Novel Ligands for the Separation of Trivalent Lanthanides and Actinides – Tetrakis(phosphane sulfide) and -(phosphinic acid) Cavitands

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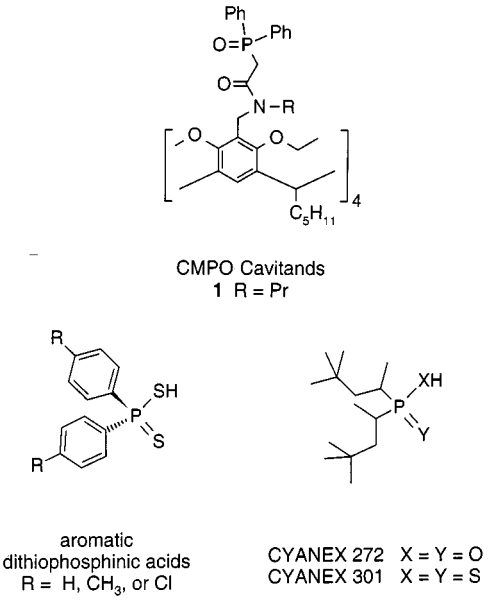
Cavitands with phosphane sulfide moieties **4** and **8a**,**b** were prepared in good yields from their phosphane oxide analogues, as more stable alternatives for the dithiophosphinic acids used at present. The cavitands **7a** and **7b** with flexible butoxyphosphane oxide ligating sites are more efficient than cavitand **3** having rigid methylphosphane oxide groups as was studied with Eu^{III} picrate extractions. Due to the absence of an ionic functionality in the phosphane sulfides **4** and **8a**,**b** Am^{III} and Eu^{III} are not extracted, not even in the presence of synergents (e.g. TBP, TOPO, HDNNS). Cavitand **10** with phosphinic acid groups efficiently extracts Eu^{III} in 1:1 or 2:1 complexes, depending on the metal-to-ligand concentration ratio (extraction constants $K_{ex}{}^1 = 3.9 \cdot 10^{-5}$ M^2 and $K_{ex}{}^2 = 1.9 \cdot 10^2$ M, respectively). Furthermore, in the case of **10** Eu^{III} is preferentially extracted over Am^{III} with a separation factor $S_{Eu/Am}$ up to 5.

Introduction

At present time, nearly all commercial nuclear fission plants are using uranium as their basic fuel. After burn-up the spent fuel is reprocessed in the PUREX (*P*lutonium *UR*anium *EX*traction) process to recover the uranium and plutonium.[1] The removal of the transplutonium actinides from liquid waste streams generated in the PUREX process, and their separation of the lanthanide fission products, is necessary to allow differentation in the radioactive wastes, and the subsequent handling, treatment, and storage.

Previously, we described the synthesis and extraction properties of CMP(O) and phosphoryl cavitands.[2,3] These ligands, and especially CMPO-based ligand **1** (Scheme 1), are very effective extractants for the removal of trivalent actinides and lanthanides from solutions simulating nuclear-waste conditions.[4] However, this (type of) ligand(s) does not show selectivity for the actinide element americium over the lanthanides, e.g. europium. To date, the most selective extractants for actinide/lanthanide separation are dithiophosphinic acids (the major component of the commercial CYANEX 301 extractant[5]). These sulfur donor atoms containing ligands (Scheme 1) are capable of efficiently extracting Am with selectivities ($S_{Am/Ln}$) of up to 4500 over the lanthanides. The disadvantage of these extractants with P(S)SH functionalities is their sensitivity for oxidative degradation, resulting in side products that rapidly diminish the selectivity, viz. formation of P(S)OH and P(O)OH compounds.[6,7] In the light of these counter-acting properties of the dithiophosphinic acid extractants, it would be desirable to develop more stable extractants with similar extraction abilities.



Scheme 1. CMPO cavitand **1**, aromatic dithiophosphinic acids, and CYANEX extractants

The advantage of phosphane sulfides over dithio acids is the higher stability under various conditions. However, the extraction efficiency of dithio extractant CYANEX 301 is significantly lower than of its phosphinic acid analogue (e.g. CYANEX 272)[8] because of the "softer" character of the donor atoms (sulfur vs. oxygen).[9,10] In the same line phosphane sulfides (e.g. CYANEX 471X[11]) will be even weaker extractants as they contain only one P–S donor site and lack the additional ionic interactions of the dithiophosphinic acid functionality. The strength of complexation decreases in the order of $R_2P(O)O^- > R_2P(S)S^- > R_3P(S)$. However, lower extraction *efficiencies* are no obstacle when high extraction *selectivities* can be consolidated.

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In this paper the results are described of a study on cavitands with phosphane sulfide functionalities as a possible alternative for the dithiophosphinic acid extractants (e.g. CYANEX 301). By preorganization of four phosphane sulfides on a cavitand template the complexation strength might be sufficient to selectively extract Am^{III} over the Ln^{III}s. First, the influence of the flexibility of the ligating sites was studied with the phosphane oxide precursors of the sulfides. Subsequently, the effect of the presence of (an)ionic ligating sites was studied with a tetrakis(phosphinic acid) cavitand.

Results and Discussion

Phosphane Sulfide Cavitand

A cavitand with phosphane sulfide functionalities was prepared straightforwardly from tetrakis(phosphane oxide) cavitand **3** which was prepared from the well-known tetrakis(bromomethyl) cavitand **2**.[2] Reaction of cavitand **3** with Lawesson's reagent[12] in refluxing toluene afforded tetrakis(diphenylmethylphosphane sulfide) cavitand **4** in 42% yield (Scheme 2). In contrast to the CMP(O) and phosphoryl cavitands the phosphane sulfide **4** could easily be purified with standard silica-gel column chromatography.[2] The formation of the phosphane sulfide **4** followed from the characteristic ^{1}H-NMR signals for tetrasubstituted cavitands: singlets for the aromatic (H_p) and benzylic hydrogen atoms (H_b) and doublets for the outer (H_o) and inner bridge hydrogen atoms (H_i). The introduction of the sulfur atom induced a downfield shift for the benzylic proton (H_b) signal from δ = 3.46 to 3.74 ($^2J_{PH}$ = 14.5 Hz) and a ^{31}P-NMR shift from δ = 29.36 to 41.71.

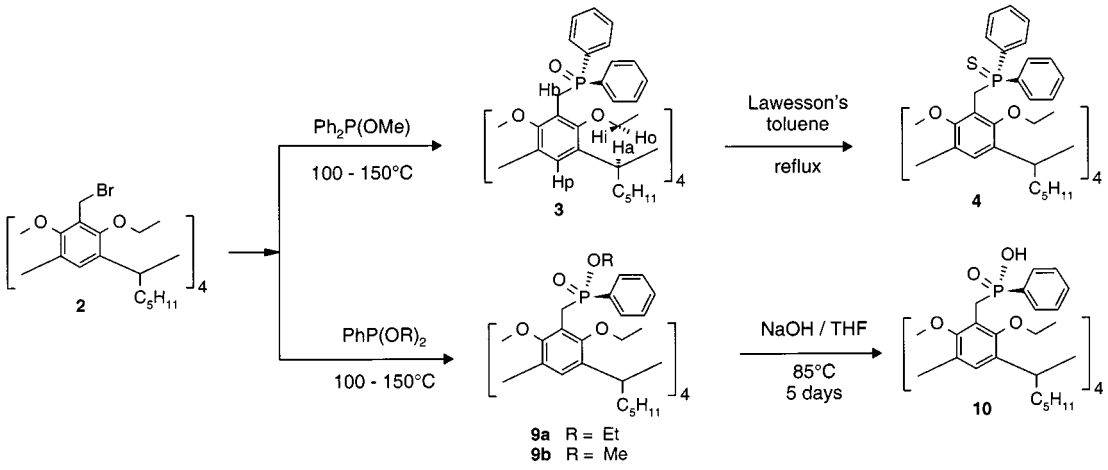
Flexible Phosphane Sulfides

In cavitand **4** the functional phosphane sulfide moieties are rigidly attached to the cavitand template via methylene ($-CH_2-$) spacers. The synthesis of cavitands with phosphane sulfide moieties attached to the cavitand template with a prolonged spacer starts from the hydroxy cavitands **5a**,**b** (Scheme 3). Tetrol **5a** was prepared according to literature procedures[13][14] and in the synthesis of **5a** the analogous cavitand with three hydroxy groups (cavitand **5b**) is generally formed as a by-product in varying yields (approximately 5−20%).

