Calix[*n*]arene Phosphine Oxides. A New Series of Cation Receptors for Extraction of Europium, Thorium, Plutonium and Americium in Nuclear Waste Treatment

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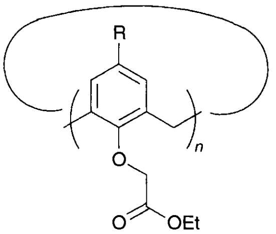
A novel class of calixarene derivatives with phosphine oxide residues [calix-$(OCH_2CH_2POPh_2)_n$] attached to the lower rim showing high efficiency in extraction of Eu^{III}, Th^{IV}, Pu^{IV}, and Am^{IV} from simulated nuclear waste is reported.

Inter- and intra-group separations of lanthanides and actinides, among the most difficult of all metal ion separations, are important processes in strategies for management and storage of high-level radioactive waste and clean-up of decommissioned nuclear facilities.[1] Environmental concerns demand that such processes be conducted with stringent attention to safety. Of particular importance in separation processes are liquid–liquid extraction and ion-exchange both of which involve, in their simplest forms, the transfer of a charged metal ion, or a complex, from a polar aqueous phase (usually highly acidic in nuclear waste) to another immiscible phase with concomitant charge neutralisation. Of the various extractants used in actinide process chemistry, neutral organophosphorus compounds are among the most useful.[1] The PUREX process for plutonium/uranium separation, for example, is based on the extracting ability of tributylphosphate.[2] Efforts to improve the performance of simple monofunctional organophosphorus extractants led to the development of a group of bifunctional analogues which include carbamoylmethylphosphonates [$(RO)_2PO(CO)NR'_2$](CMPs) and carbamoylmethylphosphine oxides [$R_2POCH_2(CO)NR'_2$](CMPOs).[3]

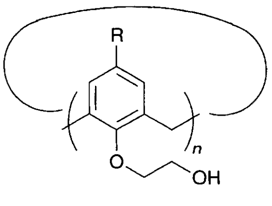
We now report the synthesis of a new generation of polyfunctional phosphine oxides **5a–f** and demonstrate their superiority over CMPO-like substances in extraction and complexation of selected lanthanides and actinides. In designing these structures we sought to exploit the synergism that might accrue from combining several phosphine oxide and ether podands with the receptor potential of macrocycles of the calixarene family. Additionally, the calixarenes offer versatility with respect to the number of podands to be deployed per molecule. These lower-rim derivatives were synthesised from the known ethyl acetates **1a–f**[4] *via* reduction to primary alcohols **2a–f** using DIBAL in toluene, conversion of the alcohols into tosylates **3a–f** with toluene-*p*-sulfonyl chloride in pyridine, introduction of diphenylphosphine residues through exposure of the tosylates to sodium diphenyl phosphide in dioxane–THF, and finally oxidation of the resulting phosphines **4a–f** to phosphine oxides **5a–f** using either dimethyldioxirane or hydrogen peroxide in acetone.† ^1H NMR analysis revealed that the *p-tert*-butyl tetramer derivative **5a** and its dealkylated counterpart **5d** exist in stable cone conformations in solution. The hexamers and octamers **5b,c,e,f** are conformationally mobile at ordinary temperatures as is the case with many of the larger calixarene derivatives. The isolation of good quality crystals of tetramer phosphine oxide **5a** offered the opportunity to probe the solid-state structure by X-ray diffraction, in particular, the disposition of the putative binding sites and their degree of preorganisation about the lower rim cavity.‡

The molecule exists in a distorted cone conformation (shown in Fig. 1) which is best described by the angles between the four aromatic rings and the mean plane of the macrocyclic ring methylene groups [(A) 145, (B) 81, (C) 131, (D) 100°]. The methylene carbon atoms are themselves almost coplanar. Aromatic rings A and C are almost normal to one another (96°), whereas rings B and D are almost parallel (2°). The confines of the lower rim hydrophilic cavity are defined by the positions of the four phenolic oxygen atoms and the four phosphine oxide residues, the distortion of the cone being highlighted by the distances 3.50 Å (A–C) and 5.22 Å (B–D) between phenolic oxygen atoms across the cavity. All four phosphine oxide oxygen atoms point away from the cavity though this effect is less pronounced with O(2A). Four methanol molecules of crystallisation are present within the lattice, two with their oxygen atoms disordered over two sites. The hydrogen atoms of the methanol molecules could not be located unequivocally but the O···O distances between three of the methanol oxygen atoms and the nearest phosphine oxide oxygen atoms are consistent with the presence of intermolecular hydrogen bonds [O(1MD)···O(2A), 2.79 Å], [O(1MA)···O(2D), 2.64 Å] and [O(1MC)···O(2B), 2.73 Å].

