Multicoordinate ligands for actinide/lanthanide separations

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In nuclear waste treatment processes there is a need for improved ligands for the separation of actinides (An(III)) and lanthanides (Ln(III)). Several research groups are involved in the design and synthesis of new An(III) ligands and in the confinement of these and existing An(III) ligands onto molecular platforms giving multicoordinate ligands. The preorganization of ligands considerably improves the An(III) extraction properties, which are largely dependent on the solubility and rigidity of the platform. This *tutorial review* summarizes the most important An(III) ligands with emphasis on the preorganization strategy using (macrocyclic) platforms.

1. Introduction

Currently, about 15% of the world's electricity is generated by over 400 nuclear power plants. This is likely to increase in order to meet future energy needs without emitting carbon dioxide and other atmospheric pollutants. As a consequence, the already large nuclear waste depositories will continue to expand. In recent decennia a great deal of research has been devoted to the subject of proper nuclear waste management in order to reduce its burden on the environment. Yet, there is no satisfactory solution for this problem and the need for reducing current and future waste disposal remains.

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Nuclear waste management processes that are presently in operation start with the PUREX[1] process in which almost all uranium and plutonium is separated from the depleted fuel. The residual waste stream HLLW (high level liquid waste) contains the remaining fission products along with the minor actinides Np, Am, and Cm. The long lasting radioactivity ($T_{1/2}$ = 10^3–10^4 years) of the latter makes storage of HLLW a serious environmental problem (risk of leaking) and economically unfavorable.

The radiotoxicity of HLLW can be reduced by neutron-irradiation (transmutation) of the minor actinides into short-lived ($T_{1/2}$ = 10^1 years) nuclides or stable nuclides. However, the lanthanides (especially Sm, Gd, and Eu) have high neutron capture cross sections and preferably absorb the neutrons with regard to the actinides.[2] For a satisfactory transmutation process it becomes imperative to separate the

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Henk Dam, born in 1975, studied organic chemistry at the University of Professional Education Enschede, The Netherlands, where he received his degree in June 1999. He continued to study organic chemistry at the Free University (VU) at Amsterdam. His final project involved the synthesis of novel bifunctionalized ligands and their ruthenium complexes, which was performed in the group of Prof. dr. G. van Koten (metal-mediated synthesis) at Utrecht University. He received his master degree in June 2002. Since September 2002 he has been a PhD candidate in the group of Prof. dr. ir. D. N. Reinhoudt at the University of Twente. The aim of his project is the synthesis of new actinide receptors using a combinatorial chemistry approach.

David N. Reinhoudt

Professor David N. Reinhoudt was born in 1942 in The Netherlands. He studied Chemical Technology at the Delft University of Technology and graduated (suma cum laude) in chemistry in 1969 with Professor H. C. Beijerman. In the period 1970–1975 he worked at Shell where he started the crown ether research program. In 1975 he was appointed as a part-time professor (extraordinarius) at the University of Twente followed by the appointment as a full professor in 1978. The major part of his research deals with supramolecular chemistry and technology. Nanotechnology, molecular recognition, and non-covalent combinatorial synthesis are the major fields. Application of supramolecular chemistry e.g. in "lab-on-a-chip", in the field of electronic or optical sensor systems, catalysis, and molecular materials. Professor Reinhoudt is the scientific director of the MESA+ Research Institute. Since 2002 he has been the chairman of the Board of NanoNed, the Dutch Network for Nanotechnology. He is a member of the Royal Dutch Academy of Sciences, Fellow of the American Association for the Advancement of Science, and Fellow of the Institute of Physics. He is the author of about 825 scientific publications, patents, review articles, and books. He has been honored with the Izatt–Christensen award (1995), the Simon Stevin Mastership (1998) and Knight of the Order of the Dutch Lion (2002).

actinides from the chemically similar but relatively harmless lanthanides.

