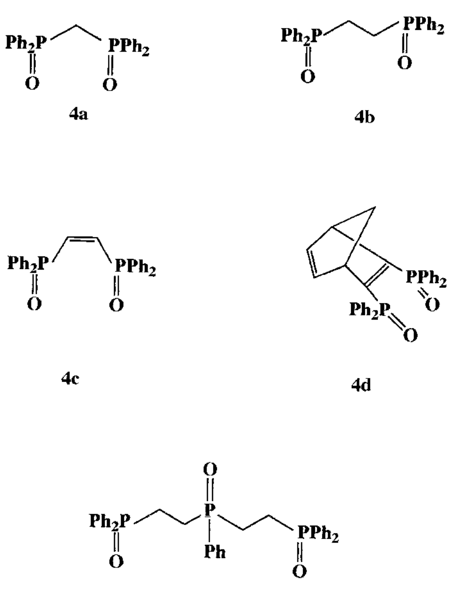
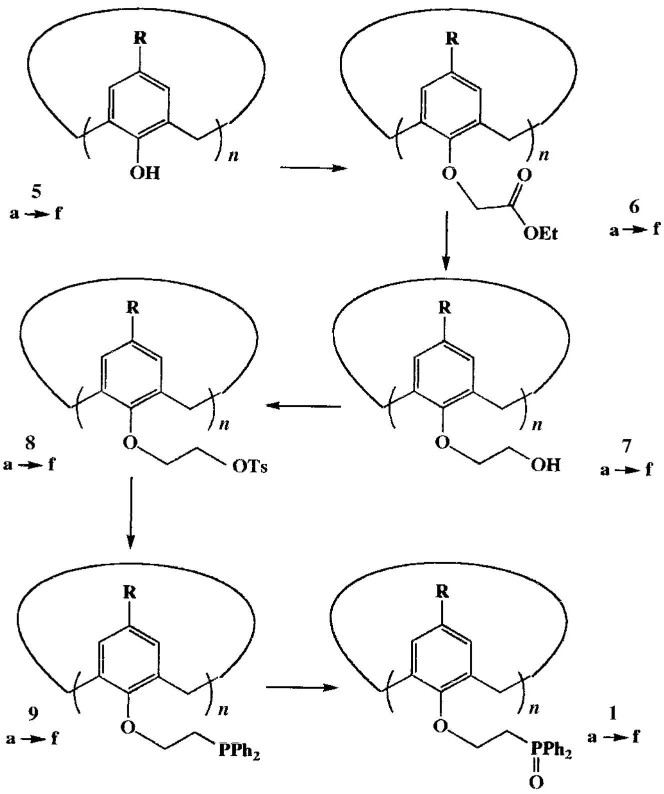


Scheme 2. The noncalixarene polyphosphine oxides studied.



Scheme 3. Synthesis procedure of the calixarene phosphine oxides. **a**: $n=4$, $R=t$Bu; **b**: $n=6$, $R=t$Bu; **c**: $n=8$, $R=t$Bu; **d**: $n=4$, R = H; **e**: $n=6$, R = H; **f**: $n=8$, R = H.

crystal structure[6] of the former reveals the disposition of the putative P–O binding sites and their degree of preorganisation about the lower rim cavity. Compound **2b** exist as a stable cone conformation, whereas the hexamers and octamers are conformationally mobile at ordinary temperatures, as is the case with many of the larger calixarene derivatives.

The diamide diphosphine oxide **3a** has been previously investigated in extraction studies with alkali and silver cations.[11, 12] Our studies include both extraction and complexation studies of the alkali and alkaline earth cations with all three groups of phosphine oxides. We have extended our extraction studies of compounds **1a–f** and **2a** to europium(III) and thorium(IV), for use as models for extraction of trivalent lanthanides and tetravalent actinides. Some additional results concerning the stability in methanol of the complexes of thorium by the various compounds are also presented.

Experimental Section

General: Melting points are uncorrected. Infrared spectra were obtained with a Perkin–Elmer 983G grating spectrophotometer with solid samples dispersed in KBr clear pressed discs. ^{1}H NMR spectra were recorded at 300 MHz on a General Electric QC300 spectrometer and at 500 MHz on a General Electric QE500 instrument. ^{13}C and ^{31}P NMR spectra were recorded at 125 MHz and 202 MHz respectively, with a General Electric QE500 spectrometer. In all cases tetramethylsilane was used as an internal standard. Elemental analyses were determined on a Perkin–Elmer 2400 CHN microanalyser. Carbon values in microanalysis are frequently low for calixarenes with cavities capable of retaining solvent molecules. In some instances acceptable elemental analysis was only observed if one assumed the inclusion of one or more molecules of solvent. EI mass spectra were recorded at 70 eV on a VG Autospec instrument with a heated inlet system. Accurate molecular weights were determined by the peak-matching method with perfluorokerosene as standard reference. ES mass spectra were recorded on a Fisons VG-Quatro instrument with electrospray inlet. Analytical TLC was performed on Merck Kieselgel 60_{254} plates. Preparative TLC was carried out with glass plates (20 × 20 cm) coated with Merck Kieselgel $PF_{254+366}$ (21 g in 58 mL H_2O per plate). Flash chromatography was effected with Merck Kieselgel 60 (230–400 mesh). All reactions were performed under a nitrogen atmosphere. Commercial grade solvents were dried and purified by the standard procedures.[13] The following calixarenes were prepared as previously described in the literature: 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene **5a**,[14] 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetraethoxycarbonylmethyleneoxycalix[4]arene **6a**,[15] 25,26,27,28-tetrahydroxycalix[4]arene **5d**,[16] 25,26,27,28-tetraethoxycarbonylmethyleneoxycalix[4]arene **6d**,[15] 5,11,17,23,29-penta-*tert*-butyl-31,32,33,34,35-pentahydroxycalix[5]arene,[17] 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene **5b**,[18] 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexaethoxycarbonylmethyleneoxycalix[6]arene **6b**,[15] 37,38,39,40,41,42-hexahydroxycalix[6]arene **5e**,[16] 37,38,39,40,41,42-hexaethoxycarbonylmethyleneoxycalix[6]arene **6e**,[15] 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene **5c**,[19] 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octaethoxycarbonylmethyleneoxycalix[8]arene **6c**,[15] 49,50,51,52,53,54,55,56-octahydroxycalix[8]arene **5f**,[16] 49,50,51,52,53,54,55,56-octaethoxycarbonylmethyleneoxycalix[8]arene **6f**,[15] 5,11,17,23-tetra-*tert*-25,26,27,28-tetrahydroxyethyleneoxycalix[4]arene **7a**[20] and 25,26,27,28-tetrahydroxyethyleneoxycalix[4]arene **7d**.[20] The calixaryl phosphine oxides **2a** and **3a** were prepared by the method of Matt and coworkers.[5] Phosphine oxides **4a**[21a], **4b**[21b], **4c**[21c] and **4e**[21d] were known compounds.

General procedure for the formation of calixarene ethyleneoxy alcohols 7a–f: The following procedure was used to reduce calixarene esters **6a–f** into the corresponding primary alcohols **7**. A 300% molar excess of DIBAL (1.5 M solution in toluene) was added to a solution of the calixarene ester (ca. 5%) in dry toluene under N_2. The reaction mixture was stirred at room temperature for 24 h. Excess reducing agent was destroyed by dropwise addition of methanol until hydrogen evolution had ceased. The precipitated inorganic salts were then broken up by the addition of methanol/water and were subsequently removed by filtration through Celite. The inorganic residue was washed with hot chloroform, and the organic layer separated and washed with brine; each brine wash was further backextracted with chloroform. The combined organic extracts were dried over $MgSO_4$ and concentrated at reduced pressure to afford the crude calixarene alcohol. The following ethyleneoxy alcohols were thus prepared.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxyethyleneoxycalix[6]arene (7b): Calixarene **6b** furnished the corresponding alcohol **7b** as a white solid in 77% yield after trituration at −20°C in ethanol. M.p. > 300°C (decomp); IR (KBr) $\tilde{\nu} = 3423\,\mathrm{cm^{-1}}$ (OH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$ (s, 54H; C(CH_3)$_3$), 3.40–4.00 (brs, 36H; ArCH_2Ar, OCH_2CH_2 overlapping), 4.45–4.70 (brs, 6H; OH), 7.00 (brs, 12H; ArH); MS (ES): *m/z*: 1237.4 $[M+H]^+$; $C_{78}H_{108}O_{12}\cdot 3H_2O$ (1291.72): calcd C 72.6, H 8.4; found: C 72.5, H 8.1.