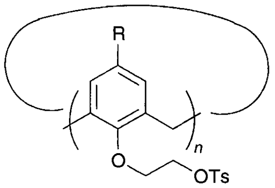
Our primary objectives initially were to study the extraction of thorium and europium, the former as a model for tetravalent, and the latter as a model for trivalent actinides, and apply the results to the extraction of simulated nuclear waste containing sodium nitrate and nitric acid. Preliminary extractions of thorium(IV) picrate and europium(III) picrate with calixarene phosphine oxides **5a–f**, and for comparison acyclic phosphine oxides **6** [$MeC(CH_2POPh_2)_3$] (obtained by oxidation of triphos), **7** [$(C_8H_{17})_3PO$] (topo), and **8** [$Ph_2POCH_2CON(C_8H_{17})_2$] (cmpo), from neutral aqueous solution into dichloromethane, demonstrated that all compounds were active phase-transfer agents under these conditions. However, neutral water provides



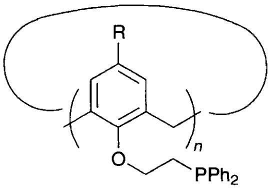
1a–f



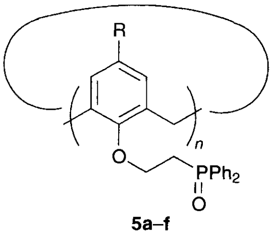
2a–f



3a–f



4a–f



5a–f

a R = Bu^t, $n = 4$
b R = Bu^t, $n = 6$
c R = Bu^t, $n = 8$
d R = H, $n = 4$
e R = H, $n = 6$
f R = H, $n = 8$

a very inadequate simulation of the conditions for extracting lanthanides or actinides from strongly acidic nuclear waste. It was decided, therefore, to study the extraction of metal nitrates from 1 mol dm^{-3} nitric acid into dichloromethane. Thorium(IV) nitrate was measured with an excess of ligand at different ligand concentrations. The linear plots of log D, the distribution coefficient for the salt between the two phases, *vs.* log C_L, the ligand concentration, are represented in Fig. 2. The values for the slopes of the linear plots for the three dealkylated calixarene phosphine oxides **5d–f** were close to 2.0, indicating that the compounds may extract thorium as 1 : 2 species. The greater deviation with respect to the ideal slope of 2.0 observed with the *p-tert*-butyl derivatives **5a–c** suggests that coextraction of complexes of different stoichiometries and/or nitric acid may also occur. Fig. 2 confirms that, without exception, all six calixarene phosphine oxides are more efficient extractants for thorium(IV) than the acyclic phosphine oxides **6**, **7** and **8**. Within the dealkylated calixarene series, the order of efficiency is **5e** > **5f** > **5d**. The corresponding order in the *tert*-butyl series is **5b** > **5a** > **5c**. In general, the absence of a *p-tert*-butyl group significantly increases the extraction efficiency towards thorium(IV). Other trends can be discerned. For example, there is a greater spread of extraction efficiency in the *tert*-butyl series than in the dealkylated series. Similar investigations using europium(III) nitrate produced the conclusions summarised graphically in Fig. 3. For compound **5b**, extraction was measured at one ligand concentration only (log D = −0.58 at C_L = 2.5 × 10^{-2} mol dm^{-3}). The order of efficiency parallels that for Th^{IV}. Eu^{III} is less well extracted than Th^{IV}.