The commonly encountered oxidation state of the lanthanides (Ln) and actinides (An) in HLLW is trivalent. The HSAB-principle classifies the An(III) and Ln(III) cations as hard Lewis acids,[3] consequently their bonding is primarily ionic and mainly governed by charge density.[4] The identical oxidation states of these metals and their nearly similar ionic radii, as result of the f-element contractions, makes the intra- and intergroup separation of An(III) and Ln(III) exceedingly difficult. Despite this, there is a modest enhancement of covalency in the An(III)–ligand bonding compared to Ln(III).[5] This results in an advantageous discrimination between An(III) and Ln(III) when using softer donor atoms compared to oxygen (*e.g.* N, S, Cl).

In many studies devoted to the improvement of An/Ln separation this feature is exploited by incorporating softer donor groups in newly designed ligands. Besides this, separation factors can also be improved by preorganizing chelating groups onto a platform creating a multicoordinate ligand. For this purpose different types of (macrocyclic) platforms have been used. This review will focus on the latest advances made into the continuously extending range of multicoordinate actinide ligands, particularly on the separation of Am(III) from Eu(III).

2. An(III) ligands

The extensive research into proper nuclear waste management of the past decennia has led to a large number of An(III) ligands. The extractability and stability of the complexes formed with these ligands are characterized by their distribution ratio (D_M), defined as the ratio between the metal concentration in the organic and in the aqueous phase at equilibrium. The separation factor ($S_{M1/M2}$), defined as the quotient of the distribution ratios, characterizes the complex extractability and stability with respect to a second metal. In the following sections ligands that are mostly encountered or that have a noteworthy complexation behavior will be highlighted.

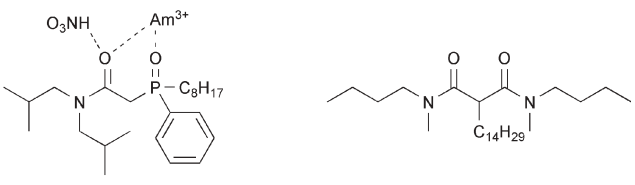
2.1 *O*-donating ligands

This group of ligands covers a broad range of *O*-bearing functionalities (*viz*. phosphonates, phosphinates, phosphine oxides, amides, carbonic acids, ketones, pyridine *N*-oxides, and phenols). Well known are the carbamoylmethylphosphonates (CMPs) and the carbamoylmethylphosphine oxides (CMPOs), a derivative of the latter (**1**, Chart 1) is presently used in the TRUEX (*trans*uranium *ex*traction) process.[6] Upon complexation with the metal cation it forms a six-membered chelate ring with, in general, a ligand to metal stoichiometry of 1 : 3.[7] It is believed that this ligand predominantly coordinates with its phosphoric oxygen and that the carbonyl oxygen only weakly coordinates to the metal cation, but instead functions as an internal buffer and coordinates with a proton. The strength of the formed complexes for these types of *O*-donors are generally phosphine oxide > phosphate > phosphonate.[8]

N,N′-Dimethyl-*N,N′*-dibutyl-tetradecylmalonamide[9] **2** is currently used in the DIAMEX process[10] for the sequestering of actinides and lanthanides. The malonamide group of ligands have the advantage of being completely incinerable and thus fulfill the *CHON*-principle (ligands that only contain elemental carbon, hydrogen, oxygen or nitrogen are preferred, since they produce less harmful waste after burn up) leading to reduced secondary wastes. The malonamides coordinate in a bidentate fashion with their carbonyl oxygens. Their extraction efficiency is generally increased upon increasing the nitric acid concentration resulting in a maximum D_{Am} at around 8 M HNO_3. The *N*-substituents greatly influence the performance of the ligand as for instance phenyl rings on this position result in less basic carbonyl oxygens improving the extraction efficiency with a steep extraction increase up to >10 M HNO_3.[11] The *O*-donor ligands are generally strong extractants owing to the hard nature of the oxygen atom, although, usually lack discrimination between Am(III) and Eu(III), resulting in relatively low $S_{Am/Eu}$ values.

