Calixarenes with diphenylphosphoryl acetamide functions at the upper rim. A new class of highly efficient extractants for lanthanides and actinides

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Various calix[4]arene tetraalkyl ethers and a calix[5]arene pentaalkyl ether substituted at the upper rim by the CMPO-like functional group $-NH-C(O)-CH_2-P(O)Ph_2$ as well as some linear model compounds have been synthesized for the first time. Their ability to extract europium, thorium, neptunium, plutonium and americium from 1 mol dm^{-3} aqueous HNO_3 into methylene chloride or o-nitrophenyl hexyl ether was studied under various conditions. All the new oligomeric ligands, but especially the calixarene derivatives, are tremendously strong extractants compared with the commonly used CMPO [(N,N-diisobutylcarbamoylmethyl)octylphenylphosphine oxide]. Also in transport studies through supported liquid membranes their efficiency is higher than that of CMPO which shows lower transport rates even at a 10-fold concentration.

Introduction

Nuclear fuel reprocessing operations produce high and medium level liquid wastes (HLLW and MLLW) containing different long-lived radioactive elements as β/γ emitters (Tc, I, Zr, Se, Cs, etc.) and α emitters (transuranium actinides: Np, Pu, Am, Cm, etc.). In order to simplify the conditioning of such wastes, it would be highly desirable to selectively remove these very long-lived radionuclides. This would decrease the volume of wastes intended for disposal in deep geological repositories using instead subsurface repositories which are easier to manage.[1] Furthermore these nuclides, separated from the matrix, could afterwards be turned into short-lived elements or non-radioactive ones through transmutation.

One of the generally used chemical separation processes in fuel treatment is liquid–liquid extraction by specific molecules. Presently two processes are well known for the decategorization of actinides: the TRUEX process using the classical CMPO

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1a
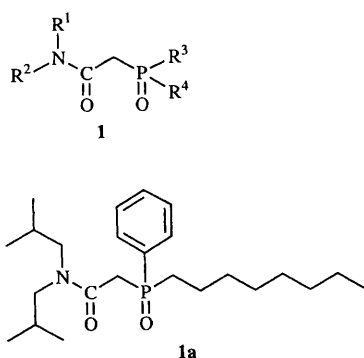
1a   [(N,N-diisobutylcarbamoylmethyl)octylphenylphosphine oxide][2,3] and the DIAMEX process involving diamide molecules.[1] Further developments include transport experiments using supported liquid membranes (SLM) which require only small amounts of ionophores.[4,5]
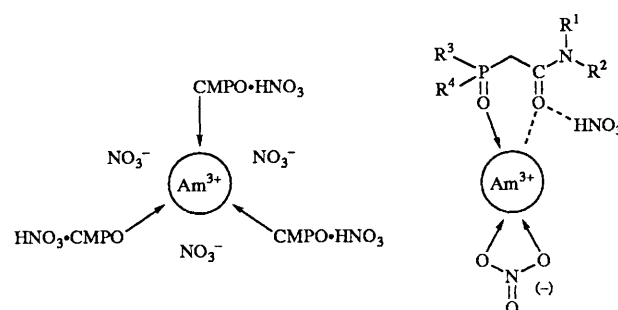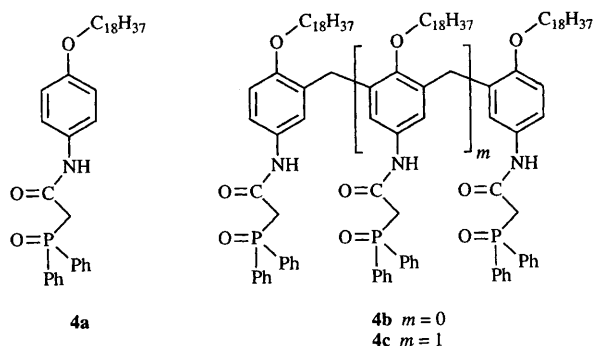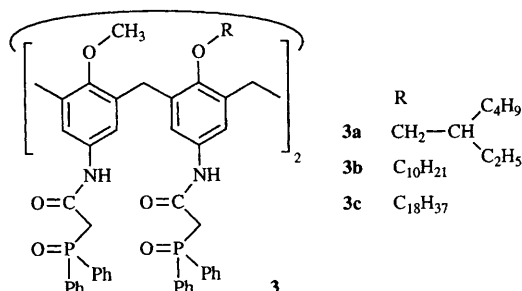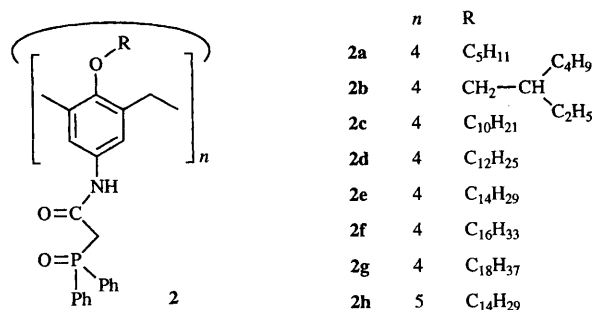

Fig. 1   Possible solution structure (schematic) of the americium(III) nitrato–CMPO complex at high HNO_3 concentration