37,38,39,40,41,42-Hexahydroxyethyleneoxycalix[6]arene (7e): Calixarene **6e** furnished the alcohol **7e** as a white solid in 68% yield after trituration in hot ethanol. M.p. > 300°C (decomp); IR (KBr) $\tilde{\nu} = 3416\,\mathrm{cm^{-1}}$ (OH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.55$ (brs, 12H; ArCH_2Ar), 3.61 (brs, 12H; OCH_2CH_2), 3.95 (brs, 12H; OCH_2CH_2), 4.20 (brs, 6H; OH), 6.95 (brs, 18H; ArH); MS (ES) *m/z*: 901.4 $[M+H]^+$; $C_{54}H_{60}O_{12}\cdot 2H_2O$ (937.07): calcd C 69.2, H 6.8; found: C 68.5, H 7.1.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxyethyleneoxycalix[8]arene (7c): Calixarene **6c** furnished the alcohol **7c** as a white solid in 81% yield following recrystallisation from ethanol/water. M.p. 255–257°C; IR (KBr): $\tilde{\nu} = 3434\,\mathrm{cm^{-1}}$ (OH); ^{1}H NMR (300 MHz $CDCl_3$): $\delta = 1.16$ (s, 72H; C(CH_3)$_3$), 3.58 (brs, 32H; OCH_2CH_2, ArCH_2Ar overlapping), 3.99 (brs, 16H; OCH_2CH_2), 4.68 (brs, 8H; OH), 6.97 (16H; s, ArH); MS (ES): *m/z*: 848.1 $[M/2+Na]^+$; $C_{104}H_{144}O_{16}\cdot 2H_2O$ (1686.3): calcd C 74.1, H 8.9; found C 73.8, H 8.8.

49,50,51,52,53,54,55,56-Octahydroxyethyleneoxycalix[8]arene (7f): Calixarene **6f** furnished the dealkylated alcohol **7f** as a white solid in 52% yield after liberating the crude material from the mixture of DIBAL salts with a hot solution of chloroform/methanol and subsequent purification by trituration in acetone. M.p. > 290°C (decomp); IR (KBr) $\tilde{\nu} = 3434\,\mathrm{cm^{-1}}$ (OH); ^{1}H NMR (300 MHz [D$_6$]DMSO) $\delta = 3.63$–3.66 (t, 16H; OCH_2CH_2), 3.76–3.78 (t, 16H; ArCH_2Ar), 4.05 (s, 16H; OCH_2CH_2), 4.81–4.85 (t, 8H; OH), 6.81 (s, 24H; ArH); MS (ES): *m/z*: 1201.6 $[M+H]^+$; $C_{72}H_{80}O_{16}\cdot CH_3OH$ (1233.48): calcd C 71.1, H 6.8; found C 70.9, H 6.7.

General procedure for the formation of calixarene tosylates 8a–f: The following procedure was used to transform calixarene ethyleneoxy alcohols **7a–f** into the corresponding tosylates **8a–f**. The calixarene was dissolved in dry pyridine (ca. 10% solution, with gentle heating as necessary). *p*-Toluenesulphonyl chloride (200% molar excess) was added and the contents shaken to dissolution. The reaction mixture was cooled to 0°C in an ice bath and stirred at that temperature for 2 h, after which time the solution was subsequently cooled further to −15°C for 3 days. The solution was then filtered to remove the precipitated pyridinium hydrochloride salt and the filtrate poured onto an ice/water mixture and stirred for 1 h. The resulting off-white precipitate was filtered, washed well with water and triturated in hot ethanol to afford the crude calixarene tosylate. The following calixarene tosylates were thus prepared.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetratosylateethyleneoxycalix[4]arene (8a): Calixarene **7a** afforded the tetratosylate **8a** as a white solid in 96.5% yield an was used without further purification. M.p. 99–101°C; IR (Kbr): $\tilde{\nu} = 1355, 1170\,\mathrm{cm^{-1}}$ (S=O); ^{1}H NMR (300 Mhz, $CDCl_3$): $\delta = 1.05$ (s, 36H, (CH_3)$_3$), 2.40 (s,12H, ArCH_3), 2.97 (d, 4H, H_B, $J_{AB} = 12$ Hz, ArCH_2Ar), 4.0–4.5 (m, 20H, −OCH_2CH_2 and H_A superimposed), 6.68 (s, 8H, ArH), 7.5 (q, 16H, ArH(CH_3)); $C_{80}H_{96}O_{16}S_4$ (1441.89): calcd C 66.57, H 6.65, S 8.54; found C 66.79, H 6.88, S 8.88.

25,26,27,28-Tetratosylateethyleneoxycalix[4]arene (8d): Calixarene **7d** furnished the dealkylated tosylate **8d** as a white crystalline solid in 91% yield after recrystallisation from ethanol/methylene chloride. M.p. 180–181°C; IR (KBr): $\tilde{\nu} = 1355, 1176\,\mathrm{cm^{-1}}$ (S=O); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.43$ (s, 12H; ArCH_3), 3.05 (d, H_B, $J_{BA} = 13.62$ Hz, 4H; ArCH_2Ar), 4.13 (t, $J = 4.32$ Hz, 8H; OCH_2CH_2), 4.30 (d, H_A, $J_{AB} = 13.55$ Hz, 4H; ArCH_2Ar), 4.39 (t, $J = 4.29$ Hz, 8H; OCH_2CH_2), 6.56 (s, 12H; ArH), 7.32 (d, $J = 8.31$ Hz, 8H; ArHCH$_3$), 7.76 (d, $J = 8.26$ Hz, 8H; SArH); MS (ES): *m/z*: 1217.3 $[M+H]^+$, 1235.5 $[M+H+H_2O]^+$; $C_{64}H_{64}O_{16}S_4$ (1217.46): calcd C 63.1, H 5.3; found C 63.0, H 5.3.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexatosylateethyleneoxycalix[6]arene (8b): Calixarene **7b** afforded the hexatosylate **8b** as a white solid in 74% yield following recrystallisation from ethanol/methylene chloride. M.p. 170–172°C; IR (KBr) $\tilde{\nu} = 1361, 1178\,\mathrm{cm^{-1}}$ (S=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 54H; C(CH_3)$_3$), 1.95 (s, 18H; ArCH_3), 3.20 (d, H_B, $J_{BA} = 12.08$ Hz, 6H; ArCH_2Ar), 3.75 (brs, 12H; OCH_2CH_2), 4.25 (m, 18H; H_A, ArCH_2Ar, OCH_2CH_2 overlapping), 6.75 (s, 12H; ArH), 7.31 (d, $J = 7.98$ Hz, 12H; ArHCH$_3$), 7.80 (d, $J = 8.23$ Hz, 12H; SArH); MS (ES): *m/z*: 558.1 $[M/4+H_2O]^+$; $C_{120}H_{144}O_{24}S_6$ (2162.83): calcd C 66.7, H 6.7; found C 66.7, H 6.9.

37,38,39,40,41,42-Hexatosylateethyleneoxycalix[6]arene (8e): Calixarene **7e** furnished the dealkylated tosylate **8e** as a white solid in 83% yield following recrystallisation from ethanol/methylene chloride. M.p. 152–155°C; IR (KBr) $\tilde{\nu} = 1358, 1177\,\mathrm{cm^{-1}}$ (S=O); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.38$ (s, 18H; ArCH_3), 3.60 (brs 12H;, OCH_2CH_2), 3.78 (brs, 12H; ArCH_2Ar), 4.03 (brs, 12H; OCH_2CH_2), 6.65 (s, 18H; ArH), 7.30 (d, $J = 7.88$ Hz, 12H; ArHCH$_3$), 7.80 (d, $J = 8.18$ Hz, 12H; SArH); MS (ES): *m/z*: 1732.6 $[M+H-C_7H_7]^+$; $C_{96}H_{96}O_{24}S_6$ (1826.18): calcd C 63.1, H 5.3; found C 62.7, H 5.1.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octatosylateethyleneoxycalix[8]arene (8c): Calixarene **7c** furnished the tosylate **8c** as a white solid in 77% yield after recrystallisation from ethanol/methylene chloride. M.p. 128–130°C; IR (KBr): $\tilde{\nu} = 1361, 1176\,\mathrm{cm^{-1}}$ (S=O); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.96$ (s, 72H; C(CH_3)$_3$), 2.17 (s, 24H; ArCH_3), 3.78 (brs, 16H; OCH_2CH_2), 3.87 (brs, 16H; ArCH_2Ar), 4.23 (brs, 16H; OCH_2CH_2), 6.80 (s, 16H; ArH), 7.12 (d, $J = 7.91$ Hz, 16H; ArHCH$_3$), 7.66 (d, $J = 8.09$ Hz, 16H; SArH); MS (ES): *m/z*: 1442.3 $[M/2+H]^+$, 1465.9 $[M/2+2H+Na]^+$; $C_{160}H_{192}O_{32}S_8$ (2883.78); calcd C 66.6, H 6.7, S, 8.9; found C 66.7, H 6.7, S 8.5.