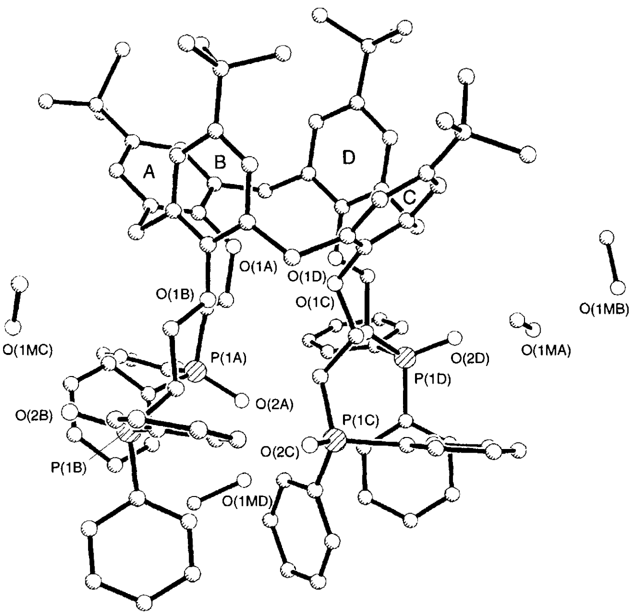


Fig. 1 A side view of **5a**. Phosphorus atoms are represented by shaded spheres.

Supported liquid membrane (SLM) technology was used to assess the efficacy of these phosphine oxides in extraction of ^{237}Np, ^{239}Pu, and ^{241}Am. Here, the source and receiving phases were separated by a microporous membrane impregnated with a solution of the extractant in a very lipophilic diluent (1,2-nitrophenyl hexyl ether, NPHE). The choice of NPHE as solvent is due to its very low solubility in water and its relatively high dielectric constant which favours the extraction of cations and anions through better solvation. The source solution, 1 mol dm^{-3} in HNO$_3$ and 4 mol dm^{-3} in NaNO$_3$ to simulate nuclear waste conditions, contained one of the actinide radionuclides ^{237}Np, ^{239}Pu or ^{241}Am. The stripping phase was an aqueous solution of a standard complexing agent of the actinides, sodium citrate or methylenediphosphonic acid. Table 1 contains the distribution coefficients D of the three nuclides between the source phase and solutions of calixarenes **5a–d**, **5f** and CMPO **8** in NPHE. It is clear that, among the alkylated oligomers, hexamer **5b** is the best extractant for all three nuclides. However, the performance does depend on the nature of the upper rim substituent. Because of insufficient solubility, **5d** was studied at a concentration of 10^{-3} instead of 10^{-2} mol dm^{-3}. This compound seems more effective than the previous derivatives, particularly for plutonium extraction. But a very strong improvement is obtained with the dealkylated compound **5f**, particularly for americium, its distribution coefficient being by far greater than that for CMPO. The data for Pu^{IV} and Am^{III} can be compared with the earlier data of Fig. 2, *i.e.* the D values for extraction of Th^{IV} and Eu^{III} into CH$_2$Cl$_2$, where the same order of decreasing extraction efficiency is found in both series, with the exception of one inversion between **5a** and **5c**.

The permeability P_{strip} of the membrane, is according to Danesi's transport model [eqn. (1)] where C = activity of

$$\ln[1 - (C/C_0)] = \varepsilon SPt/V \qquad (1)$$

the radionuclide in the strip solution at time t (Bq cm^{-3}); C_0 = initial activity of the radionuclide in the feed solution

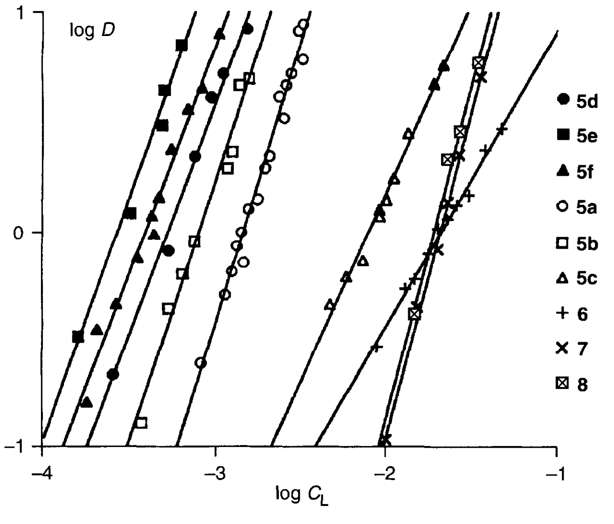


Fig. 2 Log D *vs.* log of ligand concentration C_L for the extraction of thorium(IV) from an aqueous thorium nitrate aqueous solution (10^{-4} mol dm^{-3}) in the presence of 1 mol dm^{-3} HNO$_3$ into dichloromethane at 20 °C.