In carbamoylmethylphosphine oxides (CMPOs, 1) the C=O and P=O groups act as the ligating functions. During the last decades the general structure 1 was modified in many ways and compounds bearing numerous residues at the nitrogen (R^1, R^2) and phosphorus (R^3, R^4) in various combinations have been checked.[6] Horwitz et al. investigated the solution structure of the americium(III) complex formed with CMPO under the technical conditions of the TRUEX process. Their results show that the americium(III) ion is co-ordinated by three CMPO molecules and three nitrate anions in an overall neutral complex as indicated in Fig. 1. A further molecule of HNO_3 is hydrogen bound to each of the carbamoyl oxygens.[7] Two to four molecules of CMPO have been suggested to be included in the complex formed with plutonium(IV) and more than one molecule of CMPO will be also involved in the CMPO complexes of other cations.[7] Therefore it seems reasonable to construct molecules, in which several (three or four) CMPO functions are combined in a suitable mutual arrangement. This may not only lead to new ligands which show in general improved extraction properties on the basis of chelate effects (favourable entropic factors), but also to ligands which show selectivity in extraction due to the different stoichiometry (or

	n	R
2a	4	C_5H_{11}
2b	4	$CH_2-CH\langle^{C_4H_9}_{C_2H_5}$
2c	4	$C_{10}H_{21}$
2d	4	$C_{12}H_{25}$
2e	4	$C_{14}H_{29}$
2f	4	$C_{16}H_{33}$
2g	4	$C_{18}H_{37}$
2h	5	$C_{14}H_{29}$

	R
3a	$CH_2-CH\langle^{C_4H_9}_{C_2H_5}$
3b	$C_{10}H_{21}$
3c	$C_{18}H_{37}$

4a

4b $m = 0$
4c $m = 1$

composition) of complexes and to differences in the steric requirements.

The easily available calixarenes represent a class of macrocyclic compounds that offers an ideal platform for the arrangement of various ligating functions.[8] Modifications are possible both at the upper[9] and the lower[10] rim which allow an independent control of other factors like solubility in organic solvents and insolubility in aqueous phases by the introduction of further residues. We report here on the synthesis of calixarenes 2 and 3 bearing the CMPO-analogous functions $-NH-C(O)-CH_2-P(O)Ph_2$ at the upper rim and of the corresponding linear analogues 4. These compounds have been used in extraction of lanthanides and actinides and in transport studies with supported liquid membranes.[11]

Experimental

Syntheses

General remarks. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, with Me_4Si as reference. δ Values are given in ppm and J values in Hz. Melting points were determined on Dr Tottoli's (Büchi) or Kofler's (Reichert) melting point apparatus and are uncorrected. FD mass spectra were recorded on a Finnigan MAT 8230 spectrometer.

(Diphenylphosphoryl)acetic acid 7. Isopropyl ester of diphenyl-phosphinous acid (48 g, 0.2 mol) (prepared according to standard literature procedures from chlorodiphenylphosphine and propan-2-ol) and ethyl bromoacetate (25 cm³, 37 g, 0.22 mol) were mixed in an open 500 cm³ flask at room temperature. After a short time the mixture rapidly warmed up and isopropyl

bromide was evolved. When the reaction had ceased, the solution was heated to 100 °C for 30 min. The crude product was added to a solution of sodium hydroxide (40 g, 1 mol) in water–ethanol 1 : 1 (v/v) (300 cm³) and kept at 70 °C for three days. Then the ethanol was evaporated, water (200 cm³) was added and this solution was extracted with chloroform (100 cm³) to remove the undesired Arbuzov rearrangement products. The aqueous layer was acidified to pH 1 and the crude acid extracted with chloroform (3 × 200 cm³). The combined extracts were washed with brine, dried (anhydrous sodium sulfate) and evaporated in vacuo. If the acid (45 g, 85%) was obtained as an oil, the crystallization could be accelerated by trituration with benzene. Mp 136–138 °C; δ_H(200 MHz, $CDCl_3$) 3.50 (2 H, d, J 14.5, CH_2), 7.30–7.60 (6 H, m, ArH), 7.65–7.80 (4 H, m, ArH) and 11.80 (1 H, s, COOH); δ_C(50 MHz, $CDCl_3$) 38.4 (d, J 62, CH_2), 128.3–132.5 (m, Ar) and 167.1 (d, J 6, COOH); m/z (FD) 261.1 (M$^+$ + 1).

p-Nitrophenyl (diphenylphosphoryl)acetate 8. Diphenylphos-phorylacetic acid 7 (5.00 g, 19 mmol) and p-nitrophenol (2.64 g, 19 mmol) were dissolved together with thionyl chloride (2.24 cm³, 3.67 g, 31 mmol) in ethanol-free dry chloroform (35 cm³). The mixture was kept at 40 °C for 5 h and stirred overnight at room temperature. After addition of chloroform (20 cm³), the organic solution was washed with cold (!) 5% sodium hydrogen carbonate solution (50 cm³) and water (3 × 50 cm³), dried (anhydrous sodium sulfate) and evaporated under reduced pressure to give an orange–yellow sticky mass, which crystallized after treatment with ethyl acetate (20 cm³). It was filtered by suction and washed with cold ethyl acetate (5 cm³); a second crop of the p-nitrophenyl ester was obtained from the filtrate on cooling. Total yield 5.46 g, 75%, mp 114–116 °C (Found: C, 62.95; H, 4.25; N, 3.6. $C_{20}H_{16}NO_5P$ requires C, 63.0; H, 4.25; N, 3.65%); δ_H(200 MHz, $CDCl_3$) 3.75 (2 H, d, J 14.5, CH_2), 6.94 (2 H, d, J 9.2, NO_2ArH), 7.31–7.89 (10 H, m, other ArH) and 8.16 (2 H, d, J 9.2, NO_2ArH); δ_C(50 MHz, $CDCl_3$) 39.3 (d, J 58, CH_2), 122.3–132.7 (P-Ar), 130.2, 132.4, 145.5, 154.9 (NO_2-Ar) and 164.1 (d, J 6, COOR); m/z (FD) 382.0 (M$^+$ + 1).