The tetra- and trihydroxy cavitands **5a** and **5b** were treated with a large excess of 1,4-dibromobutane in the presence of also large excesses of K_2CO_3 and NaI to give the corresponding tetrakis- and tris(bromobutoxy) cavitands **6a** and **6b** in 83 and 92% yield, respectively (Scheme 3). The ^{1}H-NMR spectrum of the tetrasubstituted cavitand **6a** exhibits one singlet at δ = 6.77 for the aromatic hydrogen atoms (H_p) and doublets for both the outer (H_o) and inner bridge hydrogen atoms (H_i) at δ = 5.78 and 4.35, respectively. The trisubstituted cavitand **6b** can be clearly distinguished by the three signals in the aromatic region, viz. at δ = 7.03, 6.79, and 6.59 with a ratio of 1:3:1. Furthermore, due to the lower degree of symmetry, the spectrum shows two doublets for the inner bridge hydrogen atoms (H_i).

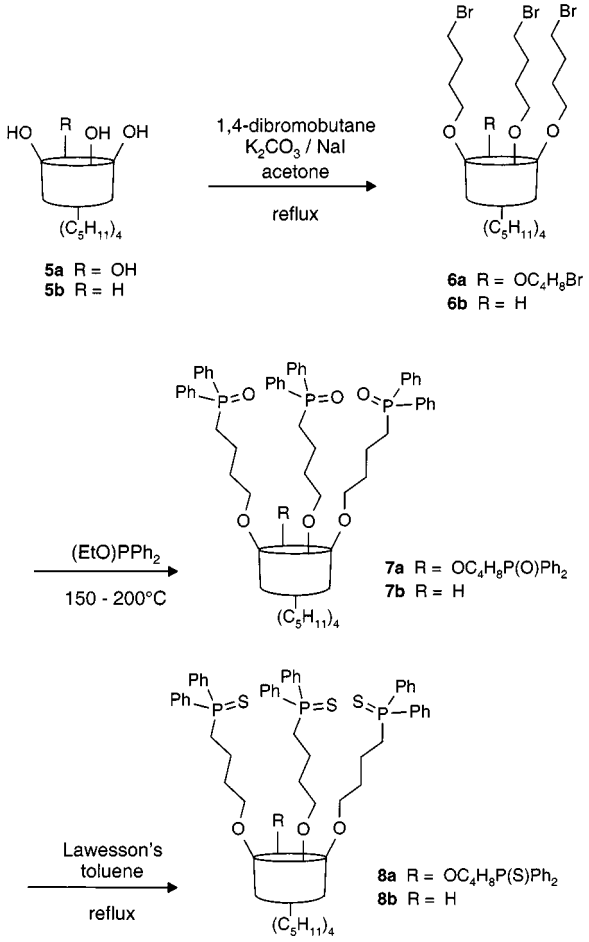
Arbusov reaction[15] of cavitand **6a** with ethyl diphenylphosphinite gave tetrakis(butoxydiphenylphosphane oxide) cavitand **7a** in 93% yield.[16,17] In the case of cavitand **6b** the corresponding tris(butoxydiphenylphosphane oxide) cavitand **7b** was obtained in 96% yield. Although the reactions are similar as in the synthesis of the diphenyl-CMPO and phosphoryl cavitands (e.g. cavitands **1** and **3**),[2] some important variations in the Arbusov reaction conditions were necessary. In order to prevent decomposition, the reactions with the bromobutoxy cavitands required higher temperatures (150−200°C), *ethyl* diphenylphosphinite as Arbusov reagent, and a reaction time of no longer than 10 min.

The synthesis of the flexible phosphane sulfides was performed similarly to that of **4**. Reaction of (butoxydiphenylphosphane oxide) cavitands **7a** and **7b** with Lawesson's reagent in refluxing toluene afforded tetrakis(butoxydiphenylphosphane sulfide) cavitand **8a** and tris(butoxydiphenylphosphane sulfide) cavitand **8b** in 95 and 81% yield,



Scheme 2. Synthesis of phosphane sulfide and phosphinic acid cavitands

respectively. The completion of the substitution reaction followed from the disappearance in the ^{31}P-NMR spectra of **7a** and **7b** of the phosphorus P=O signals at δ = 32.14 and 32.2, respectively. Due to the introduction of the sulfur atom the signals shifted downfield to δ = 40.44 and 42.55, respectively. In contrast to the dithiophosphinic acids,[6,7] the phosphane sulfide cavitands are very stable.[18] Also after γ radiation of a solid sample of cavitand **4** no decomposition was observed.[19]



Scheme 3. Synthesis of alkylphosphane oxide and sulfide cavitands

Phosphinic Acid Cavitand

A cavitand with four phosphinic acid moieties[20] was prepared starting from bromomethyl cavitand **2** in two steps (Scheme 2). The literature procedure for the Arbusov reaction (temperature 100−150°C and reaction time 20 min)[2] on bromomethyl cavitand **2** with diethyl phenylphosphonite afforded tetrakis(ethyl phenylmethylphosphinate) cavitand **9a** in 47% yield. The corresponding reaction with *dimethyl* phenylphosphonite afforded tetrakis(methyl phenylmethylphosphinate) cavitand **9b** in 94% yield. Treatment of the methyl phosphinate cavitand **9b** with NaOH[20,21] in THF at 85°C gave the tetrakis(phenylmethylphosphinic acid) cavitand **10** in 81% yield. The hydrolysis only reached completion after five days, whereas the corresponding ethyl phosphinate **9a** did not hydrolyse under these conditions.[22] The acid **10** was purified by converting it into its ammonium salt, washing it with CH_2Cl_2 and subsequently acidifying it to recover the free acid.

The ^{1}H-NMR spectra in $CDCl_3$ of **9a** and **9b** are very complicated and show multiple signals for all the cavitand signals.[2,23] The ^{1}H-NMR spectrum of acid **10** in $CDCl_3$ is broad and shows a similar multiplicity of all signals, probably due to (intermolecular) association or slow rotation of the benzylic substituents. However, when recorded in more polar solvents (e.g. [D$_6$]DMSO; [D$_6$]acetone/CD$_3$OD, 6:1) the spectra sharpen and exhibit all characteristic signals for tetrasubstituted cavitands.

Extractions with Phosphane Oxides

To study the influence of the prolonged spacer between the cavitand frame and the phosphoryl functionality picrate (= 2,4,6-trinitrophenolate) extractions were performed with the alkylphosphane oxide cavitands **7a** and **7b**. The europium(III) extraction properties were compared with the data of cavitand **3**.[2] The extraction procedure followed and the calculation of the extraction coefficients (K_{ex}) for the 1:1 complexes are described in earlier papers.[2,24]

In Figure 1 the relations between the distribution ratios (logD_{Eu}) and the initial ligand concentrations (log[L]$_{o,i}$) are linear in the region with excess cation over ligand ([L]$_{o,i}$ < [Eu]$_{w,i}$ = 10^{-4} M). At higher (initial) ligand concentration the variations of logD_{Eu} as a function of log[L]$_{o,i}$ are larger. This may be attributed to changes in the stoichiometry of the predominantly extracted complexes from 1:1 to 2:1 ligand-to-cation ratio. The butoxyphosphane oxide extractants **7a** and **7b** both reach a maximum extraction (distribution) comparable with the CMPO cavitands.[2]