2.2 *S*-donating ligands

Cyanex 301 (**3a**, Chart 2) is a good example of an Am(III) chelator having a very high $S_{Am/Eu}$ due to the preferable

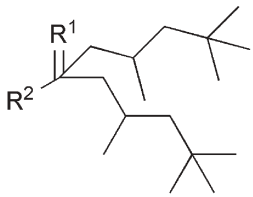


1 2

Chart 1

Willem Verboom

Willem Verboom was born in 1954 in Goes, The Netherlands. He studied chemistry at Utrecht University, where he also received his PhD with Prof. Dr. H. J. T. Bos with a thesis entitled ''Thermal and photochemical rearrangements of γ-oxo-α,β-unsaturated carboxamides and esters''. Subsequently, he joined the group of Prof. Dr. Ir. D. N. Reinhoudt at the University of Twente, where he now is an associate professor in organic chemistry. Over the years the research interests moved from heterocyclic chemistry to supramolecular chemistry. His present research topics involve the functionalization and application of suitable molecular building blocks, in particular calixarenes and cavitands, for the development of specific receptors and larger (non-)covalent assemblies and recently, chemistry in microchips. He is the (co-)author of about 300 scientific publications. He served as a board member of the International Society of Heterocyclic Chemistry in the period 1992–1995. He was a member of the editorial board of the Dutch journal Recl. Trav. Chim. Pays-Bas (1992–1996). For a long time he has been a member of the refereeing panel of different journals of the Royal Chemical Society (UK). Currently, he is secretary of the 'Design and Synthesis' study group of the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) (2001-).



3a R^1 = S, R^2 = SH (Cyanex 301)
3b R^1 = S, R^2 = OH (Cyanex 302)
3c R^1 = O, R^2 = OH (Cyanex 272)

Chart 2

covalent binding of Am(III) to the relatively softer sulfur donor atom. A difference of -25.6 kJ mol^{-1} was observed between the enthalpies of Am(III) and Eu(III) extraction by **3a** into kerosene.[5c] $S_{Am/Eu}$ values well over one thousand are found with **3a**, however, the selectivity is considerably lowered upon oxidation of the compound to Cyanex 302 (**3b**) and is reversed when further oxidized to Cyanex 272 (**3c**).

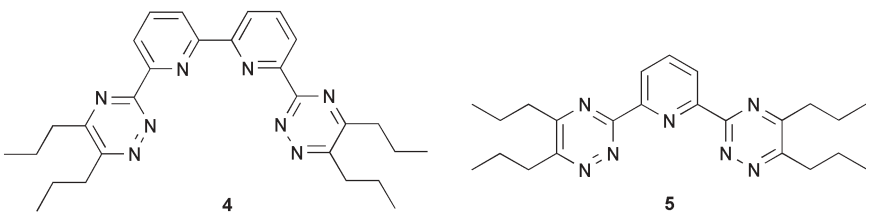
This reduces the applicability of this type of compounds for the use in industrial processes. No shortening in the Am–S bonds was found compared to the Ln–S bonds in extracted complexes. Whether the differences in structure and stoichiometries of the extracted An and Ln complexes contribute to the high selectivity of **3a** is not yet fully understood.[5c,12] In synergistic mixtures with *O*- or *N*-donating ligands the D_{Am} is greatly improved. With 2,2′-bipyridyl or 1,10-phenanthroline auxiliary ligands $S_{Am/Eu}$ values of over 40 000 are obtained resulting from the combination of two softer Lewis bases.[13] The synergistic mixtures also suffer from oxidation and protonation at lower pH, resulting in strong decreases of D_{Am}.

2.3 *N*-donating ligands

With regard to extraction efficiency and Am(III) selectivity the *N*-donor ligands are placed more or less in between the *O*- and *S*-donor ligands. In most *N*-donor ligands the nitrogen is incorporated into an aromatic ring. Ligands based on pyridine, pyrimidine, pyrazine, 1,2,4-triazine, 1,3,5-triazine, 1,2,4-triazole, benzimidazole, benzothiazole, and benzoxazole ring systems in various combinations have been studied for Am(III) extraction and complex properties.