General procedure for the calixarenes 2 and 3. A tetra-O-alkyl tetra-p-amino calix[4]arene (1 mmol) or penta-O-alkyl penta-p-amino calix[5]arene (0.8 mmol) and p-nitrophenyl (diphenylphosphoryl)acetate (1.91 g, 5 mmol) were stirred in dry and ethanol-free chloroform (80 cm³) at 45 °C for three days. After cooling to room temperature, water (80 cm³) and a few cm³ of concentrated potassium hydroxide solution were added. The mixture was stirred for 3–4 h. Then the organic layer was separated and subsequently washed with 5% sodium carbonate solution and water. After drying (anhydrous sodium sulfate) the solvent was removed in vacuo and the residue was recrystallized from methanol or (in the case of alkyl chains below C_{12}) precipitated from methanol–half-saturated brine; yield ca. 70%. The melting points are not sharp; the samples melt after softening in a temperature range between 150 and 180 °C under decomposition. The molecular masses of all compounds have been affirmed by FAB mass spectra.

General δ_H(200 MHz, $CDCl_3$) for calix[4]arenes 2a–g: 0.87 (12 H, t, J 6.5, CH_3), 1.26 (m, CH_2 of alkyl chains), 1.81 (8 H, m, OCH_2CH_2), 2.99 (4 H, d, J 13.2, $ArCH_2Ar$), 3.42 (8 H, d, J 13.6, $POCH_2CO$), 3.74 (8 H, t, J 7.2, OCH_2), 4.29 (4 H, d, J 13.2, $ArCH_2Ar$), 6.56 (8 H, s, Calix-ArH), 7.37–7.75 (40 H, m, P-ArH) and 8.96 (4 H, s, NH). Associated water appears as a broad singlet at ca. 2 ppm.

General δ_H(200 MHz, $CDCl_3$) for calix[4]arenes 3 (owing to the conformational flexibility various conformers are present and the NMR spectra are more complicated than the spectra of the compounds with four equal O-alkyl groups which are fixed in the cone conformation): 0.80–2.00 (br m, alkyl chains), 2.75–4.25 ($ArCH_2Ar$, OCH_2, OCH_3, $POCH_2CO$), 5.90–6.80 (together 8 H, 3 s, Calix-ArH), 7.25–8.00 (40 H, m, P-ArH) and 8.30–9.60 (together 4 H, 3 or 4 s, NH).

standard experiment were the following: the aqueous phase consisted of a solution of europium or thorium nitrate ($C_M = 10^{-4}$ mol dm^{-3}) and HNO$_3$ (1 mol dm^{-3}) in bidistilled water; the organic phase was a solution of the ligand in dichloromethane, at a concentration C_L suited for an extraction percentage ranging between 10 and 90%. A 1 cm^3 aliquot of each phase was stirred in a stoppered tube immersed in a thermostatted bath at 20 ± 0.1 °C for 12 h. After separation of the two phases, the concentration of the cation remaining in the aqueous phase was monitored spectrophotometrically using Arsenazo III as reagent. The arsenazo solution (5 cm^3, $c = 6.4 \times 10^{-4}$ mol dm^{-3}) was added to a 0.7 cm^3 aliquot of the aqueous phase. The volume of this sample was then adjusted to 50 cm^3 with a sodium formiate–formic acid buffer (pH 2.80) for the determination of europium(III) and with HNO$_3$ (4 mol dm^{-3}) for the determination of thorium(IV). The absorbances (A) were measured 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 percentages %E were derived from eqn. (1), where A^0 is the

$$\%E = 100 \frac{A^1 - A}{A^1 - A^0} \qquad (1)$$

absorbance of the arsenazo solution without cation and A^1 the absorbance of the arsenazo solution containing a known concentration of the cation before extraction.

Log–log plot analysis. To characterize the extraction ability the dependence of the distribution coefficient D of the cation between the two phases upon the calixarene concentration was examined at [HNO$_3$] = 1 mol dm^{-3}. If the general extraction equilibrium is assumed to be given by eqn. (2) the overall

$$M^{x+} + xNO_3^- + n\overline{L} \rightleftharpoons \overline{ML_n(NO_3)_x} \qquad (2)$$
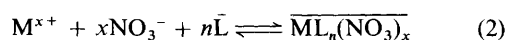
extraction equilibrium constant is expressed as eqn. (3).

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

Introducing the distribution ratio D, defined by eqn. (4) one

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

obtains eqn. (5). With these assumptions a plot of the log D vs.

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

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 our method a log–log plot for the extraction of thorium(IV) and europium(III) nitrates ($C_M = 10^{-4}$ mol dm^{-3}) by CMPO was investigated under our experimental conditions. As expected from previous studies,[16] a slope of 3.1 is found for thorium, while a lower value of 2.4 is observed for europium. A similar deviation with respect to the expected slope of 3 was observed by Horwitz and co-workers[17] for the extraction of Am(III) into toluene by CMPO, and attributed to a marked decrease in the activity coefficient of CMPO in toluene as water and nitric acid are also extracted.

Liquid–liquid extraction of actinides
The aqueous phase was choosen to simulate real occurring waste solutions. It consisted of 4 mol dm^{-3} NaNO$_3$, 1 mol dm^{-3} HNO$_3$ spiked with ^{152}Eu, ^{237}Np, ^{239}Pu and ^{241}Am. The activity was 1500 kBq dm^{-3} for Eu, Pu and Am and 3000 kBq dm^{-3} for Np which corresponds to the following concentrations in mol dm^{-3}: [Eu] = 1.5 $\times$ 10^{-9}, [Np] = 5 $\times$ 10^{-4}, [Pu] = 2.7 $\times$ 10^{-6} and [Am] = 5.2 $\times$ 10^{-8}. A 10^{-3} mol dm^{-3} solution