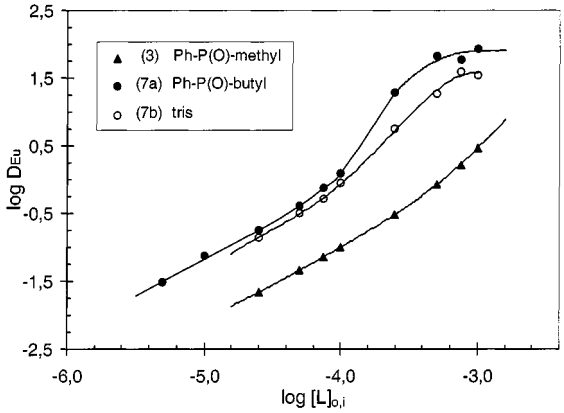


Figure 1. Plots of logD_{Eu} vs. log[L]$_{o,i}$; [Eu^{3+}]$_{w,i}$ = 10^{-4} M, [LiPic]$_w$ = 10^{-2} M, [HNO$_3$]$_w$ = 10^{-3} M; pH = 3.0

The K_{ex} values for the 1:1 complexes of the ligands **7a** and **7b** with Eu(picrate)$_3$ are $2.8\cdot10^{10}$ and $1.7\cdot10^{10}$ M^{-4}, respectively, and for phosphane oxide **3** a K_{ex} value of $1.1\cdot10^{9}$ M^{-4} was found.[2] The large difference in the K_{ex} values of both tetrakis(phosphane oxide) cavitands **3** and **7a** is striking (25 times lower). The rigid positioning of the

phosphane oxide groups in **3** obviously does not allow an optimal complexation ("geometrical fit") of the europium cation. The (small) difference between the K_{ex} values of the tetra- and trisubstituted cavitands **7a** and **7b** (1.6 times higher for **7a**) is similar to that found for the tetra- and trisubstituted CMPO cavitands (with R = H).[24]

The extraction constant of **7a** is only 1.3 times lower than that of the tetrakis(diphenyl-*N*-methylcarbamoylmethylphosphane oxide) cavitand (viz. $3.7 \cdot 10^{10}$ M^{-4}),[2] indicating that bidentate extraction behavior is not an important factor in complexations with the latter compound. The comparable properties of a CMPO cavitand (R = H) and phosphane oxide **7a** are in agreement with Am^{III} extraction results from (non-acidic) $LiNO_3$ solutions with the "simple" bidentate dihexyl-*N*,*N*-diethyl-CMPO and the monofunctional TOPO.[25]

Extractions with Phosphane Sulfides

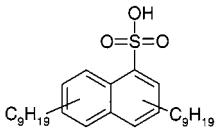
In similar picrate extraction experiments with phosphane sulfide cavitands **4** and **8a** Eu^{III} was not extracted. This result was expected as cavitands **4** and **8a** are designed to be selective for trivalent actinides over lanthanides. In extraction experiments with cavitand **4** and *tracer* concentrations ($< 10^{-6}$ M) of Am^{III} and Eu^{III} both elements were extracted with average distribution ratios of $D = 0.032$ and 0.018, respectively, while with ligand **8a** both Am^{III} and Eu^{III} were not extracted ($D < 10^{-3}$). The extraction of Am^{III} and Eu^{III} may be attributed to the large excess of ligand, however, the separation factor $S_{Am/Eu}$ of 1.7 is very poor. The difference between **4** and **8a** might be the decreased rigidity in **8a** compared to **4** and thus weaker preorganization. Furthermore, no extraction was measured in experiments with cavitand **4** or **8a** from nitrate (4 M $LiNO_3$ and 0.1 M HNO_3) and perchlorate (4 M $LiClO_4$ and 0.1 M $HClO_4$) aqueous solutions.

Synergents

From the literature it is known that the addition of a so-called *synergent* to an extraction system can increase the extraction efficiency and/or the selectivity of the separation.[9,10,26] Especially, tributylphosphate (TBP), and tri-*n*-octylphosphane oxide (TOPO) are frequently used as synergents. Using mixtures of cavitand **4** or **8a** and TBP in CH_2Cl_2 did not result in extraction of Am^{III} or Eu^{III} from aqueous solutions with various compositions (e.g. varying the anion, the salt concentration, and/or pH). A mixture of cavitand **4** ($5 \cdot 10^{-4}$ M) and TOPO (10^{-3} M) in CH_2Cl_2 extracted both Am^{III} and Eu^{III} with distribution ratios of $D = 0.055$ and 0.051, respectively ($S_{Am/Eu} = 1.1$). Under these conditions with 10^{-4} M cavitand **8a** distribution ratios of $D = 0.38$ and 0.32 were found for Am^{III} and Eu^{III}, respectively ($S_{Am/Eu} = 1.2$). The higher distribution for phosphane sulfide **8a** compared to **4** is in agreement with the differences found for the Eu^{III} extraction of their phosphane oxide analogues **7a** and **3** (vide supra). These effects cannot solely be attributed to the extracting ability of TOPO, so the phosphane sulfide cavitands do play a role in the extraction. However, the lack of any significant selectivity of the extraction of Am^{III} over Eu^{III} suggests the absence of the phosphane sulfide extractants in the *"first"* or *"inner"* coordination sphere.

Dinonylnaphthalenesulfonic Acid (HDNNS)[27]

With the phosphane sulfides **4** and **8a** Am^{III} and Eu^{III} are not significantly extracted, even in the presence of synergents. This indicates that the acid function in CYANEX 301 is essential to achieve extraction, viz. the extraction follows a proton-exchange mechanism and the ligand associates with the cation via an interaction with an ionic character.[28] The phosphane sulfides associate via ion-dipole interactions and have to extract the cation accompanied by its counter anion(s).[9b] In order to study the influence of the proton-exchange mechanism an ionic synergent was used, viz. HDNNS (Scheme 4). The sulfonic acid HDNNS is an organic acid and can facilitate the extraction of the cations to the organic phase by proton exchange. The cation might then be complexed by a ligand which is not strong enough to extract the salt itself.



Scheme 4. HDNNS (isomere mixture)

"Synergistic" mixtures of HDNNS ($5 \cdot 10^{-3}$ M) and cavitands **4** or **8a** ($5 \cdot 10^{-4}$ M) extracted Am^{III} and Eu^{III} from $NaNO_3$ solutions (pH $\approx$ 3.2) with distribution ratios in the order of $D = 0.7$. However, performing the same extractions with only HDNNS in the absence of a cavitand ligand resulted in comparable distribution ratios. Therefore, the (non-selective) extraction of Am^{III} and Eu^{III} can solely be attributed to the extracting ability of HDNNS itself.

Extractions with Phosphinic Acid

From comparison of the experiments with the phosphane sulfide cavitands **4** and **8a** and the reported properties of CYANEX 301[6,7,28] it is clear that ionic interactions are essential for extractions with the sulfur-containing ligands. In order to obtain insight into the behavior of a cavitand-based ligand with four anionic ligating sites, the extraction properties of tetraphosphinic acid **10** were studied. The extraction of Eu^{III} with cavitand **10** is based on the exchange of three of its protons for an Eu^{III} cation. This is in contrast to the CMP(O) cavitands that are neutral ligands and complex Eu^{III} with ion-dipole interactions. The equilibrium for the extraction of an Eu^{III} cation with tetraacid ligand **10** is then described by the general Equation 1. For tetraacid ligand **10** (H_4L) is used and the assumption is made that the partition of the ligand to the aqueous phase is negligible ($[H_4L]_w \approx 0$).

$$[Eu^{3+}]_w + p \times [H_4L]_o \rightleftharpoons [Eu{\cdot}HL{\cdot}(H_4L)_{p-1}]_o + 3 \times [H^+]_w \quad (1)$$

For "simple" phosphinic acids [$R^1R^2P(O)OH$ or HL*] it is known that they associate and form aggregates in (non-polar) solutions. In extractions they are generally assumed to be present as dimers, viz. $(HL^*)_2$.[29] In relation to this it is possible that at higher concentrations in CH_2Cl_2 tetrakis(phosphinic acid) cavitand H_4L is (to some extent) present as the $(H_4L)_2$ dimer. However, from the extraction experiments no proof was obtained for this association in the concentration range studied (vide infra).