49,50,51,52,53,54,55,56-Octatosylateethyleneoxycalix[8]arene (8f): Calixarene **7f** furnished the cone isomer of the dealkylated tosylate **8f** as a white solid in 28% yield after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 15:1). M.p. 128–132°C; IR (KBr): $\tilde{\nu} = 1358, 1177\,\mathrm{cm^{-1}}$ (S=O); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.30$ (s, 24H; ArCH_3), 3.80–3.95 (brs, 32H; OCH_2CH_2, ArCH_2Ar overlapping), 4.20 (brs, 16H; OCH_2CH_2), 6.70 (s, 24H; ArH), 7.15–7.23 (d, $J = 7.98$ Hz, 16H; ArHCH$_3$), 7.70 (d, $J = 8.12$ Hz, 16H; SArH); MS (ES): *m/z*: 1240.2 $[M/2+Na]^+$; $C_{128}H_{128}O_{32}S_8$ (2434.91): calcd C 62.2, H 5.3; found C 61.8, H 5.2.

General procedure for the formation of calixarene phosphines 9a–f: The following procedure was used to transform calixarene tosylates **8a–f** into the corresponding phosphines **9a–f**. Distilled chlorodiphenylphosphine (150% molar excess to calixarene) was dissolved in dry dioxane (ca. 10% solution) under N_2. Sodium metal (300% molar excess to chlorodiphenylphosphine; cut into small slivers) was added slowly. The mixture was then heated to reflux for 7 h with strong mechanical stirring. The intensely yellow reaction mixture was then allowed to cool to room temperature whilst stirring was continued. The calixarene dissolved in dry THF (ca. 10% solution) was slowly added dropwise through a pressure-equalizing dropping funnel and the mixture allowed to stir at room temperature for 2 days. The red reaction mixture was filtered through Celite and the inorganic residue washed with dry toluene. The yellow/orange organic solution was concentrated under reduced pressure to yield a sticky orange/red semisolid. Methylene chloride was added to the residue and the organic solution washed with a distilled water/brine (50:50) mixture. The organic layer was separated and dried over $MgSO_4$ to afford the crude calixphosphine as a cream solid. The following calixarene phosphines were thus prepared. Satisfactory analytical data were not obtained for all of these phosphines due to their ready oxidation in air.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetradiphenylphosphineethyleneoxycalix[4]arene (9a): Calixarene **8a** furnished the phosphine **9a** as a white solid in 61% yield after purification by column chromatography (SiO_2, CH_2Cl_2/hexane 5:1). M.p. 187–189°C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.05$ (s, 36H; C(CH_3)$_3$), 2.65 (m, 8H; OCH_2CH_2), 2.95 (d, H_B, $J_{BA} = 13.28$ Hz, 4H; ArCH_2Ar), 3.95 (m, 8H; OCH_2CH_2), 4.20 (d, H_A, $J_{AB} = 13.15$ Hz, 4H; ArCH_2Ar), 6.70 (s, 8H; ArH), 7.10–7.30 (m, 40H; PPh_2); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = -22.79$ (d, PPh$_2$); $C_{100}H_{108}P_4O_4\cdot H_2O$ (1515.86): calcd C 79.3, H 7.3; found C 78.9, H 7.1.

25,26,27,28-Tetradiphenylphosphineethyleneoxycalix[4]arene (9d): Calixarene **8d** furnished the phosphine **9d** as a white solid in 68% yield after purification by column chromatography (SiO_2, CH_2Cl_2/hexane 5:1). M.p. 136–138 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.56$ (t, $J = 7.97$ Hz, 8H; OCH_2CH_2), 2.97 (d, H_B, $J_{BA} = 13.45$ Hz, 4H; $ArCH_2Ar$), 3.96 (m, 8H; OCH_2CH_2), 4.28 (d, H_A, $J_{AB} = 13.35$ Hz, 4H; $ArCH_2Ar$), 6.56 (s, 12H; Ar*H*), 7.19–7.31 (m, 40H; P*Ph*$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = -22.69$ (d, *P*Ph$_2$); $C_{84}H_{76}P_4O_4 \cdot 2\,H_2O$ (1309.43): calcd C 77.1, H 6.2; found C 77.2, H 5.8.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexadiphenylphosphineethyleneoxycalix[6]arene (9b): Calixarene **8b** afforded the hexaphosphine **9b** as a white solid in 66% yield after purification by column chromatography (SiO_2, CH_2Cl_2/hexanes 5:1). M.p. 125–130 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.10–1.20$ (m, 54H; $C(CH_3)_3$), 2.65 (m, 12H; OCH_2CH_2), 3.60–4.20 (m, 24H; OCH_2CH_2, $ArCH_2Ar$ overlapping), 6.80–7.60 (m, 72H; Ar*H*, P*Ph*$_2$ overlapping); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = -22.05$ (s, *P*Ph$_2$); $C_{150}H_{162}P_6O_6$ (2246.79): calcd C 80.2, H 7.2; found C 79.8, H 7.5.

37,38,39,40,41,42-Hexadiphenylphosphineethyleneoxycalix[6]arene (9e): Calixarene **8e** furnished the hexaphosphine **9e** as a white solid in 51% yield after purification by column chromatography (SiO_2, CH_2Cl_2/hexane 5:1) and subsequent trituration in methanol. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.35$ (m, 12H; OCH_2CH_2), 3.70 (m, 12H; $ArCH_2Ar$), 3.80 (m, 12H; OCH_2CH_2), 6.40 (t, 6H; Ar*H*), 6.60 (d, 12H; Ar*H*), 7.30–7.40 (m, 60H; P*Ph*$_2$). Correct elemental analysis could not be obtained for this compound due to its susceptibility to undergo oxidation in air.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octadiphenylphosphineethyleneoxycalix[8]arene (9c): Calixarene **8c** afforded the octaphosphine **9c** as a white powdery solid in 62% yield after purification by column chromatography (SiO_2, CH_2Cl_2/hexane 5:1). M.p. 229–231 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.94$ (s, 72H; $C(CH_3)_3$), 2.49 (brs, 16H; OCH_2CH_2), 3.85 (brs, 16H; OCH_2CH_2), 3.93 (brs, 16H; $ArCH_2Ar$), 6.75 (s, 16H; Ar*H*), 7.10 (brs, 48H; P*Ph*$_2$), 7.27 (brs, 32H; P*Ph*$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = -22.90$ (*P*Ph$_2$). Correct elemental analysis could not be obtained for this compound due to its susceptibility to undergo oxidation in air.

49,50,51,52,53,54,55,56-Octadiphenylphosphineethyleneoxycalix[8]arene (9f): Calixarene **8f** furnished the octaphosphine **9f** as a grey solid in 48% yield upon trituration from ice-cold ethanol. The product was subject to ready oxidation and was used for subsequent conversion to the corresponding phosphine oxide without purification.

Formation of calixarene phosphine oxides 1a–f: Oxidation of the calixarene phosphines **9a–f** to the corresponding phosphine oxides was carried out using either dimethyldioxirane (DMD)[22] or hydrogen peroxide in acetone according to the procedures subsequently outlined.

Oxidation with dimethyldioxirane: The calixarene phosphine was suspended in dry acetone (ca. 5% solution) and the solution cooled to 0 °C with an ice bath. Distilled dimethyldioxirane (DMD) (50% molar excess) was added and the solution stirred at this temperature for 10 min. The yellow solution was then allowed to warm to room temperature and was stirred at that temperature for a further 30 min. Removal of the solvent at reduced pressure furnished the crude calixarene phosphine oxide as a pale yellow solid.

Oxidation with hydrogen peroxide: Calixarene phosphine was suspended in dry acetone (ca. 5% solution) and the solution cooled to 0 °C with an ice bath. Hydrogen peroxide (30% solution; ca. 5% molar excess) was added and the solution stirred at this temperature for 10 min at which point it was allowed to warm to room temperature and was stirred at that temperature for a further 30 min. Methylene chloride was added and the solution washed in turn with saturated sodium iodide solution (containing a drop of acetic acid), 0.1 N sodium thiosulphate solution and distilled water. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to afford the crude calixarene phosphine oxide as an off-white solid. The following calixarene phosphine oxides were thus prepared.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetradiphenylphosphorylethyleneoxycalix[4]arene (1a): Calixarene **9a** was oxidized with DMD as described to furnish the phosphine oxide **1a** as a white crystalline solid in 84% yield after recrystallisation from methanol. M.p. 289–290 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.05$ (s, 36H; $C(CH_3)_3$), 2.90–3.10 (m, 12H; OCH_2CH_2, H_B, $ArCH_2Ar$ overlapping), 4.00–4.10 (d, H_A, $J_{AB} = 13.24$ Hz, 4H; $ArCH_2Ar$), 4.15–4.20 (m, 8H; OCH_2CH_2), 6.68 (s, 8H; Ar*H*), 7.31–7.45 (m, 24H; PO*Ph*$_2$), 7.69–7.80 (m, 16H; PO*Ph*$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = +30.03$ (*P*OPh$_2$); MS (ES): *m/z*: 1561.6 $[M+H]^+$; $C_{100}H_{108}P_4O_8 \cdot CH_3OH$ (1593.90): calcd C 76.2, H 7.1; found C 76.4, H, 6.7.