of the extractant in *o*-nitrophenyl hexyl ether (NPHE), a solvent also taken in the SLM studies, was used as the organic phase. Equal volumes (1 cm^3) of both phases were shaken in sealed tubes for an hour. Control experiments showed that the distribution equilibrium was reached for these low metal ion concentrations already after less than 10 min. The concentration of actinides in each phase was determined by liquid scintillation using a Tri Carb liquid scintillation analyser (Packard, a Canberra Company).[18] Therefore 100 mm^3 of each phase were added to 19.9 cm^3 of a scintillating liquid (insta gel) before the measurements. The distribution coefficients of the cations are defined by D where $\Sigma[M_{org}]$ and $\Sigma[M_{aq}]$ denote the total

$$D = \frac{\Sigma[M_{org}]}{\Sigma[M_{aq}]} \qquad (6)$$

concentration of metal species in the organic and in the aqueous phase, respectively. From the distribution coefficients the percentage extracted %E was calculated by eqn. (7). Back

$$\%E = \frac{D}{D + 1} \times 100 \qquad (7)$$

extraction was performed using Thermally Unstable Complexants (TUCs) recommended by Horwitz *et al.* to remove metal ions from organic solutions.[19] Here methylenediphosphonic acid (MDPA) and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) were used.

Transport studies
The experiments were carried out with an apparatus designed by Reinhoudt *et al.*[20] using the same phases as those used for liquid–liquid extraction experiments. The organic phase impregnated a microporous support of polypropylene placed between the aqueous phases. The mass of organic phase incorporated in a membrane was determined by weighing the membrane before and after impregnation: 1.5 mg cm^{-2} for a CELGARD 2500 membrane (thickness: 25 μm, porosity 45%). The receiving phase corresponds to the aqueous phase used for the back extraction in liquid–liquid experiments.

We have induced a coupled co-transport of the metal cations and nitrate anions, establishing a chemical gradient between the feed solution and the receiving one. According to the mass transfer model described by Danesi,[5] the permeability P is obtained using eqns. (8) and (9), where C is concentration of

Feed solution: $\quad \ln\left(\frac{C}{C^0}\right) = -\varepsilon\frac{S}{V}P_F t \qquad (8)$

Strip solution: $\quad \ln\left(1 - \frac{C'}{C^0}\right) = -\varepsilon\frac{S}{V}P_S t \qquad (9)$

the cation in the feed solution at time t, C' is concentration of the cation in the strip solution at time t and C^0 is initial concentration in the feed solution C^0: 2.7 $\times$ 10^{-6} ^{239}Pu, 1.5 $\times$ 10^{-9} ^{152}Eu, 5.2 $\times$ 10^{-8} ^{241}Am and 5 $\times$ 10^{-4} ^{237}Np mol dm^{-3}. ε, the volumic porosity of the SLM is 0.45, S, the membrane surface area is 11.4 cm^2 and V, the volume of feed and stripping solutions, is 53 cm^3.

P_F and P_S were determined graphically from the slope of plots $\ln(C/C^0)$ and $\ln(1 - C'/C^0)$, respectively, *versus* t. In ideal cases, P_F is equal to P_S. Values lower than P_F may be due to slow decomplexation kinetics, resulting in an accumulation of the cation in the membrane.

Results and discussion

Synthesis
The calixarene derivatives **2** and **3** were prepared in four (**2a–h**) or five (**3a–c**) steps starting from *p-tert*-butylcalix[4]- or *p-*

tert-butylcalix[5]-arene. (*a*) *O*-Alkylation in DMF using NaH as base gives the tetra- or penta-ethers in the cone-conformation in yields of 60–70%. The mixed tetraethers, necessary for the preparation of **3**, were synthesized in two steps introducing first the larger alkyl group R^1, which cannot pass the annulus, followed by *O*-methylation of these *syn*-1,3-diethers in DMF–THF with NaH as base. (*b*) Ipso-nitration of the tetra- or penta-ethers with yields of pure products in the range of 80–85%. (*c*) Reduction of the nitro groups by catalytic hydrogenation (Raney-Ni, 60 °C, normal pressure) leading to the amino calixarene ethers in *ca.* 80% yield. (*d*) Introduction of the –C(O)–CH$_2$–P(O)Ph$_2$ groups by acylation with an activated ester. The first steps (*a*)–(*c*), leading on a large scale to compounds which are interesting as starting material for various syntheses, have been described elsewhere.[21]

Initially we tried to introduce the phosphoryl functions by acylation of the amino compounds **I** with chloro- or bromo-acetylchloride followed by an Arbuzov reaction of **II** with the methyl or isopropyl ester of diphenylphosphinous acid (Scheme 1). Although this reaction was successful with model

Scheme 1
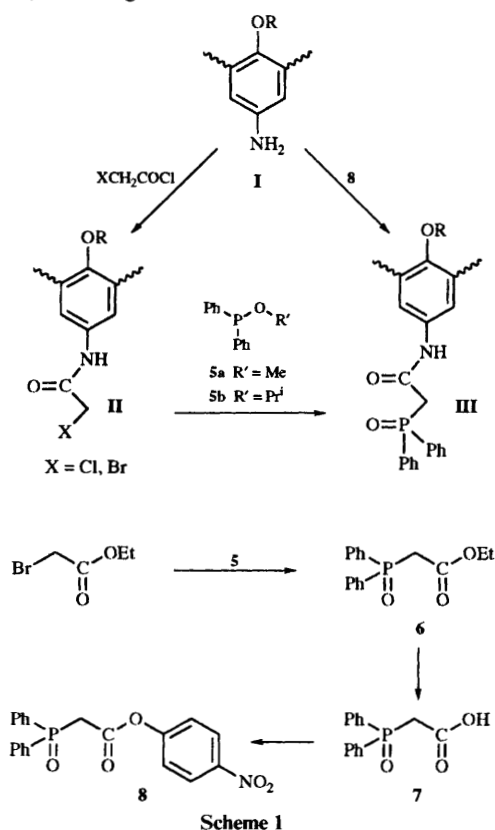
compounds, *e.g.* **4a**, it failed (in our hands) with calixarenes. While the tetrachloroacetamido compound **II** was still available, its further reaction gave only ill-defined products. (Decomposition of calixarenes of type **II** under slightly basic conditions was also observed in other reactions.)