$NaNO_3$ and H^+ Concentrations

From the extraction mechanism in Equation 1 it follows that the extraction should be insensitive to the presence (and concentration) of a salting agent. Furthermore, the pH of the aqueous phase should have a large influence on the extraction. To confirm this mechanism the possible influence was studied of the presence of $NaNO_3$ on the extraction with acid **10**. From Figure 2 it follows that at $[H^+] = 10^{-3}$ M $\log D_{Eu}$ is nearly insensitive to the presence of $NaNO_3$ in the concentration range of 0−4 M. At increasing concentration the extraction increases slightly, but this may

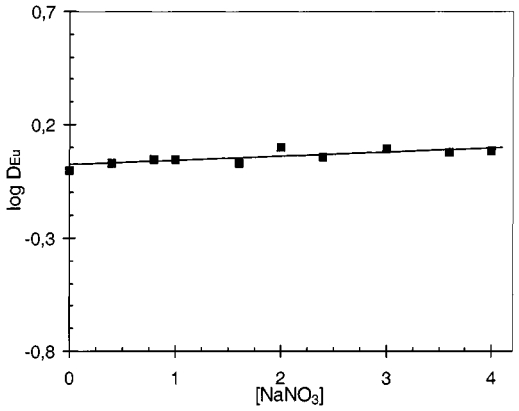


Figure 2. Dependency on $NaNO_3$ concentration; plot of $\log D_{Eu}$ vs. $[NaNO_3]$; $[\mathbf{10}]_{o,i} = 10^{-4}$ M in CH_2Cl_2, $[Eu^{3+}]_{w,i} = 10^{-4}$ M, $[H^+] = 10^{-3}$ M

be attributed to the salting-out effect of saline solutions.[30]

An $NaNO_3$ concentration of 0.5 M was chosen to perform the experiments at varying H^+ concentration. The plot in Figure 3 shows that the $\log D_{Eu}$ remains fairly constant at $[H^+] < 10^{-3}$ M but at higher concentrations the extraction decreases rapidly on account of the unfavorable deprotonation of the phoshinic acid moieties, necessary to complex the Eu^{III} cation. Further experiments were performed with $[H^+] = 10^{-3}$ M, comparable to the picrate extractions (vide supra).

Extraction Constants

The dependency of the extraction on the ligand concentration was studied from aqueous phases both in the presence and the absence of 0.5 M $NaNO_3$ as salting agent, while

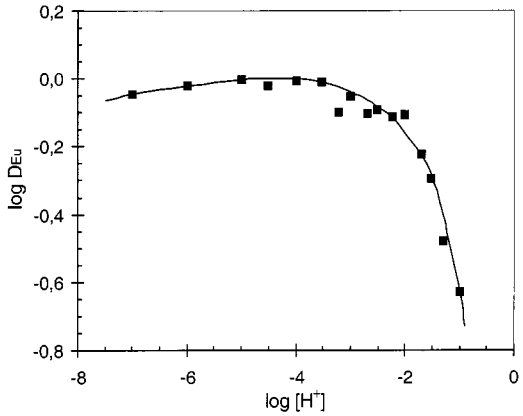


Figure 3. Dependency on H^+ concentration; plots of $\log D_{Eu}$ vs. $\log[H^+]$; $[\mathbf{10}]_{o,i} = 10^{-4}$ M in CH_2Cl_2, $[Eu^{3+}]_{w,i} = 10^{-4}$ M, $[NaNO_3] = 0.5$ M

the H^+ concentration was kept at 10^{-3} M. From the plot of $\log D_{Eu}$ vs. $\log[L]_{o,i}$ in Figure 4 it follows that the presence of a salting agent has no effect on the extraction, which is in agreement with the previously obtained results.

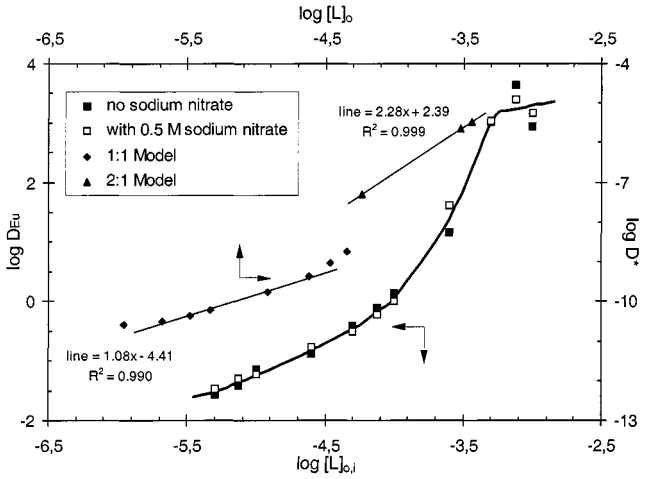


Figure 4. Dependency of $\log D_{Eu}$ on $\log[L]_{o,i}$ and $\log D^*$ on $\log[L]_o$; ligand **10** in CH_2Cl_2, $[NaNO_3] = 0$ or 0.5 M, $[H^+]_{w,i} = 10^{-3}$ M, $[Eu^{3+}]_{w,i} = 10^{-4}$ M

In the plot two regions can be distinguished with different slopes, while at higher [L] a maximum is reached corresponding to quantitative extraction (> 99.8%). The region at $\log[L]_{o,i} < -4$ corresponds to the situation of excess metal over ligand which results in the formation of 1:1 complexes ($p = 1$ in Equation 1). While in the region of $\log[L]_{o,i} > -4$ the presence of an excess ligand allows the formation of 2:1 complexes (ligand-to-metal ratio; $p = 2$). The general expression for the extraction constants K_{ex} for the 1:1 and 2:1 complexes is given by Equation 2.

$$K^p_{ex} = \frac{[Eu{\cdot}HL{\cdot}(H_4L)_{p-1}]_o \times [H^+]^3_w}{[Eu^{3+}]_w \times [H_4L]^p_o} \quad (2)$$

The distribution coefficient D_{Eu} is defined as the ratio of the metal concentration in the organic and in the aqueous phase, viz. $D_{Eu} = \Sigma(M)_o/\Sigma(M)_w$. Under the conditions that only one complex (p:1 stoichiometry, ligand-to-metal ratio)

is present and Eu^{3+} is unassociated in the aqueous phase (thus neglecting $[EuNO_3]^{2+}$ and $[Eu(NO_3)_2]^{+}$ species), the distribution coefficient D_{Eu} for the p:1 complexation is then expressed by $[Eu{\cdot}HL{\cdot}(H_4L)_{p-1}]_o/[Eu^{3+}]_w$. Substitution of D_{Eu} in Equation 2 gives Equation 3 in which the dependency of the $logD^*$ is described as a function of the K^p_{ex} and the concentration of the ligand (logD* is introduced for simplicity).

$$\log D = \log D_{Eu} + 3 \times \log [H^+]_w = \log K^p_{ex} + p \times \log[H_4L]_o \quad (3)$$

A plot of $\log D^*$ vs. $\log[H_4L]_o$ should be linear with a slope of p; where p indicates the number of ligand molecules involved per cation in the extracted species. The intercept of the plots with the $\log D^*$ axis is equal to $\log K^p_{ex}$, which allows the determination of the value of the extraction coefficient by slope analysis.

The equilibrium $[H^+]_w$ and $[H_4L]_o$ concentrations could be calculated from the mass balances under the previously given assumptions. In Figure 4 the plots of $\log D^*$ vs. $\log[H_4L]_o$ for both regions are plotted. From the slopes of the plots it is clear that the regions indeed correspond to situations of 1:1 and 2:1 complexation with $[L]_{o,i} < 10^{-4}$ M and $[L]_{o,i} > 10^{-4}$ M, respectively. The slope in the 2:1 region is slightly higher than expected (viz. 2.28), however, this may be attributed to the small number of points in the graph. From the values of the intercepts the values of the constants for the extraction of Eu^{III} with ligand **10** in CH_2Cl_2 were calculated to be $K^1_{ex} = 3.9{\cdot}10^{-5}$ M^2 and $K^2_{ex} = 1.9{\cdot}10^2$ M.