25,26,27,28-Tetradiphenylphosphorylethyleneoxycalix[4]arene (1d): Calixarene **9d** was oxidized with DMD as described to afford dealkylated phosphine oxide **1d** as a white crystalline solid in quantitative yield after recrystallisation from methanol. M.p. 124–126 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.83$ (m, 8H; OCH_2CH_2), 2.92 (d, H_B, $J_{BA} = 13.62$ Hz, 4H; $ArCH_2Ar$), 4.02 (d, H_A, $J_{AB} = 13.41$ Hz, 4H; $ArCH_2Ar$), 4.17 (m, 8H; OCH_2CH_2), 6.54 (s, 12H; Ar*H*), 7.31–7.46 (m, 24H; PO*Ph*$_2$), 7.67–7.74 (m, 16H; PO*Ph*$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = +29.81$ (*P*OPh$_2$); MS (ES): *m/z*: 1337.6 $[M+H]^+$; $C_{84}H_{76}P_4O_8 \cdot H_2O$ (1355.43): calcd C 74.4, H 5.8; found C 74.1, H 5.7.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexadiphenylphosphorylethyleneoxycalix[6]arene (1b): Calixarene **9b** was oxidized with DMD as described to furnish the corresponding phosphine oxide **1b** as a white solid in 68% yield after recrystallisation from methanol. M.p. 289–290 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.10$ (54H; brs, $C(CH_3)_3$), 2.95 (12H; brs, OCH_2CH_2), 3.90–4.25 (24H; brs, OCH_2CH_2, $ArCH_2Ar$ overlapping), 7.40 (brs, 36H; Ar*H*, PO*Ph*$_2$ overlapping), 7.85 (brs, 36H; PO*Ph*$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = +29.92$ (*P*OPh$_2$); MS (ES): *m/z*: 1172.2 $[M/2+H]^+$; $C_{150}H_{162}P_6O_{12} \cdot 4\,H_2O$ (2414.79): calcd C 74.6, H 7.1; found C 74.9, H 6.7.

37,38,39,40,41,42-Hexadiphenylphosphorylethyleneoxycalix[6]arene (1e): Calixarene **9e** was oxidized with hydrogen peroxide as described to furnish the corresponding dealkylated phosphine oxide **1e** as a cream solid in 62% yield after trituration from ether. M.p. 98–102 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.65$ (m, 12H; OCH_2CH_2), 3.65 (m, 12H; $ArCH_2Ar$), 3.93 (m, 12H; OCH_2CH_2), 6.43 (m, 6H; Ar*H*), 6.49 (m, 12H; Ar*H*), 7.35 (m, 24H; PO*Ph*$_2$), 7.45 (m, 12H; PO*Ph*$_2$), 7.68 (m, 24H; PO*Ph*$_2$); MS (ES): *m/z*: 1003.6 $[M/2+H]^+$, 2006.5 $[M+2H]^+$; $C_{126}H_{114}P_6O_{12}$ (2006.14): calcd C 75.5, H 5.7; found C 75.9, H 5.6.

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octadiphenylphosphorylethyleneoxycalix[8]arene (1c): Calixarene **9c** was oxidized with DMD as described to furnish the corresponding phosphine oxide **1c** as a white powdery solid in 89% yield after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 19:1). M.p. 160–162 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (brs, 72H; $C(CH_3)_3$), 2.81 (brs, 16H; OCH_2CH_2), 3.98 (brs, 32H; OCH_2CH_2, $ArCH_2Ar$ overlapping), 6.75 (brs, 16H; Ar*H*), 7.24 (brs, 48H; PO*Ph*$_2$), 7.66 (brs, 32H; PO*Ph*$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = +29.65$ (*P*OPh$_2$); MS (ES): *m/z*: 1562.0 $[M/2+H]^+$; $C_{200}H_{216}P_8O_{16} \cdot H_2O$ (3141.72); calcd C 76.5, H 7.0; found: C 76.3, H 7.0.

49,50,51,52,53,54,55,56-Octadiphenylphosphorylethyleneoxycalix[8]arene (1f): Calixarene **9f** was oxidized with DMD as described to afford the corresponding dealkylated phosphine oxide **1f** as a cream solid in 48% yield after dissolution of the crude material in methanol, filtration to remove traces of tosylate, and concentration of the filtrate to dryness. M.p. 116–118 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.75$ (m, 16H; OCH_2CH_2), 3.76 (s, 16H; $ArCH_2Ar$), 4.05 (m, 16H; OCH_2CH_2), 6.58 (s, 24H; Ar*H*), 7.30 (m, 48H; PO*Ph*$_2$), 7.65 (m, 32H; PO*Ph*$_2$); MS (ES): *m/z*: 1338.0 $[M/2+H]^+$, 2674.0 $[M+H]^+$; $C_{168}H_{152}P_8O_{16} \cdot 3\,H_2O$ (2728.86): calcd C 74.0, H 5.8; found C 73.9, H 5.8.

5,11,17,23,29-penta-*tert*-butyl-31,32,33,34,35-penta-diphenylphosphorylmethyleneoxycalix[5]arene (2b): *p-tert*-Butylcalix[5]arene[17] was treated with $Ph_2P(O)CH_2OTs$ in dry toluene containing sodium hydride exactly as described by Matt and co-workers[5] for the tetramer analogue **2a** to afford the pentaphosphine oxide **2b** in 61% yield. M.p. 220–221 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.89$ (s, 45H; $C(CH_3)_3$), 3.05 (d, H_B, $J_{BA} = 14.73$ Hz, 4H; $ArCH_2Ar$), 5.00 (s, 10H; $OCH_2P(O)Ph_2$), 5.06 (d, H_A, $J_{AB} = 14{,}65$ Hz, 4H; $ArCH_2Ar$), 6.51 (s, 10H, Ar*H*), 7.25 (brs, 30H; *m*- and *p*-P(O)*Ph*$_2$), 7.71–7.75 (m, 20H; *o*-P(O)*Ph*$_2$); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = +26.32$ (*P*(O)Ph$_2$); MS (ES): *m/z*: 1880.9 $[M]^+$; $C_{120}H_{125}0_{10}P_5$ (1882.19): calcd C 76.6, H 6.7; found C 76.2, H 6.4.

Di-*tert*-butylesterdiphenylphosphorylmethyleneoxycalix[4]arene (3b): The known di-*tert*-butylacetate of *tert*-butylcalix[4]arene was treated with $Ph_2P(O)CH_2OTs$ in dry THF/DMF containing sodium *tert*-butoxide exactly as described by Matt and coworkers[5] for the diamidediphosphine oxide **3a** to afford the diesterdiphosphine oxide **3b** in 69% yield. M.p. 319–320 °C (decomp); IR (Kbr): $\tilde{\nu} = 1743$ cm^{-1} (s, C=O); ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 0.88$ (s, 18H; C(C*H*$_3$)$_3$), 1.13 (s, 18H; C(C*H*$_3$)$_3$), 1.37 (s, 18H; C(C*H*$_3$)$_3$), 2.88 (d, H$_B$, $J_{BA} = 13.08$ Hz, 4H; ArC*H*$_2$Ar), 4.47 (s, 4H; OC*H*$_2$CO$_2$*t*Bu), 4.60 (d, H$_A$, $J_{AB} = 12.92$ Hz, 4H; ArC*H*$_2$Ar), 5.78 (s, 4H; OC*H*$_2$P(O)Ph$_2$), 6.46 (s, 4H; *m*-Ar*H*), 6.59 (s, 4H; *m*-Ar*H*), 7.26–7.43 and 7.74-7.78 (m, 20H; P(O)*Ph*$_2$); ^{31}P NMR (202 MHz, CDCl$_3$): $\delta = +25.31$ (P(O)*Ph*$_2$); MS (ES): *m/z*: 1304.2 [*M*]$^+$; C$_{82}$H$_{98}$0$_{10}$P$_2$ (1305.63): calcd C 75.4, H 7.6; found C 75.5, H 7.3.