However, the (diphenylphosphoryl)acetic acid **7** is available in good yields by the Arbuzov reaction of ethyl bromoacetate and subsequent alkaline hydrolysis of the ester **6**. First attempts to acylate amines **I** with the anhydride of **7** were unsatisfactory, while the direct coupling of **7** using dicyclohexylcarbodiimide (DCC) furnished the desired product in a form which was difficult to purify. By far the best results to date were obtained by aminolysis of the *p*-nitrophenyl ester **8** in chloroform at 45 °C. Various calixarenes of type **2** and **3** were prepared in this way in yields of 70% of the pure product (see below) on a gram-scale and attempts are presently directed towards a scaling-up of this reaction. The ester **8** itself can be obtained best in large quantities by reaction of **7** with *p*-nitrophenol in CHCl$_3$ in the presence of thionyl chloride.
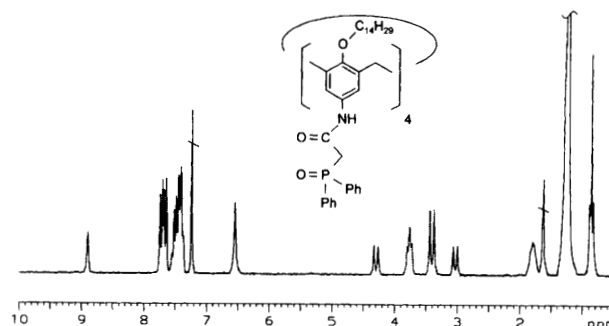
Fig. 2 ^{1}H NMR spectrum of the calix[4]arene **2d** in CDCl$_3$

Synthesis of the linear oligomers **4** was achieved in a similar way, starting however with the methylene bridged dimer or trimer of *p*-nitrophenol. These are easily available by acid-catalysed condensation of *p*-nitrophenol with formaldehyde and by condensation of bis-bromomethylated *p*-nitrophenol with excess *p*-nitrophenol.[13] *O*-Alkylation, reduction of the nitro group and subsequent acylation with **8** lead to **4**.

All compounds were characterized by FABMS and ^{1}H NMR spectra and partly also by ^{13}C NMR spectra. Their purity was further checked by thin layer chromatography. Considering the fact that incompletely acylated compounds are the most likely impurities, a clear ^{1}H NMR spectrum, as shown in Fig. 2, is the most convincing proof for the purity, while 'bulk values' like elemental analysis (troubled often by the unpredictable inclusion of solvent) for C, H and N are less indicative. A pure calix[4]arene derivative in the cone conformation is distinguished here for instance by a single pair of doublets for the protons of the bridging methylene groups (Ar–CH$_2$–Ar) and a singlet for the aromatic protons of the calixarene skeleton. However, with compounds **3** which can assume the cone, partial cone and 1,3-alternate conformation and obviously are present as a mixture of these conformers, this NMR analysis is not so easy. The purity is here mainly based on analogous experience with compounds **2**.

Extraction of europium(III) and thorium(IV)

Lanthanides are often used as models for actinides in extraction and complexation studies owing to the similarity of their ionic radii and their co-ordination behaviour. Thus, first extraction experiments were carried out with europium(III) as a model for americium(III) in order to check the complexation properties of the newly synthesized ligands in a simple way with non-radioactive material. Thorium(IV) was studied for similar reasons as a model of plutonium(IV).

Table 1 gives the percentages of thorium(IV) and europium(III) extracted into methylene chloride by the various ligands **2**, **3** and **4**. For comparison, results obtained with the classical extractants TOPO and CMPO are also reported. It should be emphasized that, owing to the different efficiencies of the ligands, their concentrations had to be varied from 10^{-4} to 0.25 mol dm^{-3}.

The data may be summarized as follows. (*a*) All the new calixarene compounds are highly efficient extractants for thorium(IV), since for a cation concentration of 10^{-4} mol dm^{-3}, ligand concentrations of 10^{-4} mol dm^{-3} are sufficient to extract comparable amounts. The non-cyclic compounds **4** require ligand concentrations of 10^{-3} mol dm^{-3}, while TOPO and CMPO must be present at a concentration of 10^{-2} mol dm^{-3} for a decent extraction level. Thus, even these linear oligomers **4b** and **4c** are stronger extractants than the classical ligands TOPO and CMPO, although less efficient than the calixarenes **2** and **3**. (*b*) Calixarenes **2** and **3** also extract europium(III) more efficiently than compounds **4**, TOPO and CMPO. (*c*) Like CMPO, all the new compounds are stronger extractants for thorium(IV) than for europium(III), since similar extraction