Am^{III}/Eu^{III} Separation

Phosphinic acid derivatives extract both the lanthanides [e.g. Eu^{III}] and the trivalent actinides, however, with a small preference for the lanthanides.[8] This is also the reason of the rapidly diminishing selectivity upon degradation of the dithiophosphinic acids, as compounds with P(S)OH and P(O)OH functionalities are the most important degradation products.[6,7] In Figure 5 the extraction of tracer concentrations Am^{III} and Eu^{III} with phosphinic acid cavitand **10** at variable $[HNO_3]$ is shown. At low acid concentrations ($\log[H^+] < -2$) both elements are quantitatively extracted (> 99.5%) but at higher H^+ concentrations Eu^{III} is preferentially extracted with a separation factor of $S_{Eu/Am}$ up to 5. The Eu/Am selectivity of **10** is comparable to extractions with CYANEX 272 (12.5 wt-% in *n*-dodecane[7] or 1 M in kerosene[8]) from 1 M $NaNO_3$, however, the extraction with CYANEX 272 under these conditions is 12 times lower than with 10^{-4} M **10** in CH_2Cl_2 at $\log[H^+] = -1.5$ M.[7,8]

Conclusions

Ligands with phosphane oxide moieties attached to the cavitand template via butoxy spacers were prepared in two steps from the hydroxy cavitands **5a** and **5b** in good overall yields (77 and 88% for **7a** and **7b**, respectively). The influence of the spacer length and the flexibility of the ligating sites was studied in Eu^{III} picrate extractions with extractants **3** and **7a**, **b**. The cavitands with the flexible butoxyphosphane oxide ligating sites (**7a** and **7b**) are more efficient than cavitand **1** having more rigid methylphosphane oxide groups.

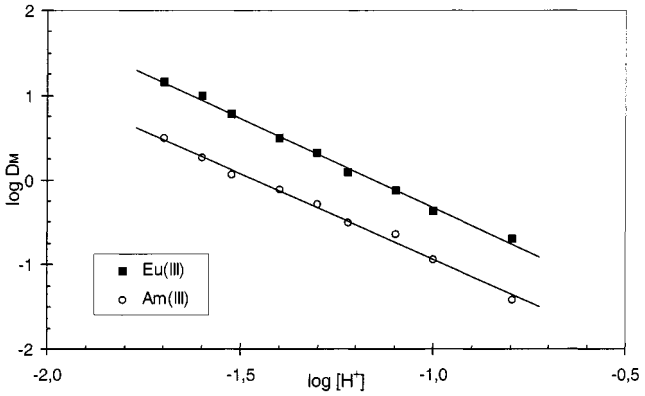


Figure 5. Dependency on the HNO_3 concentration of the Eu^{III} and Am^{III} extraction; ligand $[\mathbf{10}]_{o,i} = 10^{-4}$ M in CH_2Cl_2, tracer Am^{III} and Eu^{III}, variable $[HNO_3]$, $[NaNO_3] = 0.5$ M

Corresponding cavitands with phosphane sulfide (**4**, **8a**, and **8b**) moieties were synthesized in good yields from the phosphane oxides. These ligands were prepared as (more stable) alternatives for CYANEX 301. However, the phosphane sulfides did not extract Am^{III} or Eu^{III}, not even in the presence of synergents (e.g. TPB, TOPO). This indicates that ionic interactions are essential for the application of sulfur-containing extractants. However, the addition of the organic acid HDNNS to facilitate the complexation did not result in significant extraction.

The tetraphosphinic acid cavitand **10** was prepared in two steps from bromomethyl cavitand **2** and extracts Eu^{III} by a proton-exchange mechanism (by ionic interactions). Ligand **10** very distinctly extracts Eu^{III} in 2:1 complexes when excess ligand is present and in 1:1 complexes when excess metal is present. With cavitand **10**, compared to its "simple" dialkyl analogue CYANEX 272, similar extraction efficiencies are established with ca. 10^3 times lower extractant concentration (although in CH_2Cl_2 vs. in the less polar dodecane). The selectivity for Eu^{III} over Am^{III} remains of the same order ($S_{Eu/Am} = 5$).

Our results clearly show that preorganization of ligating sites on a rigid cavitand platform increases the extraction efficiencies significantly. Unfortunately, preorganization does not afford suitable extractants for Am^{III} in the case of the tetrakis(phosphane sulfide) cavitands. The extraction properties of the phosphinic acid cavitand **10** are an indication that a cavitand with four dithiophosphinic acid groups will have improved properties compared to the "simple" dialkyl and aromatic analogues.

Experimental Section

Syntheses: All reactions were carried out under argon, unless otherwise stated. Flash column chromatography was performed with

Merck silica gel 60 (0.040−0.063 mm, 230−400 mesh) and Sephadex column chromatography was performed using Pharmicia BioTech Sephadex LH-20. − Melting points (uncorrected): Reichert melting point apparatus. − (FAB) MS : Finnigan MAT 90 spectrometer with *m*-nitrobenzyl alcohol as a matrix. − NMR: Bruker AC 250 spectrometer (250 MHz and 62.5 MHz, respectively, for ^1H and ^{13}C) in $CDCl_3$ at ambient temperature, and the chemical shifts were expressed relative to $CDCl_3$ (δ = 7.26 and 76.91, respectively, for ^1H and ^{13}C NMR). Elemental analyses: Model 1106 Carlo Erba Strumentazione Elemental Analyzer; the presence of solvent molecules in the analytical samples was confirmed by ^1H-NMR spectroscopy. In the ^1H-NMR spectra the signals for the aromatic hydrogen atoms (H_p), the outer (H_o), and inner (H_i) bridge hydrogen atoms, and the methylene bridge (H_a) and benzylic hydrogen atoms (H_b) are specifically assigned. The signals for the pentyl side chains (CHCH_2, [CH_2]$_3$, and CH_3) are not assigned. For explanations of the symbols see the Schemes in the text.

Materials and Isotopes: The compounds **1**−**3**[2] and **5a**[13] were prepared according to literature procedures. TBP (Acros) and TOPO (Lancaster) are commercial products and used as received. Dinonylnaphthalenesulfonic acid (HDNNS)[27] was a kind gift from King Industries, Waddinxveen (The Netherlands). The ^{152}Eu radiotracer was prepared by neutron radiation of the corresponding carbonate in the ECN High Flux Reactor. The ^{241}Am and ^{152}Eu isotope tracer solution was used from ECN stocks and contained, in addition, small amounts of ^{144}Ce and ^{137}Cs isotopes.

General Procedure for the Lawesson-Type Reactions: The solution of the starting material and Lawesson′s reagent was refluxed in toluene overnight. Subsequently, the solvent was evaporated and the residue was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH, 100:0, and gradient to 98:2 when necessary).