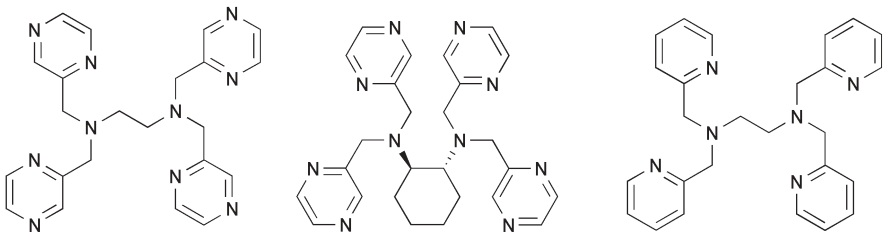
The 1,2,4-triazine-pyridine ligands **4** and **5** (Chart 3) possess the highest D_{Am} (>100) and $S_{Am/Eu}$ (>100) values of the nitrogen donor ligands up to now.[14] These values are obtained at a nitric acid concentration of 1 M, which is relatively high for *N*-donor type of ligands, since they are rather easily protonated. The high preference of **4** and **5** for Am(III) complexation is believed to originate from the two adjacent nitrogen atoms in the 1,2,4-triazine rings. These two nitrogens possess a partial charge that is considerably lower than that of the nitrogens in a 1,3,5-triazine ring (0.312 *e versus* 0.559 *e*) which essentially means a softer character for the two adjacent nitrogens and thus a more covalent Am(III) binding. Besides the electronic nature of the coordinating atoms, there is also an important role reserved for the ligand architecture and complexation geometry. This was demonstrated by showing the large difference in the $S_{Am/Eu}$ values for ligands **6** and **7** (Chart 4) which have different spatial orientations of their coordinating groups.[15] Stronger *N*–metal bonds are formed in **6** owing to the ability of the ligand to resemble the preferred complexation geometry more closely resulting in an approximately 30 times higher $S_{Am/Eu}$.

Furthermore, due to the chelate effect extraction efficiencies are also generally better for ligands having a higher multivalency as shown for ligand **8** ($S_{Am/Eu} > 100$).[16] Such ligands are also more able to replace all coordinated water molecules and to encapsulate the ligand creating a lipophilic exterior which facilitates phase transfer. This is most likely also one of the reasons for the high extraction efficiency of ligands **4** and **5** which coordinate in a 2 : 1 and 3 : 1 ligand to metal stoichiometry, respectively.[17]



4 **5**

Chart 3



6 **7** **8**

Chart 4

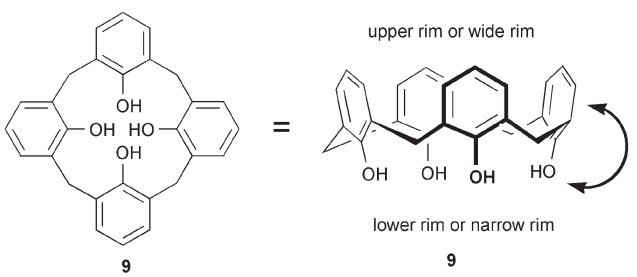
3. Platforms for preorganization of An(III) ligands

Preorganization is the extent to which the free ligand is fixed in the conformation required for complexing the target metal ion. Trivalent f-elements have high coordination numbers (>8) and prefer a tricapped trigonal prismatic complexation geometry (*e.g.* $[Eu(H_2O)_9]^{3+}$ (D_{3h})). The high coordination numbers result in the binding of several chelating groups at the same time by this group of metals. The preorganization of chelators results in better extractants (more favorable entropic changes) with higher metal selectivities. The extent to which the chelating groups match the preorganization necessary for successful binding of a cation is strongly influenced by the structural parameters of the platform. How this is influencing the metal extraction properties will be shown by various examples throughout this section.

3.1 Macrocyclic platforms

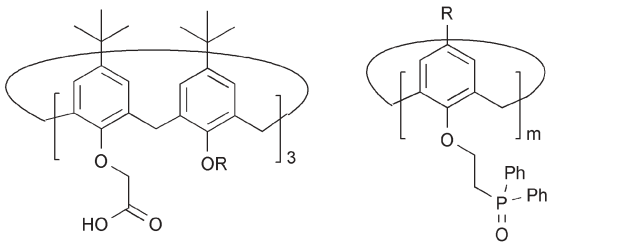
3.1.1 Calixarenes. Calixarenes are appealing macrocyclic platforms for the preorganization of chelating groups. Functionalization of the calixarene platform is possible in two ways, at the narrow lower rim (smaller cavity) and at the wide upper rim (larger cavity). Additionally one or both rims can be used for tuning the solubility or conformation of the calixarene platform. Each phenyl ring can rotate through the annulus of the macrocycle which results in the existence of several conformers.[18] This rotation around the methylene axis is inhibited by the attachment of groups larger than ethyl to the narrow rim. In the cone-shaped conformer (point group C_{2v}, C_{4v}) (Chart 5), the rings still possess some rotational freedom, which is transferred in a certain degree of flexibility of the chelating groups attached to it.