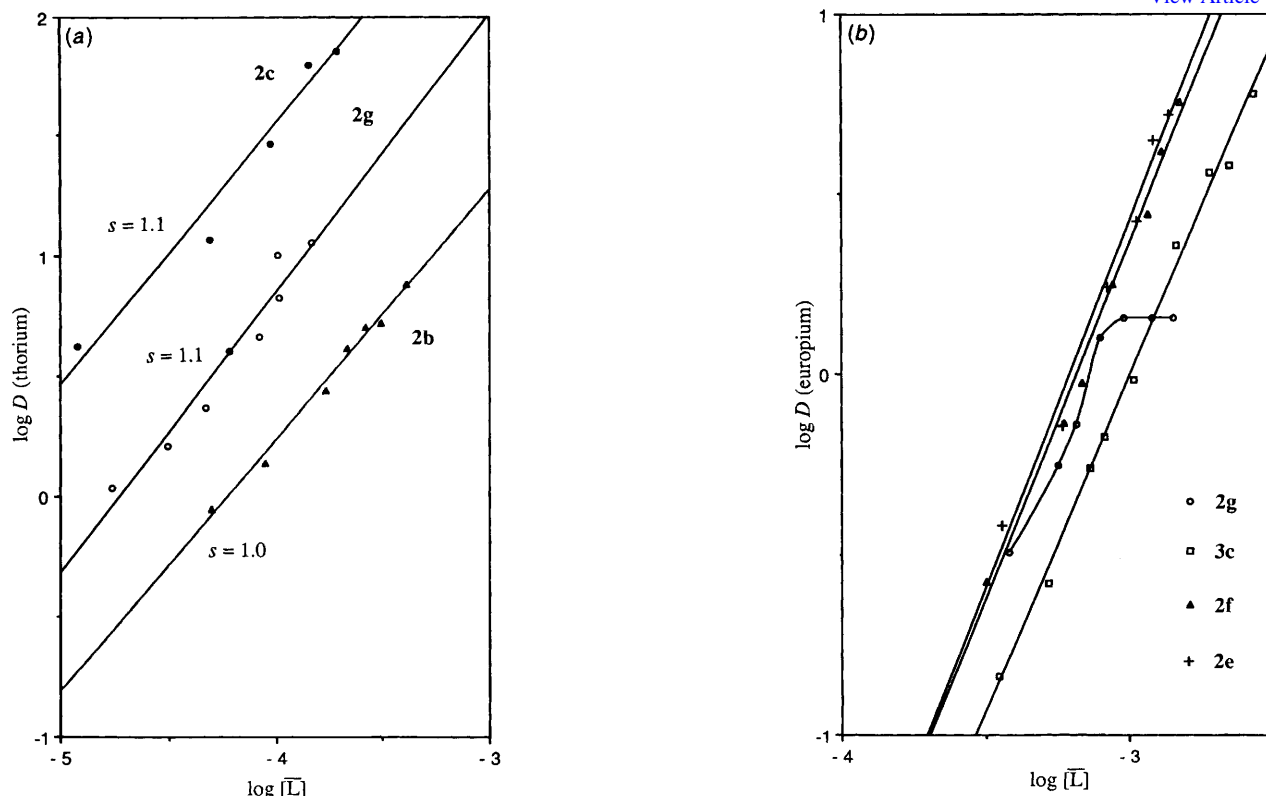**Fig. 3** Log D *versus* log $[\bar{L}]$ for the extraction of (a) thorium nitrate and (b) europium nitrate ($c_M = 10^{-4}$ mol dm^{-3}) by selected calixarenes **2** and **3**, from an aqueous phase (1 mol dm^{-3} HNO$_3$) into dichloromethane, at 20 °C (s = slopes of the linear plots)

Table 1 Extraction ($\%E$) of thorium(IV) and europium(III) by calixarenes **2** and **3** and their acyclic analogues **4** in comparison with CMPO and TOPO; $t = 20$ °C. Aqueous phase: cation nitrate $c_M = 10^{-4}$ mol dm^{-3} in 1 mol dm^{-3} HNO$_3$; organic phase: ligand (c_L) in dichloromethane

Ligand	$\%E$ (Th^{4+}) ($c_L = 10^{-4}$ mol dm^{-3})	$\%E$ (Eu^{3+}) ($c_L = 10^{-3}$ mol dm^{-3})
2a	39	47
2b	26	24
2c	53	68
2d	63	68
2e	54	72
2f	51.5	69.5
2g	50	59
2h	46	—
3a	32	20
3b	39	40
3c	43	49
4a	<3^a	<3
4b	17^a	<3
4c	78^a	<3
CMPO	12.2^b	69.5^c
TOPO	10.2^b	18^c

$^a c_L = 10^{-3}$ mol dm^{-3}. $^b c_L = 10^{-2}$ mol dm^{-3}. $^c c_L = 0.25$ mol dm^{-3}.

efficiencies require ligand concentrations of 10^{-3} mol dm^{-3} for europium(III) and only 10^{-4} mol dm^{-3} for thorium(IV). (d) Within the series **2**, an increase in the alkyl chain length from C$_{10}$ to C$_{18}$ does not cause any regular change in the extraction efficiency. (e) The 1,3-dialkyl-2,4-dimethyl ethers **3** give extraction percentages for thorium(IV) comparable to those obtained with the tetrapentyl ether **2a**. (f) The pentamer **2h** extracts thorium slightly less than its homologous tetramer **2c** (46% instead of 54%).

Log D vs. log $[\bar{L}]$ plots for the extraction of thorium(IV) by compounds **2b**, **2c** and **2g** are represented in Fig. 3(a). The plots

are linear with slopes close to one, in agreement with the formation of 1:1 complexes. For compounds **3a** and **3c**, the plots are not linear suggesting the formation of at least two complexes of different stoichiometries.

Corresponding plots for europium with the compounds **2e–g** and **3c** are shown in Fig. 3(b). With the exception of **2g**, the plots are linear with slopes of 2.0, suggesting that the stoichiometry of the europium complexes extracted is 1:2, under these conditions, *i.e.* in the presence of an excess of ligand. However, further studies are being carried out to establish the exact complex composition in all these cases.

The log–log plot for the extraction of europium(III) by compound **2g** bearing four octadecyl chains is not linear. The extraction tends towards saturation. This may be due to precipitation of the regular shaped ligand in which the four long alkyl chains in the cone conformation may show a kind of 'intramolecular crystallization' or to aggregation of the amphiphilic ligand at the water–dichloromethane interface. As stressed before, the related mixed compound **3c**, having only two octadecyl chains and assuming partly the partial cone conformation, does not show such behaviour.