Synthesis of the bicyclic diphosphine oxide 4d: Bis-(diphenylphosphinyl)acetylene[21e] (0.5 g, 1.18 mmol) in chloroform (20 mL) was stirred under nitrogen for 10 min. Cyclopentadiene (0.4 mL, 4.4 mmol) was added through a syringe and the reaction mixture stirred under reflux for several hours. The solvent was removed in vacuo and the residue evaporated under high vacuum overnight to afford **4d** as a white crystalline solid (0.56 g, 95%). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 1.9$ (d, $J = 7.3$ Hz, 1H; C*H*$_2$), 2.25 (d, $J = 6.9$ Hz, 1H; C*H*$_2$), 4.07 (s, 2H; C*H*), 6.60 (d, $J = 2.2$ Hz, 2H; C=C*H*), 7.29–7.61 (m, 20H; P*Ph*$_2$); ^{31}P NMR (202 MHz, CDCl$_3$): $\delta = +24.75$ (*P*(O)Ph$_2$); MS (EI): *m/z*: 492.14 [*M*]$^+$; C$_{31}$H$_{26}$O$_2$P$_2$ (492.14): calcd C 75.7, H 5.3; found C 76.2, H 5.4.

Extraction measurements

Picrate extraction method: The classical picrate extraction method for alkali and alkaline earth cations with calixarenes has already been described.[22] In summary, the percentage cation extracted (%E) or the distribution coefficient D [$D = \%E/(100-\%E)$] from water into dichloromethane, at 20 °C, was determined from the measured absorbance of the picrate anion remaining in the aqueous phase after extraction at 355 nm. The same concentration (2.5×10^{-4} M) was used for the ligand in the organic phase and the picrate in the aqueous phase.

Nitrate extraction method: The extrapolation of the picrate extraction method to the trivalent lanthanides and tetravalent thorium led to unusual and so far unexplained selectivities in the lanthanide series, that is, a strong extraction maximum for Eu^{3+}. Since our objective was to develop extraction processes for lanthanides and actinides that would mimic their removal from nuclear waste, it was necessary to find an alternative to the picrate extraction method, which would allow the extraction of metal nitrates. Furthermore, because liquid nuclear waste has a relatively high concentration of nitric acid, extractants were needed which would function in acidic media. For these reasons we have developed a new method for monitoring metal nitrate extraction in the presence of excess nitric acid, which is also applicable, with certain approximations, to the determination of the stoichiometries of the extracted species.

Metal nitrate extraction procedure: A standard experimental set up consisted of an aqueous phase containing europium or thorium nitrate (10^{-4} M) in 1 M HNO$_3$; the organic phase was a solution of calixarene in dichloromethane, at a concentration adapted to an extraction percentage ranging from 10–90%. Each phase (1 mL) was thoroughly mixed by stirring in a stoppered tube at 20 °C for 12 h. After separation of the two phases, the concentration of the cation remaining in the aqueous phase was monitored spectrophotometrically with arsenazo(III) (2,2″-[1,8-dihydroxy-3,6-disulpho-2,7-naphtalenebis(azo)]dibenzenearsenic acid) as a coloured indicator.[23] Arsenazo solution (0.5 mL of 6×10^{-4} M) was added to a 0.7 mL aliquot of the aqueous phase and the volume was finally adjusted to 50 mL with either a sodium formate/formic acid buffer (pH 2.80) for the determination of europium or with a 4 M nitric acid solution for the determination of thorium. The absorbances were then determined at 665 nm for thorium and 655 nm for europium. Since the concentration of arsenazo(III) is at least 30 times higher than the concentration of the cation, complete complexation of the cation can be assumed. The extraction percentage was derived from Equation (1), in which A_0 is the absorbance of the arsenazo solution without the cation and A_1 the absorbance of the blank.

$$\%E = 100[(A_1 - A)/(A_1 - A_0)] \qquad (1)$$

Log–log plot analysis: In order to characterize the extraction ability, the dependence of the distribution coefficient D of a cation between the two phases upon the calixarene concentration has been examined. If the general extraction equilibrium is assumed to be Equation (2) with M^{x+} = metal ion, L = neutral ligand and with the overlined species referring to species in the organic phase, the overall extraction equilibrium constant is given by Equation (3). If we introduce the distribution coefficient D, as given in Equation (4), we obtain Equation (5).

$$M^{x+} + xNO_3^- + n\overline{L} \rightleftharpoons \overline{ML_n(NO_3)_x} \qquad (2)$$

$$K_{ex} = [\overline{ML_n(NO_3)_x}]/[M^{x+}][NO_3^-]^x[\overline{L}]^n \qquad (3)$$

$$D = [\overline{ML_n(NO_3)_x}]/[M^{x+}] \qquad (4)$$

$$\log D = \log K_{ex}[NO_3^-]^x + n\log[\overline{L}] \qquad (5)$$

With these assumptions, a plot of a log$D$ versus log[$\overline{L}$] should be linear and its slope should be equal to the number of ligand molecules per cation in the extracted species. To check the validity of the method, a log–log plot analysis for the extraction of thorium(IV) and europium(III) nitrates 10^{-4} M by CMPO has been investigated. In agreement with previous studies, a slope of 3.1 was found for thorium, while a lower value of 2.4 was observed for europium.[24]

Loading capacity measurements: The loading capacity of the organic phase for thorium has been determined according to the following procedure: 5 mL of the organic phase (2×10^{-4} M) were vigorously shaken with 5 mL of an aqueous phase containing increasing amounts of cation nitrate (10^{-3}–0.1 M) and 1 M HNO$_3$ during 15 h. After two hours to allow phase separation, a given aliquot of the organic phase was mineralized by evaporation at 100 °C in the presence of a few drops of 65% HNO$_3$ followed by calcination at 800 °C. The residual thorium was determined by titration according to the procedure described above.

Stability constant determinations: The stability constant of a complex formed in a homogeneous medium is strictly speaking a more representative physicochemical characteristics of the intrinsic affinity of a ligand for a cation in this given medium than an extraction constant. Stability constants enable comparison to be made between different ligands, without any interference from lipophilicity differences which do arise in extraction. Furthermore, they allow comparison with other more classical macrocyclic ligands. The stability constants β_{xy} of the complexes, expressed as concentration ratios according to the general complexation equilibrium [Eq. (6)] were determined in methanol, at 25 °C and constant ionic strength I (Et$_4$NCl), by UV spectrophotometry. Upon addition of the metal chlorides to a solution of the ligand in methanol, the UV-visible spectrum of the ligand generally undergoes small changes, in the 250 to 300 nm range, which, in most cases, are sufficient to allow a multiwavelength treatment of the data by the computer programs Letagrop-Spefo[25] or Sirko.[26] As evidence was only found for 1:1 complexes, β_{11} can be abbreviated in the following text as β. The values given in the data tables correspond to the arithmetic means of at least three independent determinations. The method is only appropriate in the stability range $1 \leq \log\beta \leq 6$.

$$mM^{x+} + nL \rightleftharpoons M_mL_n^{mx+} \qquad (6)$$

In the case of the short, that is, with one methylene spacer pentamer phosphine oxide **2b** (hereafter, for convenience the phosphine oxides with two methylene spacers are referred to as long) with the alkaline earth cations, the stability constants were also investigated by a competitive potentiometric method with Ag$^+$ as the auxiliary cation. Nevertheless the magnitude of the stability constant of the silver complex (3.62 log units) only allowed a determination of logβ for Mg^{2+} (4.72 log units), the other complexes being too strong.

Results and Discussion

Alkali cations: The results obtained with tetramers **1a**, **1d** and **2a**, pentamer **2b** and the two mixed tetramers **3a** and **3b** are given in Table 1 and are illustrated graphically in Figure 1. The results clearly reveal an enormous difference in behaviour between the tetrameric long phosphine oxide **1a**, which

Table 1. Alkali cations: Percentage extraction %E from water into dichloromethane and, in brackets, logβ in methanol ($10^{-2} \leq$ ionic strength $I \leq 4.5 \times 10^{-2}$ M in Et_4NCl).