Tetrakis(diphenylmethylphosphane sulfide) Cavitand 4: The general procedure for the Lawesson-type reaction was applied to (diphenylmethylphosphane oxide) cavitand **3** (263 mg, 157 μmol) and Lawesson′s reagent (0.39 g, 0.96 mmol) to afford 115 mg of **4** (42%), yellowish powder, m.p. 107−109°C (CH_2Cl_2). − ^1H NMR: δ = 7.85−7.75 and 7.5−7.35 (2 m, P-phenyl, 16 + 24 H), 6.77 (s, H_p, 4 H), 5.07 (d, *J* = 7.1 Hz, H_o, 4 H), 4.32 (t, *J* = 7.9 Hz, H_a, 4 H), 4.19 (d, *J* = 7.2 Hz, H_i, 4 H), 3.74 (d, $^2J_{PH}$ = 14.5 Hz, H_b, 8 H), 1.97 (q, *J* = 6.9 Hz, 8 H), 1.45−1.3 (m, 24 H), 0.93 (t, *J* = 6.5 Hz, 12 H). − ^{13}C NMR: δ = 153.4, 153.3 (Ar*C*OCH_2O), 137.5, 137.4 (Ar*C*CH), 133.6, 132.4−128.0 (P-phenyl), 119.8, 119.6, 119.0 (ArCH), 98.0 (OCH_2O), 36.8 (ArCHAr), 34.5 [CH_2P(S)]. − ^{31}P NMR: δ = 41.71. − MS; *m*/*z* (%): 1738.5 (100) [M^+]. − $C_{104}H_{108}O_8P_4S_4$·CH_2Cl_2 (1823.1): calcd. C 71.87, H 6.26, S 7.38; found C 71.44, H 6.56, S 7.02.

Trihydroxy Cavitand 5b: This compound is generally formed as a side-product in the synthesis of tetrahydroxy cavitand **5a** and isolated after flash column chromatography (SiO_2; EtOAc/hexanes, 70:30), general yield: 5−20%, white powder, m.p. 268−270°C (EtOAc/hexanes). − ^1H NMR: δ = 7.09 (s, free H_p, 1 H), 6.64 (s, H_p, 3 H), 6.51 (s, free ArH, 1 H), 5.94, 5.84 (2d, *J* = 7.0 Hz, H_o, 4 H), 4.70, 4.69 (2t, *J* = 8.0 Hz, H_a, 4 H), 4.44, 4.42 (2d, *J* = 7.0 Hz, H_i, 4 H), 2.2−2.15 (m, 8 H), 1.5−1.25 (m, 24 H), 0.91 (t, *J* = 6.4 Hz, 12 H). − ^{13}C NMR: δ = 154.8, 138.5, 138.4 (s, Ar*C*OCH_2O), 141.9 (s, ArCOH), 140.9 (s, Ar*C*CH), 121.3 [d, *p*-H-ArCH], 114.2 (d, free ArCH), 109.8 [d, *p*-HO-ArCH], 99.7 (t, OCH_2O), 36.8, 36.6 (d, ArCHAr). − MS; *m*/*z* (%): 864.8 (100) [M^+]. − $C_{52}H_{64}O_{11}$·H_2O (833.1): calcd. C 70.73, H 7.53; found C 70.91, H 7.71.

Tetrakis(bromobutoxy) Cavitand 6a: A solution of tetrahydroxy cavitand **5a** (2.3 g, 2.6 mmol), 1,4-dibromobutane (16 mL), potassium carbonate (9.5 g), and sodium iodide (2.5 g) in acetone (500 mL) was refluxed for 48 h. After evaporation of the solvent, the residual mixture and the excess 1,4-dibromobutane was redissolved in CH_2Cl_2 (100 mL) and the solution was washed with 1 M HCl (2 × 50 mL), H_2O (25 mL), and dried with $MgSO_4$. The solvent was removed, hexanes (50 mL) were added, and the solution was passed through a short silica-gel column and flushed with hexanes to remove the excess 1,4-dibromobutane. Flushing the column with CH_2Cl_2 provided the crude product which was recrystallized from CH_2Cl_2/MeOH to afford 2.19 g of **6a** (83%), white powder, m.p. 138°C (CH_2Cl_2/MeOH). − ^1H NMR: δ = 6.77 (s, H_p, 4 H), 5.78 (d, *J* = 7.1 Hz, H_o, 4 H), 4.67 (t, *J* = 8.0 Hz, H_a, 4 H), 4.35 (d, *J* = 7.2 Hz, H_i, 4 H), 3.92 (t, *J* = 5.9 Hz, OCH_2, 8 H), 3.49 (t, *J* = 6.7 Hz, CH_2Br, 8 H), 2.2−2.05 (m, 8 H), 2.04 (quint, *J* = 6.8 Hz, C$H_2$$CH_2$Br, 8 H), 1.85−1.7 [m, OCH_2CH_2, 8 H], 1.45−1.2 (m, 24 H), 0.91 (t, *J* = 6.9 Hz, 12 H). − MS; *m*/*z* (%): 1420.3 (100) [M^+]; calcd. for $C_{68}H_{92}Br_4O_{12}$ (1421.1).

Tris(bromobutoxy) Cavitand 6b: A solution of trihydroxy cavitand **5b** (0.25 g, 0.29 mmol), 1,4-dibromobutane (5 mL), potassium carbonate (2.0 g), and sodium iodide (0.15 g) in acetone (70 mL) was refluxed for 48 h. After evaporation of the solvent, the residual mixture and the excess 1,4-dibromobutane was redissolved in CH_2Cl_2 (50 mL) and the solution was washed with 1 M HCl (2 × 25 mL), H_2O (25 mL), and dried with $MgSO_4$. The solvent was removed, hexanes (50 mL) were added, and the solution was passed through a short silica-gel column and flushed with hexanes to remove the excess 1,4-dibromobutane. Flushing the column with CH_2Cl_2 afforded 337 mg of **6b** (92%), white powder which became a colorless oil upon standing under atmospheric pressure. − ^1H NMR: δ = 7.03 (s, free H_p, 1 H), 6.79 (s, H_p, 3 H), 6.59 (s, free ArH, 1 H), 5.79, 5.76 (2d, *J* = 7.2 Hz, H_o, 4 H), 4.68 (t, *J* = 7.3 Hz, H_a, 4 H), 4.40, 4.34 (2d, *J* = 7.2 Hz, H_i, 4 H), 3.93 (t, *J* = 6.9 Hz, OCH_2, 6 H), 3.49 (t, *J* = 5.3 Hz, CH_2Br, 6 H), 2.25−2.1 (m, 8 H), 2.04 (quint, *J* = 6.8 Hz, C$H_2$$CH_2$Br, 6 H), 1.79 (quint, *J* = 6.3 Hz, OCH_2CH_2, 6 H), 1.45−1.2 (m, 24 H), 0.91 (t, *J* = 6.9 Hz, 12 H). − ^{13}C NMR: δ = 154.9, 148.3, 148.2 (s, Ar*C*OCH_2O), 144.2 (s, Ar*C*CH), 139.0, 138.2 (s, ArCOH), 121.2 (d, *p*-H-ArCH), 113.9 (d, free ArCH), 109.8 (d, *p*-OCH_2-ArCH), 99.5 (t, OCH_2O), 72.5 (t, OCH_2), 37.0, 36.6 (d, ArCHAr). − MS; *m*/*z* (%): 1270.5 (100) [M^+]; calcd. for $C_{64}H_{85}Br_3O_{11}$ (1270.1).

General Procedure for the Arbusov Reactions: In an open flask the starting material was dissolved/suspended in a small amount of ethyl diphenylphosphinite while the temperature was gradually increased from 150°C to 200°C, at which temperature the mixture was stirred for 10 min. After cooling of the reaction mixture to room temp., the solution was subjected to column chromatography (Sephadex LH-20; MeOH/CH_2Cl_2, 1:1).

Tetrakis(butoxydiphenylphosphane oxide) Cavitand 7a: The general procedure for the Arbusov reaction was applied to (bromobutoxy) cavitand **6a** (119 mg, 85 μmol) and ethyl diphenylphosphinite (0.3 mL) to afford 0.15 g of **7a** (93%), white powder, m.p. 102−104°C (CH_2Cl_2/MeOH). − ^1H NMR: δ = 7.8−7.7 and 7.5−7.4 (2 m, P-phenyl, 16 + 24 H), 6.70 (s, H_p, 4 H), 5.53 (d, *J* = 7.2 Hz, H_o, 4 H), 4.60 (t, *J* = 7.8 Hz, H_a, 4 H), 4.18 (d, *J* = 7.2 Hz, H_i, 4 H), 3.9−3.8 (m, OCH_2, 8 H), 2.4−2.25 [m, CH_2P(O), 8 H], 2.2−2.05 (m, 8 H), 1.95−1.75 (m, OCH_2[CH_2]$_2$, 16 H), 1.4−1.2 (m, 24 H), 0.89 (t, *J* = 6.8 Hz, 12 H). − ^{13}C NMR: δ = 148.2 (s, Ar*C*OCH_2O), 144.2 (s, Ar*C*CH), 138.7 (s, ArCO), 133.8, 132.2−128.6 (P-phenyl), 114.0 (d, ArCH), 99.4 (t, OCH_2O), 72.8 (t, OCH_2), 36.9 (d, ArCHAr), 31.3 [CH_2P(O)]. − ^{31}P NMR: δ = 32.14. − MS; *m*/*z* (%): 1906.2 (100) [M^+]. − $C_{116}H_{132}O_{16}P_4$ (1906.2): calcd. C 73.09, H 6.98; found C 72.96, H 7.12.