Calixarenes have been extensively studied for the preorganization of chelating groups in nuclear waste treatment.[19] The size of the calixarene macrocycle can vary from three phenyl rings (calix[3]arene)[20] to more than eight (calix[8]arene). With increasing size of the macrocycle more conformations are possible and the platform becomes more flexible affecting its preorganizing properties. Calix[6]arene **10b** (Chart 6) extracts Am(III) more than 10-times better ($D_{Am} \approx 250$, $c_L = 5 \times 10^{-3}$ M, $CHCl_3$, 10^{-3} M HNO_3) than calix[4]arenes functionalized at the lower rim with COOH groups at a given pH.[21] Most likely the conformation of the calix[6]arene plays an important role as well as the increased number of coordinating groups. A higher number of coordinating groups not only raises the extraction efficiency of the ligand by more closely



9 **9**

Chart 5 Representation of the structure of calix[4]arene. Left: top view, right: side view.



10a R = CH_3
10b R = CH_2COOH

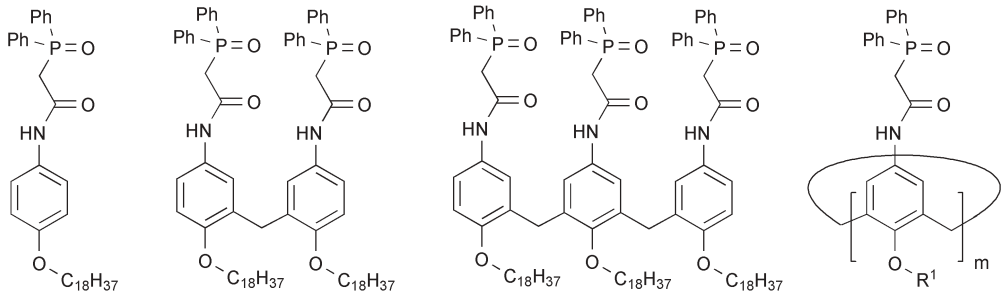
11a R = t-butyl or H, m = 4, 6, or 8
11b R = H, m = 8

Chart 6

matching the coordination number of the metal, but can also provide for shielding of the complexed cation from the competing water molecules. Ligand **10a** lacks an effective shielding and thus the tendency of the cation to interact with the competing water molecules is larger, giving rise to a lower D_{Am} value. Shielding of complexed cations from water molecules is an effective means of improving the extractability of a ligand, which can more easily be accomplished by multicoordinate ligands. According to the log *D*/pH slope of **10b** three protons are exchanged for Am(III) in agreement with the charge. The anionic coordination of the –COOH functionalized calixarenes causes a steep decrease in the extractability of the respective ligands on going to higher acidities. This is a main drawback when industrial applications are considered. In this respect calix[*m*]arenes **11a**, equipped with monodentate phosphine oxide groups, behave much better.[22] These type of multicoordinate ligands were studied for their liquid membrane transport properties of Np, Pu, and Am cations. The most promising results have been obtained using **11b**, which behaves much better than normal CMP.

Generally, better extraction properties are obtained when bidentate chelating groups are attached to a platform, mostly CMPO-derivatives are being studied. A clear example of this cooperative effect is shown by the differences in extraction efficiencies of **12** to **15a** (Chart 7). An increase in cation (*i.e.* Eu(III), Np(III), Am(III), and Th(IV)) extraction is observed going from the monomer **12** to the oligomers **13**, **14** and finally calix[4]arene **15a**.[23] Furthermore, on extending the macrocyclic calix[4]arene ring with one phenoxy ring, resulting in calix[5]arene **15b**, a significant improvement is obtained in the extraction of linear NpO_2^+, NpO^{2+}, and NpO_2^{2+} cations. The extraction of Th(IV) by **15b** is, however, lowered compared to **15a**, which stresses the influence a spatial change or the number of preorganized chelating groups can have on the extraction properties of a multicoordinate ligand without changing the chelating group itself. Ligand **15c** exhibits a size selectivity in the lanthanide series ($S_{La/Yb} \sim 730$),[24] a property more often observed resulting from the preorganization of ligating groups (*vide infra*).