	Li^+	Na^+	K^+	Rb^+	Cs^+
1a	0.7[a] –	0.5[a] –	0.3[a] –	0.5[a] –	0.4[a] –
1d	3.5[a] –	3.7[a] –	3.8[a] –	3.6[a] –	3.6[a] –
2a	7.6[a] (≤1)	6.0[a] (≤1)	22.3[a] (1.9)[b]	17.0[a] (1.4)[b]	6.4[a] –
2b	28.5[e] (≤1)	37.9[e] (2.34)[i]	45.0[f] (3.28)[j]	50.7[g] (3.9)[c]	56.9[h] (4.02)[i]
3a	53.4[a] (2.6)[b]	65.1[a] (4.5)[b]	42.6[a] (3.3)[b]	20.0[a] (2.8)[b]	13.0[a] (≤1)
3b	8.5[a] –	17.9[a] (2.9)[d]	13.7[a] (2.4)[b]	5.3[a] –	5.0[a] –

[a] $0.1 \leq \sigma_{N-1} \leq 0.5$; [b] $\sigma_{N-1} < 0.1$; [c] $\sigma_{N-1} = 0.05$; [d] $\sigma_{N-1} = 0.03$; [e] $\sigma_{N-1} = 0.8$; [f] $\sigma_{N-1} = 0.7$; [g] $\sigma_{N-1} = 0.1$; [h] $\sigma_{N-1} = 0.3$; [i] $\sigma_{N-1} = 0.02$; [j] $\sigma_{N-1} = 0.01$

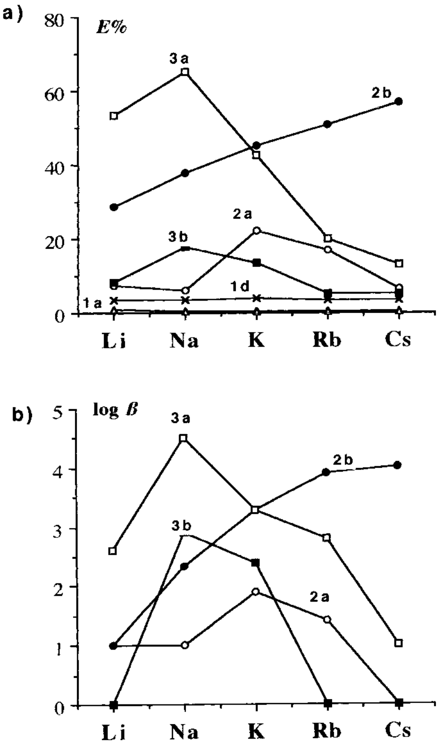


Figure 1. a) Extraction percentages (%E) of alkali picrates from water into dichoromethane by selected phosphine oxide calixarenes at 20 °C; b) Logβ values in methanol for the complexation of alkali cations by selected phosphine oxide calixarenes at 25 °C, ionic strength between 10^{-2} and 4.5×10^{-2} M in Et_4NCl.

does not extract the alkalis (or very little when *p*-dealkylated as in **1d**), and the tetrameric short phosphine oxide **2a**, which displays an extraction and complexation peak selectivity in favour of K^+ (%$E = 22$, log$\beta = 1.9$). The extraction ability of a short phosphine oxide is very much enhanced when the condensation is increased up to five, along with a change in the selectivity pattern, which now displays a continuous increase in extraction efficacy as the cation ionic radius increases; this increase from tetramer **2a** to pentamer **2b** cannot be accounted for by an increasing lipophilicity of the extractant, as the stability constants also increase and range from 2.3 for Na^+ to 4.0 for Cs^+. Clearly the larger cavity of the pentamer is better suited for the larger Cs^+ cation than its tetra analogue. The characteristics of the two mixed tetramers **3a** and **3b** are strongly dependent on the nature of the groups replacing two of the phosphine oxides. Both compounds show a peak selectivity for Na^+, as do the corresponding tetraamides and tetraesters.[3] The amide groups lead to the highest efficiency for Na^+, higher than the ester groups, as is predictable from the behaviour of the homo-substituted analogues. The efficacy order for Na^+ extraction is **3a** > **2b** > **3b** > **2a** > **1d** > **1a**. This order is unchanged in terms of stability constants, except the inversion between **2b** and **3b** and these conclusions are clearly illustrated in Figures **1a** and **b.** The results are consistent with the extraction studies made from water to dichloroethane by other authors for compound **2a**, but not for **3a** for which these authors observe a decrease from Li^+ to Na^+.[11]

Alkaline earth cations: The results for the same series of ligands are given in Table 2 and are illustrated in Figure 2. Clearly the long tetraphosphine oxides **1a** and **1d** have no extraction efficacy towards the alkaline earth cations. The *p*-dealkylation only slightly increases the extraction power of **1a**. No attempt was made to determine the stability constants of their complexes, as it was assumed, on the basis of the extraction results, that they would be very small.

The mixed short diphosphine oxide **3b** also displayed no extraction efficacy towards the alkaline earth cations, in agreement with the generally small affinity of the calixaryl esters for alkaline earths.[3] The mixed short diamide **3a** and the short phosphine oxide **2a** display medium extraction efficiencies (%$E < 25$). The stability constants of the complexes fall within the limits of the spectrophotometric method only for the calcium complex of **2a** (2.3), the calcium, strontium and barium complexes of **3a** (4.4, 4.5 and 3.4, respectively), and the calcium complex of **3b** (1.8). The stability of the calcium complex is higher for **3a** than for **2a** in

Table 2. Alkaline earth cations: extraction percentages %E from water into dichloromethane at 20 °C ($0.1 \leq \sigma_{N-1} \leq 0.5$) and, in brackets, log β values determined by spectrophotometry, in methanol, at 25 °C (one experiment only). Ionic strength I ranging from 10^{-2} to 4.5×10^{-2} M (Et_4NCl), unless otherwise stated.

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1a	0.6 –	2.6 –	0.8 –	0.5 –
1d	3.0 –	5.0 –	3.3 –	3.1 –
2a	5.6 (≤1)	23.0 (2.35)[b]	9.8 (≤1)	8.4 (≤1)
2b	18.2 (4.72)[a]	62.5 (≥6)	52.2 (≥6)	62.3 (≥6)
3a	3.7 –	15.8 (4.4)	15.4 (4.5)	12.5 (3.4)
3b	1.2 –	1.1 (1.8)	1.4 –	1.4 –

[a] Competitive potentiometry determination with Ag^+ as auxiliary cation: $I = 10^{-2}$ M in Et_4NClO_4, log $\beta(Ag^+) = 3.62 \pm 0.01$, $\sigma_{N-1} = 0.09$; [b] $\sigma_{N-1} = 0.1$

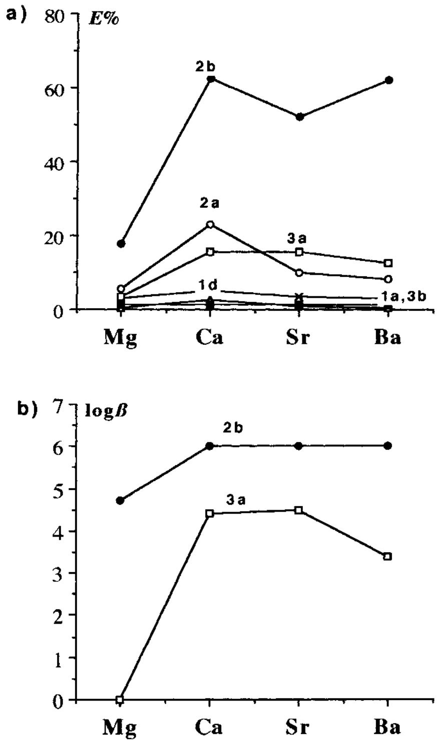


Figure 2. a) Extraction percentages (%E) of alkaline earth picrates from water into dichloromethane by selected phosphine oxide calixarenes at 20 °C; b) Logβ values in methanol for the complexation of alkaline earth cations by selected phosphine oxide calixarenes at 25 °C, ionic strength between 10^{-2} and 4.5×10^{-2} M in Et_4NCl.

contrast with the trend observed in extraction: this may reflect the greater influence of lipophilicity expected for **2a**, because of the larger number of aromatic rings. The logβ values for **3a** are approximately half the values reached with the corresponding tetradiethylamide.[22]

Evidently, the most efficient compound among the six studied is the short pentamer **2b**, for which %E reaches 62 % for Ca^{2+} and Ba^{2+}, and 18 % for Mg^{2+}. The stability constants are too high to be evaluated by any of the employed methods (competitive potentiometry gave a value of 4.7 for magnesium). Compounds **3a**, **2a** and **2b** all show an extraction selectivity for calcium, which can be considered as a plateau selectivity from calcium to barium for the pentamer and the mixed diamide, and a peak selectivity for the tetramer **2a.**

One may conclude that, in extraction as well as in stability constants for alkaline earths, the pentameric phosphine oxide **2b** is the most efficient of all compounds tested in the present work. The same conclusion was reached in the alkali series, but for cesium and rubidium only, the lighter alkalis being even better extracted or complexed by the mixed diamide tetramer.

The present results demonstrate i) the very big effect of the shortening of the carbon chain bearing the phosphine oxide groups (compare **2a** with **1a**) and ii) the tremendous effect of increasing the condensation degree from 4 to 5 (compare **2a** with **2b**). The comparison between the calix[5]phosphine oxide and the corresponding calix[4]-, calix[5]- and calix[6]-diethylamides shows that the level reached for the calcium extraction by the pentamer **2b** (62 %) is certainly inferior to the value reached by the tetraamide (98 %) and hexaamide (84 %), but is superior to that reached by the p-dealkylated hexaamide (25 %). Moreover, the extraction percentage for strontium by the pentaphosphine oxide **2b** (52 %) is almost as high as that displayed by the corresponding pentadiethylamide (55 %).