Tris(butoxydiphenylphosphane oxide) Cavitand 7b: The general procedure for the Arbusov reaction was applied to tris(bromobutoxy) cavitand **6b** (437 mg, 0.34 mmol) and ethyl diphenylphosphinite (0.5 mL) to afford 0.54 g of **7b** (96%), white powder, m.p. 100−102°C (CH_2Cl_2/MeOH). − ^{1}H NMR: δ = 7.8−7.7 and 7.6−7.45 (2 m, P-phenyl, 12 + 18 H), 6.99 (s, free H_p, 1 H), 6.74 (s, H_p, 3 H), 6.43 (s, free ArH, 1 H), 5.6−5.5 (m, H_o, 4 H), 4.63, 4.62 (2 t, J = 7.9 Hz, H_a, 4 H), 4.28, 4.17 (2d, J = 7.2 Hz, H_i, 4 H), 3.88 (br. s, OCH_2, 6 H), 2.4−2.2 [m, $CH_2P(O)$, 6 H], 2.2−2.05 (m, 8 H), 1.9−1.7 [m, $OCH_2(CH_2)_2$, 12 H], 1.45−1.2 (m, 24 H), 0.90 (t, J = 6.9 Hz, 12 H). − ^{13}C NMR: δ = 154.8, 148.2, 148.1 (s, Ar*C*OCH_2O), 144.9 (s, Ar*C*CH), 138.8, 138.7, 138.0 (s, ArCO), 133.7, 132.1−128.6 (P-phenyl), 121.3 [d, *p*-H-ArCH], 116.7 (d, free ArCH), 113.8 (d, ArCH), 99.3 (t, OCH_2O), 72.8 (t, OCH_2), 36.9, 36.6 (d, ArCHAr), 31.3 [$CH_2P(O)$]. − ^{31}P NMR: δ = 32.2. − MS; *m/z* (%): 1634.9 (100) [(M + H)$^+$]. − $C_{100}H_{115}O_{14}P_3$ (1633.9): calcd. C 73.51, H 7.09; found C 73.10, H 7.13.

Tetrakis(butoxydiphenylphosphane sulfide) Cavitand 8a: The general procedure for the Lawesson-type reaction was applied to (butoxydiphenylphosphane oxide) cavitand **7a** (0.90 g, 0.47 mmol) and Lawesson′s reagent (1.1 g, 2.7 mmol) to afford 0.88 g of **8a** (95%), yellowish powder, m.p. 102−104°C (CH_2Cl_2). − ^{1}H NMR: δ = 7.9−7.75 and 7.5−7.35 (2 m, P-phenyl, 16 + 24 H), 6.71 (s, H_p, 4 H), 5.65 (d, J = 7.1 Hz, H_o, 4 H), 4.62 (t, J = 8.0 Hz, H_a, 4 H), 4.20 (d, J = 7.2 Hz, H_i, 4 H), 3.95−3.85 (m, OCH_2, 8 H), 2.6−2.45 [m, $CH_2P(S)$, 8 H], 2.2−2.05 (m, 8 H), 1.9−1.7 (m, $OCH_2[CH_2]_2$, 16 H), 1.45−1.2 (m, 24 H), 0.89 (t, J = 6.8 Hz, 12 H). − ^{13}C NMR: δ = 148.3 (s, Ar*C*OCH_2O), 144.3 (s, Ar*C*CH), 138.8 (s, ArCO), 133.5, 132.3−128.6 (P-phenyl), 114.0 (d, ArCH), 99.5 (t, OCH_2O), 72.9 (t, OCH_2), 36.9 (d, ArCHAr), 32.1 [$CH_2P(S)$]. − ^{31}P NMR: δ = 40.44. − MS; *m/z* (%): 1969.9 (70) [M$^+$]. − $C_{116}H_{132}O_{12}P_4S_4$ (1970.5): calcd. C 70.71, H 6.75, S 6.51; found C 70.67, H 6.95, S 6.46.

Tris(butoxydiphenylphosphane sulfide) Cavitand 8b: The general procedure for the Lawesson-type reaction was applied to tris(butoxydiphenylphosphane oxide)methyl cavitand **7b** (0.30 g, 0.18 mmol) and Lawesson′s reagent (0.33 g, 0.83 mmol) to afford 0.25 g of **8b** (81%), yellowish powder, m.p. 106−108°C (CH_2Cl_2). − ^{1}H NMR: δ = 7.9−7.75 and 7.5−7.35 (2 m, P-phenyl, 12 + 18 H), 6.99 (s, free H_p, 1 H), 6.74 (s, H_p, 3 H), 6.45 (s, free ArH, 1 H), 5.66, 5.59 (2d, J = 7.2 Hz, H_o, 4 H), 4.64, 4.62 (2t, J = 8.0 Hz, H_a, 4 H), 4.29, 4.19 (2d, J = 7.2 Hz, H_i, 4 H), 3.89 (br. s, OCH_2, 6 H), 2.6−2.4 [m, $CH_2P(S)$, 6 H], 2.25−2.05 (m, 8 H), 1.9−1.6 (m, $OCH_2[CH_2]_2$, 12 H), 1.45−1.2 (m, 24 H), 0.90 (t, J = 6.9 Hz, 12 H). − ^{13}C NMR: δ = 154.8, 148.2, 148.1 (s, Ar*C*OCH_2O), 144.2 (s, Ar*C*CH), 138.9, 138.8, 138.0 (s, ArCO), 133.5, 132.2−128.5 (P-phenyl), 121.3 [d, *p*-H-ArCH], 116.7 (d, free ArCH), 113.8 (d, ArCH), 99.3 (t, OCH_2O), 72.8 (t, OCH_2), 36.9, 36.6 (d, ArCHAr). − ^{31}P NMR: δ = 42.55. − MS; *m/z* (%): 1681.7 (40) [M$^+$]. − $C_{100}H_{115}O_{11}P_3S_3$ (1506.1): calcd. C 71.40, H 6.89, S 5.72; found C 71.38, H 6.94, S 5.38.

Tetrakis(ethyl phenylmethylphosphinate) Cavitand 9a:[23] The literature procedure[2] for the Arbusov reaction (temperature 100−150°C; reaction time 2 h) was applied to bromomethyl cavitand **2** (0.52 g, 0.44 mmol) and diethyl phenylphosphonite (1.0 mL). In addition, after cooling the reaction mixture to room temp., diisopropyl ether was added, the residue filtered and purified according to the general procedure to afford 0.33 g of **9a** (47%), slightly yellow powder, m.p. 108−110°C (CH_2Cl_2/MeOH). − ^{13}C NMR: δ = 153.3 (s, Ar*C*OCH_2O), 137.4 (s, Ar*C*CH), 132.0−128.0 (P-phenyl), 118.7 (d, ArCH), 98.8 (t, OCH_2O), 62.9 (t, OCH_2CH_3), 36.7 (d, ArCHAr), 29.1 [$CH_2P(O)$], 16.4, 16.3 (t, OCH_2CH_3). − MS; *m/z* (%): 1545.9 (80) [M$^+$]. − $C_{88}H_{108}O_{16}P_4\cdot 1.5\ H_2O$ (1572.3): calcd. C 67.21, H 7.11; found C 66.95, H 6.99.