Fig. 4 describes the effect of the HNO$_3$ concentration in the aqueous phase. Calixarenes **2**, like CMPO show an increase in the extraction efficiency with increasing acidity. The slope of these curves which obviously is not constant, does not necessarily represent the number of nitrate anions in the complex, since nitric acid is also extracted without thorium.

The dependence of the extraction efficiency on the sodium nitrate concentration was also investigated. It increases, for example, for compound **2e** from 55 to 95% when the sodium nitrate concentration increases from 0 to 4 mol dm^{-3} in 1 mol dm^{-3} HNO$_3$. This can be easily understood by the formation of complexes involving NO$_3^-$ ions, compare Fig. 1. A 'salting effect' may further contribute to this increase which also indicates the comparatively poor extraction of sodium by this ligand.

Table 2 Distribution coefficient (D) and extraction (%E) of europium, neptunium, plutonium and americium by the calixarenes **2** and **3** and their acyclic analogues **4**. Aqueous phase: 1 mol dm⁻³ HNO₃, 4 mol dm⁻³ NaNO₃, 3000 kBq dm⁻³ ²³⁷Np, 1500 kBq dm⁻³ ²⁴¹Am, ²³⁹Pu and ¹⁵²Eu; organic phase: extractant concentration c_L = 0.001 mol dm⁻³ in o-nitrophenyl hexyl ether (NPHE), except CMPO c_L = 0.01 mol dm⁻³ in NPHE

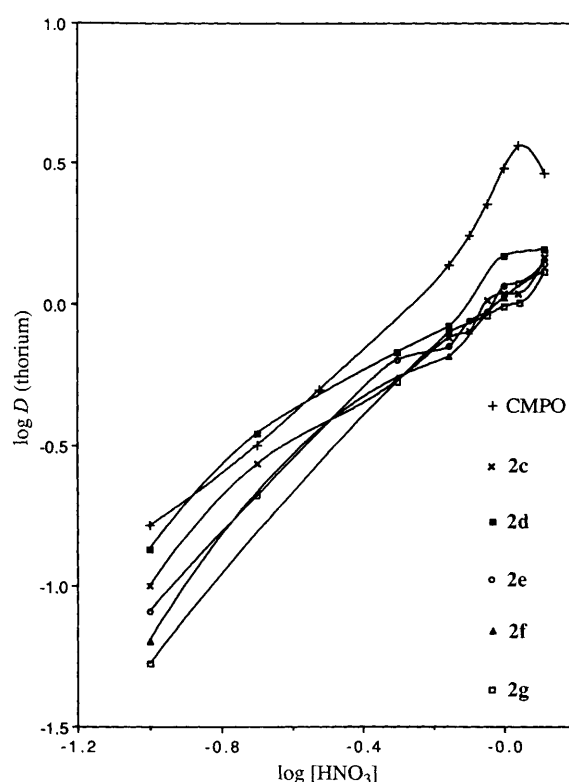| Compound	¹⁵²Eu		²³⁷Np		²³⁹Pu		²⁴¹Am	
	D	%E	D	%E	D	%E	D	%E
2a	> 100	> 99	2	67	100	99	> 100	> 99
2b	> 100	> 99	2	67	20	95	4.5	82
2c	> 100	> 99	2	67	90	98.9	> 100	> 99
2d	—	—	4	80	> 100	> 99	> 100	> 99
2e	> 100	> 99	2	67	80	98.8	> 100	> 99
2h	> 100	> 99	12	92	> 100	> 99	61	98
3a	> 100	> 99	2	67	> 100	> 99	> 100	> 99
3b	> 100	> 99	3	75	> 100	> 99	> 100	> 99
3c	> 100	> 99	3	75	> 100	> 99	> 100	> 99
4a	< 0.001	< 0.1	0.5	33	0.3	25	< 0.001	< 0.1
4b	1.2	54	0.9	47	23	96	1.8	64
4c	13	93	2	67	20	95	17	94
CMPO	—	—	0.85	46	22	96	1.2	54

Fig. 4 Effect of nitric acid concentration in the aqueous phase on the extraction of thorium nitrate by selected calixarenes **2** and CMPO into dichloromethane at 20 °C

Extraction of actinides. The high extraction efficiency for europium(III) and thorium(IV) shown by the calixarenes **2** and **3** and even by the linear analogues **4** prompted us to study the extraction of radioactive metal ions under conditions closer to the technical requirements. Table 2 summarizes the results obtained with o-nitrophenyl hexyl ether (NPHE) as the organic phase. Owing to their high polarity alkyl ethers of o-nitrophenol are frequently used as membrane solvents in supported liquid membranes[20] and the extraction experiments were carried out in analogy to the transport studies reported below. (a) Again the extraction efficiency of the calixarenes **2** and **3** is generally much higher than that of the commonly used CMPO. Even the linear compounds **4b** and **4c** reach extraction values comparable to CMPO or better. Note that the CMPO concentration in the organic phase had to be 10⁻² mol dm⁻³ while the new ligands **2**, **3** and **4** were applied at a concentration