Europium(III) and thorium(IV): It is of major environmental concern to know how to remove from liquid radioactive wastes, before their disposal, the harmful long-lived nuclides, such as caesium and strontium, and the α-emitting actinides. Of the various extractants used in actinide process chemistry, neutral organophosphorus compounds are among the most useful.[9] The PUREX process for plutonium/uranium separation, for example, is based on the extracting ability of tributylphosphate.[10] Efforts to improve the performance of a group of simple monofuntional organophosphorous extractants, such as the well-known trioctylphosphine oxide (TOPO, $[(C_8H_{17})_3PO]$), led to the development of bifunctional analogues that include carbamoylmethylphosphonates $[(RO)_2PO(CO)NR_2]$ (CMPs) and carbamoylmethylphosphine oxides $[R_2POCH_2(CO)NR_2]$ (CMPOs), among which is the classical octylphenyldiisobutylcarbamoylmethylphosphine oxide $[Ph_2POCH_2CON(C_8H_{17})_2]$ known as CMPO. In our study, we decided to extend our extraction and stability constant measurements to Eu^{III} and Th^{IV}, using the former to mimic the trivalent actinides and the latter to mimic the tetravalent actinides present in liquid nuclear waste. The calixaryl phosphine oxides used for this purpose were **1a–f**, as well as four other phosphine oxide calixarenes of group **1**, with either dodecyl groups in para position instead of *tert*-butyl groups ($n = 4$) or with n-butyl groups on the phosphorus instead of phenyl groups ($n = 4$, 6, 8). Using calixarenes as building blocks, we hoped to exploit the synergism that might accrue from combining several phosphine oxide and ether podands with the receptor potential of macrocycles of the calixarene family. For comparison purposes, the classical TOPO and CMPO extractants were also tested, as well as some bi- and trifunctional noncalixarene phosphine oxides **4a–e**.

As the picrate extraction method was not applicable to experiments intended to mimic the situation with real liquid wastes, which contain nitrates and nitric acid, we used the new nitrate extraction technique described above. The results of this study are presented in Table 3 as percentages of cation extraction into dichloromethane for selected analytical calixarene concentrations, and in Figure 3 as log$D$ versus the log of free calixarene concentration at equilibrium in the organic phase for thorium and europium (see Experimental Section for details).

The main conclusions concerning the calixarene phosphine oxides are the following:

*The long phosphine oxide series **1a–f***:

i) All calixarenes tested are better extractants for europium and thorium than TOPO and CMPO. The only exception concerns the extraction of europium by the octamer **1c.**

ii) Thorium is always better extracted than europium.

Table 3. Percentage extraction (% *E*) of thorium(IV) and europium(III) nitrates (10^{-4} M) from 1 M HNO_3 aqueous solutions into dichloromethane containing the ligand at various concentrations.

	Th^{IV}						Eu^{III}
	10^{-4} M	5×10^{-4} M	10^{-3} M	5×10^{-3} M	10^{-2} M	$2.5\cdot10^{-2}$ M	$2.5\cdot10^{-2}$ M
TOPO	0	0	0	1.4	10.2	64.2	0[a]
CMPO	0	0	0	1.6	12.2	70.4	0[b]
1a	0	5.6	26.8	96.1	100	100	0
1d	2.6	46.9	79.8	100	100	100	24.6
1g			55.0				29.6
1b	0	23.6	62.5	98.8	100	100	20.8
1e	9.4	79.4	94.8	100	100	100	94.3
1c	0	0	0	30.6	60.1	88.4	0
1f	5.1	62.6	87.9	100	100	100	92.0
2a		31.5	55.5	100			86.2
2b		[c]	[c]	[c]	[c]	[c]	[c]
4a	20		100				≥95
4b			38	–	100		8
4c			95				≥95
4d		95	100				–
4e			87				85

[a] % $E=18$ ($C_L=0.25$ M); [b] % $E=69.5$ ($C_L=0.25$ M); [c] No measurement possible, formation of a film at the interface.

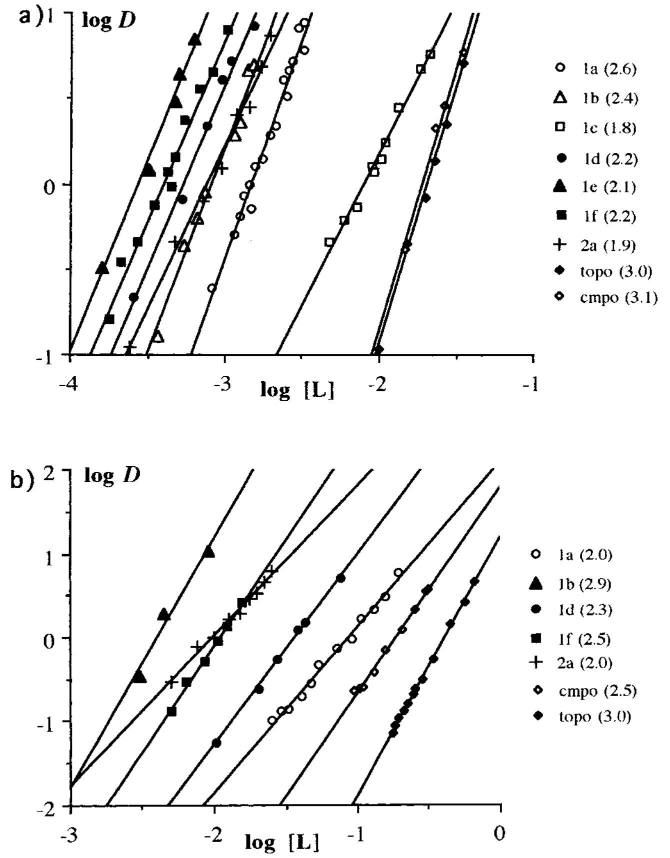


Figure 3. Extraction of a) thorium(IV) and b) europium(III) by phosphine oxide calixarenes and related classical extractants TOPO and CMPO from metal nitrate solutions (10^{-4} M) 1 M in HNO_3 into dichloromethane at 20 °C. Log*D* vs logarithm of the free ligand concentration (numbers in brackets are the values of the slopes).

iii) The dealkylated series is better than the alkylated series, both for thorium and europium. In the dealkylated series **1d–f**, the sequence of efficiency towards both cations is: hexamer > octamer > tetramer. In the alkylated series **1a–c**, the hexamer is the best extractant for thorium, followed by the tetramer and the octamer. With europium, there is no extraction by the tetramer and the octamer at concentrations lower than 0.1 M. According to the data in Table 3, the hexamer is better than the tetramer at a concentration of 2.5×10^{-2} M, but the log–log plot shows an unexpected behaviour of the hexamer, not represented on Figure 3. The replacement of the *p-tert*-butyl groups by dodecyl groups slightly decreases the extraction of thorium, but increases the extraction of europium. The replacement of the phenyl groups on the PO functions by *n*-butyl groups leads to a complete loss of extraction efficiency, since there is no extraction at a ligand concentration 10^{-3} M, that is, ten times higher than the cation concentration.

iv) With the classical extractant TOPO with only one phosphine oxide function per molecule, the slopes of the log–log plot analyses are 3 for both thorium and europium as expected from previous studies.[24] With CMPO, the slope for thorium has the expected value of 3, but in the case of europium, the slope is only 2.5. A similar deviation with respect to the expected slope of 3 was found by Horwitz and co-workers[27] for the extraction of americium(III) into toluene by CMPO, and attributed to a marked decrease in the measured activity coefficient of CMPO in toluene as water and nitric acid are also extracted.

The slopes of the linear plots for the extraction of thorium by the three dealkylated calixarene phosphine oxides **1d–f** are close to 2.0, indicating at first sight that the compounds may extract the cation as 1:2 species, that is, two calixarenes for one cation. The expected result for a 1:1 complex should be 1, assuming that one calixarene has enough PO functions to bind either thorium(IV) or europium(III). In order to verify the slope, saturation experiments of the organic phase by equilibration with increasing cation concentrations in the aqueous phase (see Experimental Section) were performed with compound **1d**, at a concentration of 2×10^{-4} M. The results, shown in Figure 4, indicate that a plateau is reached for a concentration of thorium in the organic phase equal to 10^{-4} M, that is, half the concentration of the ligand. This observation confirms the results of the log–log plot analysis for the calixarene **1d**, at least in our experimental conditions in which the ligand was in excess. The deviation from the ideal expected slope of 1 is even bigger with the *p-tert*-butyl series, for which slopes were found to range between 1.8 and 2.6. The formation of bisligand species of calixarenes with rare earth cations has already been demonstrated in the case of carboxylate derivatives of calixarenes:[28–30] it seems therefore reasonable to conclude that such bisligand species can also be formed between thorium(IV) and phosphine oxide derivatives of calixarenes. However, one cannot totally exclude the posibility of the influence of other factors on the observed slopes, such as coextraction of nitric acid and activity coefficients effects.