Tetrakis(methyl phenylmethylphosphinate) Cavitand 9b:[23] The literature procedure[2] for the Arbusov reaction (temperature 100−150°C; reaction time 20 min) was applied to bromomethyl cavitand **2** (0.60 g, 0.51 mmol) and dimethyl phenylphosphonite (1.0 mL) to afford 0.71 g of **9b** (94%), slightly yellow powder, m.p. 122−124°C (CH_2Cl_2/MeOH). − ^{13}C NMR: δ = 153.3 (s, Ar*C*OCH_2O), 137.4 (s, Ar*C*CH), 132.2−128.1 (P-phenyl), 118.8 (d, ArCH), 98.8 (t, OCH_2O), 51.4 (q, OCH_3), 36.7 (d, ArCHAr), 30.9 [$CH_2P(O)$]. − ^{31}P NMR: δ = 39.57. − MS; *m/z* (%): 1489.5 (100) [(M+H)$^+$]. − $C_{80}H_{92}O_{16}P_4\cdot 0.5H_2O$ (1442.5): calcd. C 66.61, H 6.50; found C 66.56, H 6.75.

Tetrakis(phenylmethylphosphinic acid) Cavitand 10: Tetrakis(methyl phenylmethylphosphinate) cavitand **9b** (124 mg, 83 μmol) in a 1:1 vol-% solution of THF and 2 M NaOH (20 mL) was stirred at 85°C for 5 d. Subsequently, the THF was evaporated and 3 M HCl (25 mL) was added. The solution was extracted with CH_2Cl_2 (3 × 25 mL) and the collected organic layers were washed with 1 M HCl (2 × 25 mL), H_2O (10 mL), and dried with Na_2SO_4 to afford 97 mg of **10** (81%), off-white powder, TLC (CH_2Cl_2/THF/MeOH, 8:1:1). − R_f = 0.25. − M.p. 229−231°C (CH_2Cl_2). − ^{1}H NMR: ([D$_6$]DMSO) δ = 7.6−7.45 and 7.4−7.30 (2 m, P-phenyl and H_p, 24 + 24 H), 5.32 (d, J = 7.7 Hz, H_o, 4 H), 4.35 (t, J = 7.9 Hz, H_a, 4 H), 4.22 (d, J = 7.7 Hz, H_i, 4 H), 2.92 (d, $^2J_{PH}$ = 17.6 Hz, H_b, 8 H), 2.3−2.15 (m, 8 H), 1.45−1.2 (m, 24 H), 0.88 (t, J = 6.6 Hz, 12 H). − ^{1}H NMR: ([D$_6$]acetone/CD_3OD, 6:1; selected signals): δ = 5.83 (d, J = 8.0 Hz, H_o, 4 H), 4.88 (d, J = 7.9 Hz, H_i, 4 H), 4.71 (t, J = 7.9 Hz, H_a, 4 H), 3.33 (d, $^2J_{PH}$ = 16.3 Hz, H_b, 8 H). − ^{13}C NMR: ([D$_6$]DMSO) δ = 152.6, 152.5 (s, Ar*C*OCH_2O), 137.3 (s, Ar*C*CH), 133.7−127.7 (P-phenyl), 119.9 (d, ArCH), 99.3 (t, OCH_2O), 36.9 (d, ArCHAr), 29.5 [$CH_2P(O)$]. − ^{31}P NMR: ([D$_6$]DMSO) δ = 31.96. − MS; *m/z* (%) 1730.8 (100) [(M − H)$^-$]. − $C_{80}H_{92}O_{16}P_4\cdot CH_2Cl_2$ (1518.4): calcd. C, 64.07; H, 6.24; found C, 64.33; H, 6.34.

Ammonium Salt of 10: NH_3 was bubbled through a suspension of phenylmethylphosphinic acid **10** in toluene (0.5 g in 25 mL) at room temp. for 3 h. The precipitate was filtered and washed with CH_2Cl_2. − ^{1}H NMR: ([D$_6$]DMSO) δ = 7.88 (t, J = 5.0 Hz, *m*-P-phenyl, 8 H), 7.53 (s, H_p, 4 H), 7.45−7.05 (m, P-phenyl, 12 H), 5.76 (d, J = 7.1 Hz, H_o, 4 H), 4.78 (d, J = 7.2 Hz, H_i, 4 H), 4.58 (t, J = 7.9 Hz, H_a, 4 H), 2.94 (d, $^2J_{PH}$ = 17.5 Hz, H_b, 8 H), 2.4−2.2 (m, 8 H), 1.45−1.2 (m, 24 H), 0.90 (t, J = 6.4 Hz, 12 H). − ^{31}P NMR: ([D$_6$]DMSO) δ = 18.62. − MS (spectrum shows release of NH_3 during measurement); *m/z* (%): 1433.3 (50) [(M − 4 NH_3 + H)$^+$], 1455.6 (100) [(M − 4 NH_3 + Na)$^+$]. − The free acid can be recovered by acidifying a suspension of **10**·$(NH_3)_4$ in CH_2Cl_2 with 3 M HCl (2 ×), H_2O, drying with $MgSO_4$, and removal of the solvent.

Extraction Experiments

Solutions: The 10^{-1} M Eu^{III} stock solution was prepared by dissolving the required amounts of $Eu(NO_3)\cdot 6\ H_2O$ in 0.1 M HNO_3. The 10^{-4} M Eu^{III} working solution was prepared by dissolving the appropriate amount of LiPic in 10^{-3} M HNO_3, adding 20 μL of the 10^{-1} M stock solution, and adjusting the total volume of the solution to 20 mL using volumetric glassware. The Eu^{III} picrate was prepared in situ in the stock solution resulting from the presence of an excess (10^{-2} M) of lithium picrate. The salt solution was spiked with the ^{152}Eu radiotracer by adding 100 μL of the radiotracer solution to the working solution. The solutions of the ligands were prepared by dissolving the appropriate amount of the ligands in 20 mL of CH_2Cl_2.

Procedures: Equal volumina (1.0 mL) of the organic and the aqueous solutions were pipetted in a glass-stoppered glass tube and magnetically stirred at ambient temperatures (22−24°C) for at least 30 min to ensure complete settling of the two-phase equilibration. In case of the Am/Eu extraction experiments a metal-free aqueous solution (of 10^{-2} M LiPic and 10^{-3} M HNO_3) was used to which 20 μL of the Am/Eu isotope stock solution was added. The solutions were disengaged by centrifugation (1600 rpm for 10 min) and equal aliquots (0.5 mL) of the organic and aqueous phases were pipetted out. The γ activity in both samples was determined with an LKB Wallac CompuGamma NaI(Tl) scintillation counter. In multiple isotope experiments (^{241}Am and ^{152}Eu tracers) the γ activity of the individual isotopes was determined with a Ge(Li) scintillation counter. The distribution ratio is defined as the ratio of the activity in the organic phase (A_o) and the activity in the aqueous phase (A_w): $D = \Sigma(A)_o/\Sigma(A)_w$. Variations of ligand-concentration experiments were performed by taking suitable aliquots of the stock solution and adjusting the volume to 1.0 mL by adding CH_2Cl_2. Experiments with two or three organic compounds were performed by mixing the suitable aliquots of each stock solution keeping the total organic volume to 1.0 mL. The solutions were not pre-equilibrated with the aqueous phase. The reported extraction percentages are the average of at least two experiments. The errors in the K_{ex} values are less than 15%.

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[23] The methyl and ethyl phosphinate cavitands **9a** and **9b** both have four stereocenters at the phosphorus atoms. As the product is a mixture of all possible conformers the ^{1}H-NMR spectra are very complicated and show multiple signals for most hydrogen atoms. Therefore, the ^{1}H-NMR spectra have not been assigned and are omitted. The observed phenomena are similar to those found for the *N*-propyl-substituted CMP(O) cavi-

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