of 10⁻³ mol dm⁻³. (b) The calix[4]arenes with four linear alkyl chains (**2a**, **2c**–**e**) are excellent extractants for Pu and Am with extraction levels > 98.5%. Owing to their lower solubility, precipitates occurred with calix[4]arenes **2f** and **2g** under the experimental conditions given in Table 2. If the concentration in the organic phase is reduced to 10⁻⁴ mol dm⁻³, 96% of plutonium and americium were extracted by **2f**, while **2g** still shows precipitation. (c) Introduction of branched O-alkyl chains often improves the solubility. But neither the solubility nor the extraction power of **2b** was better than those of the calixarenes with linear alkyl chains. (d) A better solubility and extraction ability was observed, however, for the mixed ether derivatives **3**. (e) Less Np (67–80%) than Pu and Am is extracted by all calix[4]arenes, which may be due to the fact that the concentration of Np is comparable to the ligand concentration while that of Pu and Am is much lower. However, 92% Np are extracted by the calix[5]arene derivate **2h**, which is especially remarkable since good extractants for Np are rare. It can be understood by the fact, that in contrast to the spherical ions Am³⁺ and Pu⁴⁺ neptunium is present under the experimental conditions in different oxidation states (IV–VI) and that cations like NpO²⁺, NpO₂⁺ and NpO₂²⁺ have a linear shape. Thus, their complexation is favoured by a larger cavity and a larger number of CMPO-like structures.[22] (f) Reasonable extraction values, although lower than those for the calixarenes, are obtained even with the dimer **4b** and the trimer **4c**. Especially remarkable is the selectivity for Pu over Am (and Np) found for **4b**. The generally observed increase in the extraction ability (**4c** > **4b** ≫ **4a**) which is more or less pronounced for the different cations demonstrates the importance of the 'chelate effect'. (g) Europium, included in this series for comparison, is extracted by all new ligands with the exception of **4** to more than 99%. (h) In all cases it was confirmed that complete back extraction was possible using MDPA or HEDPA.

Transport studies

First studies of ion transport through supported liquid membranes (NPHE) were carried out with selected examples of CMPO-like calixarenes in comparison to CMPO. The data are collected in Table 3. In general, calixarenes show strong transport abilities for actinides even when used at a low concentration of 10⁻³ mol dm⁻³. Especially high permeabilities in the range 3–7 cm h⁻¹ were obtained for all calix[4]arenes and Pu and Am. CMPO reaches a comparable value for Pu only when applied in a 10-fold higher concentration while it is still less effective for Am. With the most effective calix[4]arene **3c** (P = 7 cm h⁻¹), 92% of Pu were transported after 2 h and 99.75% after 6 h (compare Fig. 5).

Table 3 Permeabilities P for transport through supported liquid membranes by selected calixarenes **2** and **3**. Aqueous source phase: 1 mol dm^{-3} HNO$_3$, 4 mol dm^{-3} NaNO$_3$: 3000 kBq dm^{-3} ^{237}Np, 1500 kBq dm^{-3} ^{241}Am, ^{239}Pu and ^{152}Eu; membrane phase: o-nitrophenyl hexyl ether (NPHE), carrier concentration $c_L = 10^{-3}$ mol dm^{-3}, except CMPO $c_L = 10^{-2}$ mol dm^{-3}; stripping phase: 1/3 mol dm^{-3} HEDPA (**2c, 2e**); 1 mol dm^{-3} MDPA (**2a, 2h, 3a, 3b**)

Carrier	P/cm h^{-1} (^{237}Np)	P/cm h^{-1} (^{239}Pu)	P/cm h^{-1} (^{241}Am)
2a	< 0.2	3.6	3.4
2c	3.0	3.6	5.0
2e	1.2	2.9	5.3
2h	1.6	1.8	3.0
3a	1.6	4.2	2.9
3b	1.6	1.8	3.0
3c	1.3	7.0	3.2
CMPO	0.74	3.44	0.17
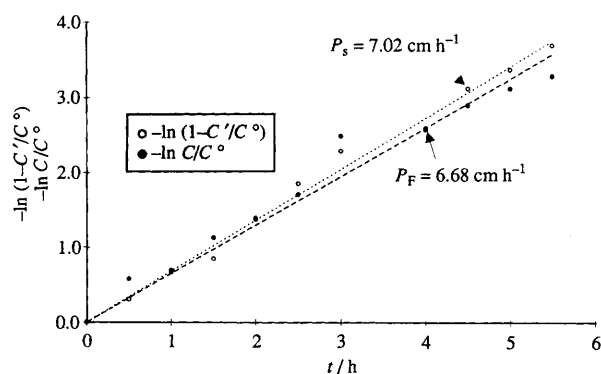
Fig. 5 ^{239}Pu transport experiment with calix[4]arene **3c**. Feed solution: 4 mol dm^{-3} NaNO$_3$, 1 mol dm^{-3} HNO$_3$, c(Pu) = 2.7 × 10^{-6} mol dm^{-3}, organic membrane: c(**3c**) = 10^{-3} mol dm^{-3} in NPHE, stripping solution: methylene diphosphonic acid (MDPA), $V_F = V_S = 53$ cm^3, $S = 11.4$ cm^2, $\varepsilon = 0.45$.

Conclusions

The standard extractant for actinides (N,N-diisobutyl-carbamoylmethyl)octylphenylphosphine oxide (CMPO) could be strongly improved by the attachment of four or five CMPO-like functions –NH–C(O)–CH$_2$–P(O)Ph$_2$ at the upper rim of calix[4]- or calix[5]-arenes. Even the analogous linear compounds show higher extraction abilities than CMPO. These results clearly demonstrate a co-operative action of several ligating groups within one molecule, although the exact composition and structure of the extracted complex is not yet known. Further studies including various spectroscopic techniques and single crystal X-ray analyses should lead to a more detailed understanding.

Since calixarenes are not only easily available in larger quantities, but also amenable to nearly unlimited chemical modifications it can be expected that even better extractants or ion carriers can be obtained on the basis of calixarenes. Variations which are presently studied concern the kind, the number and the mutual position of ligating functions, the ring size, the conformation or conformational mobility of the calixarene skeleton, or simply the solubility of the molecules. It is hoped, that in this way also the selectivity of ligands towards certain actinides or lanthanides can be improved.

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