The extraction of europium by the dealkylated tetramer **1d**, the octamer **1f** and by the *p-tert*-butyl tetramer **1a** is characterised by log–log plot slopes ranging between 2.0

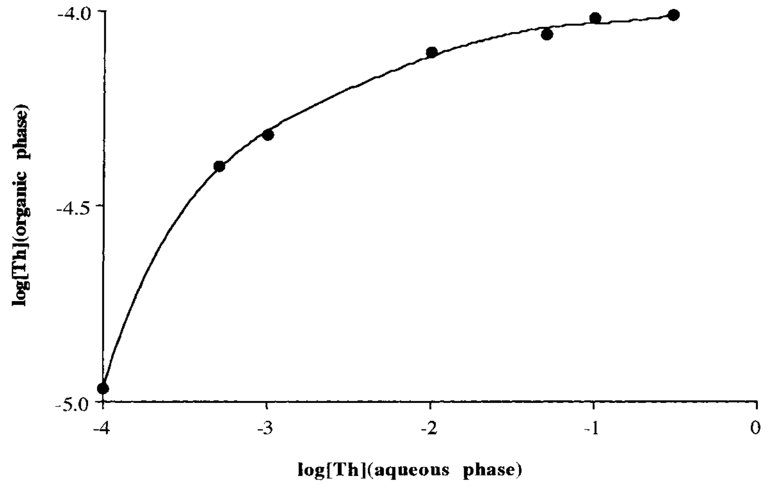


Figure 4. Loading curve for the saturation of a 2 × 10^{-4} M dichloromethane solution of calixarene **1d** by thorium nitrate from an aqueous solution 1M in HNO_3.

and 2.5, as in the case of thorium. The dealkylated hexamer **1e** gives a slope close to 3, as does TOPO just as if only one phosphine oxide per calixarene was involved in the complex formation.

*The short tetramer phosphine oxide **2a***: The shortening of the carbon chain between the phenolic oxygen and the phosphorus atom by one methylene spacer as in tetraphosphine oxide **2a** leads to a big increase of the extraction efficiency with respect to **1a**: at a calixarene concentration of 5 × 10^{-4}M, 31% Th^{IV} is extracted instead of 5.6%, and at concentration of 10^{-3}M, 55% instead of 27%. However, the changes thus induced by shortening of the spacer are not as effective as those resulting from the dealkylation of the *para* position of **1a**. For europium(III), the shortening of the spacer produces an even bigger change, as the extraction percentage increases from 0% with **1a** to 86% with **2a**, for a ligand concentration of 2.5 10^{-2}M. Compound **2a** appears to be the best extractant for europium among all the homo-substituted phosphine oxides studied in the present work.

*The short pentamer phosphine oxide **2b***: The effect of the increase of the calixarene nucleus to 5, producing the pentamer **2b**, could not be evaluated by the nitrate extraction method used here: thorium extraction was attempted with ligand concentrations ranging from 2.5 × 10^{-4}M to 4 × 10^{-2}M. The results showed surprisingly the ligand to be an extremely inefficient extractant, with $\%E = 6\%$ at 10^{-2}M and 7.4% at 4 × 10^{-2}M. A careful examination of the extraction tubes showed the presence of a sticky film on the upper surface of the aqueous layer, even more apparent at higher ligand concentrations. Europium extraction was also tried with **2b**, but the formation of a film on the upper surface of the aqueous layer was also observed. This competing phenomenon is probably the cause of the apparent poor results of the extraction power of **2b**.

*The nonmacrocyclic phosphine oxides **4a–f***: For a better understanding of the importance of the macrocyclic calixarene platform and the possibility of preorganization effects on the extraction ability of the polyfunctional phosphine oxides, some simple noncalixarene phosphine oxides have been tested as simple reference compounds. The results are given in Table 3 for the most relevant compounds.

Four compounds, the bifunctional derivatives **4a, 4c** and **4d** and the trisphosphine oxide **4e** have an extraction efficiency for thorium ranging between 87 and 100% at a ligand concentration 10^{-3}M. They can consequently be considered as good competitors of the calixarene phosphine oxides of Table 3. Compound **4a** even reaches, at a ligand concentration of 10^{-4}M, an extraction efficiency for thorium(IV) of 20%, which is only slightly lower than the good extraction performances of the CMPO-like calixarenes which reach 40–50% extraction under the same conditions.[8] It may be seen from the comparison between **4a** and **4b** that the efficiency decreases with the number of carbons between the two phosphine oxide functions. Concerning europium, **4a** and **4c** are better than all calixarenes tested.

Effect of HNO_3 and $NaNO_3$ concentrations: All the extraction work described in the previous sections refer to aqueous source solutions 1M in nitric acid. A preliminary investigation of the applicability of these results to the separation of actinides from the medium level activity liquid wastes, which are usually of high salinity and acidity (1M in HNO_3 and 4M in $NaNO_3$) before embedding of the latter in sub-surface repositories, led us to study the influence of the concentrations of acid and salt on the extraction ability of the calixarenes.

The effect of the nitric acid concentration, from 0.1 to 1.3M, is represented in Figure 5, for the *p-tert*-butyl tetramer **1a** and the dealkylated hexamer **1e**, as well as for the classical extractant TOPO, in the same experimental conditions as those described in the Experimental Section.

Below a nitric acid concentration of 1M, both calixarenes show the same decrease in extraction with HNO_3 increasing concentration, as TOPO. However, compound **1e** exhibits a slight increase of the extraction efficiency relative to TOPO when the nitric acid concentration is higher than 1M. This last trend is probably interpretable in terms of concomittant competing effects: coextraction of nitric acid, which tends to decrease the extent of extraction, and the salt effect of the anion $N0_3^-$, which leads to an increase of the extraction. This salt effect was evidenced by our study of the influence of the sodium nitrate concentration, from 0 to 4M, on the Th^{IV} extraction by the hexamer **1e** at the concentration 10^{-3}M, in presence of HNO_3 1M: we found that the higher the

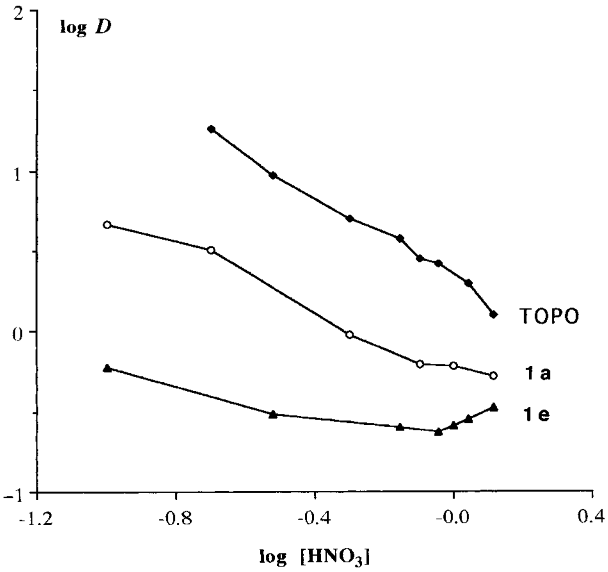


Figure 5. Influence of the nitric acid concentration in the aqueous phase on the extraction (log*D*) of thorium(IV) nitrate from aqueous solution into dichloromethane solutions of TOPO and calixarenes **1a** and **1e** at 20°C ([TOPO] = 0.025 M; [**1a**] = [**1c**] = 10^{-3} M).

concentration of $NaNO_3$, the better the extraction of Th^{IV}, a situation that is very favourable to the extension of the present studies to the further treatment of medium-level activity liquid wastes.

Stability constants: Preliminary spectrophotometric studies of the stability constants of the complexes of thorium(IV) with the calixarenic phosphine oxides **1a, 1b** and **2b** in methanol ($I = 0.01$ M Et_4NCl) have been completed. The hydroxo species of the cations have not been taken into account in these studies. The following values have been obtained for logβ of 1:1 complexes: **1a**(Th^{4+}) = 3.5; **1b**(Th^{4+}) = 3.64 ± 0.08, whereas with the same method values for Th^{4+} of 3.42 ± 0.06 and 3.64 ± 0.08 were found for the *p-tert*-tetradiethyl ester and the *p-tert*-hexadiethylamide, respectively.[31] Apparently, from these results, the nature of the functional group on the lower rim of these tetramers should play no significant role in the stability of the thorium complexes in methanol. The situation seems to be different with the short pentamer: logβ for **2b**(Th^{4+}) was found equal to 4.99 ± 0.08. The value of logβ of the 1:1 Yb^{III} complex of **2b** has also been determined and found to be very high (6.5 ± 0.1). The value for the 1:1 Th^{IV} complex of **2a** could not be obtained from spectrophotometric measurements because of insufficient spectral changes upon complexation in identical conditions. Work is in progress in order to confirm and extend these preliminary studies by other methods, in other solvents.

Acknowledgements

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