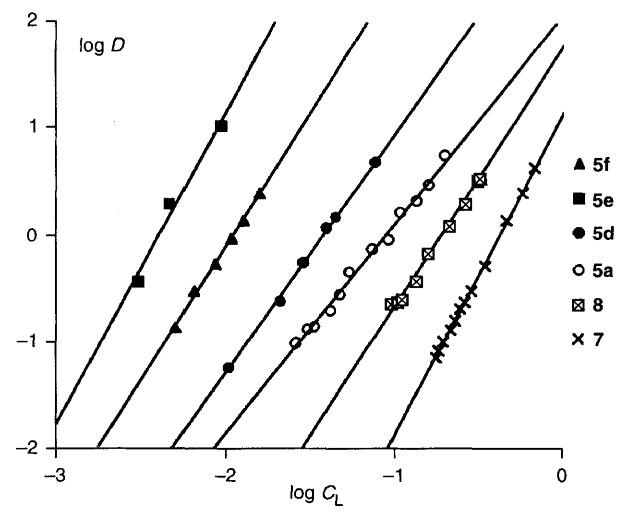


Fig. 3 Log D *vs.* log of ligand concentration C_L for the extraction of europium(III) from an aqueous europium nitrate aqueous solution (10^{-4} mol dm^{-3}) in the presence of 1 mol dm^{-3} HNO$_3$ into dichloromethane at 20 °C.

(Bq cm^{-3}); ε = volume porosity of the SLM; S = membrane surface area; V = volume of source solution; P = permeability (cm h^{-1}). The values of P_{strip} in Table 1 indicate, here also, that hexamer phosphine oxide **5b** is the best *p*-alkylated extractant for Np and Pu. But, as with the earlier liquid–liquid extraction experiments, the best compound overall is the *p*-dealkylated **5f** for which P_{strip} is comparable to that obtained with CMPO **8**.

Table 1 Distribution coefficients d of Np, Pu and Am between an aqueous phase 4 mol dm^{-3} in $NaNO_3$ and 1 mol dm^{-3} in HNO_3 and a solution of selected compounds in NPHE, and, in italics, permeability of the membrane (P_{strip}) in cm h^{-1}

Compound (0.01 mol dm^{-3} in NPHE)	^{237}Np	^{239}Pu	^{241}Am
5a[a]	1.5	22.0	0.0
	0.318	*1.92*	
5b[b]	9.2	63.5	4.0
	1.09	*2.52*	No transport
5c[b]	6.0	31.0	0.09
	0.53	*0.20*	No transport
5d[b]	1.3	24.0	0.2
	—	*1.27*	—
5f[a,b]	18.0	> 100	76.0
	0.86	*3.38*	*0.16*
8	0.85	22	1.2
	0.74	*3.44*	*0.17*

[a] Sodium citrate (0.25 mol dm^{-3}). [b] Methylene diphosphonic acid (1 mol dm^{-3}).

The low Am transfer through the membrane, even with calixarenes displaying a high D, is undoubtedly due to difficulties in stripping the actinides; even with methylenediphosphonic acid the transport rate is very low.

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Footnotes

† All new compounds showed spectroscopic and analytical data in agreement with assigned structures.

‡ *Crystal data* for **5a**: $C_{100}H_{108}O_8P_4 \cdot 4CH_3OH$, M_w 1688.8, triclinic, space group $P\bar{1}$, a = 15.725(2), b = 15.908(2), c = 20.063(3) Å, α = 79.25(1), β = 75.71(1), γ = 80.25(1)°, U = 4738(2) Å^3, Z = 2, λ (Mo-Kα) = 0.71073 Å, D_c = 1.18 g cm^{-3}, F(000) = 1808. The structure was solved by direct methods and refined by least squares to R = 0.064 for 8787 reflections measured on a Siemens P4 diffractometer at 123 K. Atomic coordinates, bond lengths and angles, and thermal parameters for **5a** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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