The rigidity of the calix[4]arene platform is considerably lowered by functionalization of the narrow rim with alkyl groups that are able to pass the annulus. A study performed to establish to what extent this influences the extraction properties revealed a significant change in metal extraction.[25] 1,3-Methyl-2,4-propyl-functionalized calix[4]arene **16b** (Chart 8)



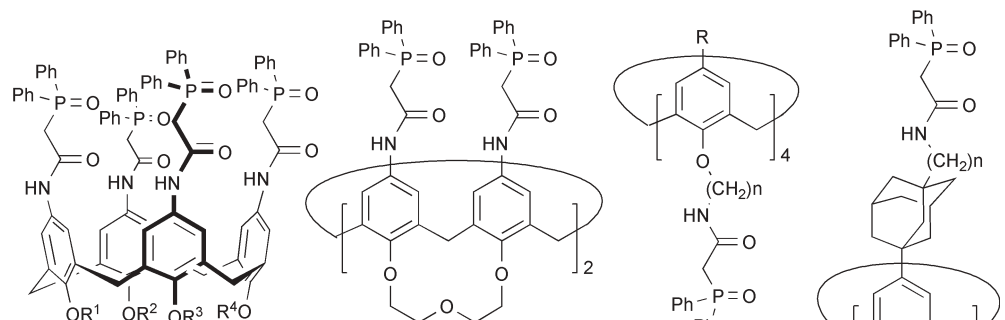
12 **13** **14**

15a m = 4, $R^1 = C_{18}H_{37}$
15b m = 5, $R^1 = C_{14}H_{29}$
15c m = 4, $R^1 = C_5H_{11}$
15d m = 4, $R^1 = C_{14}H_{29}$

Chart 7

gave the highest $D_{Am} \sim 570$ ($S_{Am/Eu} \sim 5$), whereas the highest $S_{Am/Eu} \sim 9$ ($D_{Am} \sim 440$) was obtained with 1,2-methyl-3,4-propyl derivative **16c** ($c_L = 10^{-3}$ M, NPHE (nitrophenylhexyl ether), 1 M HNO_3). Although less efficient than the former two, the most flexible tetramethyl substituted calix[4]arene **16e** is more efficient than either the tetrapropyl **16f** or tetrapentyl **15c** functionalized calix[4]arenes. Surprisingly, also rigidification of the macrocycle as in **17** results in a substantial increase of the D_{Am} (>1000) under similar conditions and a doubling of the $S_{Am/Eu}$ is observed at a ten times lower ligand concentration ($S_{Am/Eu} = 18.9$, $c_L = 10^{-4}$ M, NPHE, 1 M HNO_3).[26] This illustrates that the rigidity of the platform is not necessarily the only important factor that influences the extraction efficiency. Symmetry deformations of the macrocyclic ring induced by substituents such as those in **17** can as well alter the extraction properties and the preferred solution ligand to metal complex stoichiometry. Moreover, the influence rigidity changes has on metal complexation is certainly not always the same within the lanthanide and actinide group of metals. For instance, the lower rim substitution changes have a much less pronounced effect on the extraction of Th^{4+}. An increase of around 10% in extraction is observed ($c_L = 10^{-4}$ M, CH_2Cl_2, 1 M HNO_3) for the mixed ethers **16a** to **16d** with regard to the extraction efficiencies (~61%) of the identical ethers **16e** and **16f**.

The versatility of the calixarene platform offers the possibility of lower rim functionalization. Exploiting this strategy, CMPO moieties were attached to the phenolic oxygens using different chain lengths.[27] The lower rim preorganization of CMPO chelating groups also accounts for an increase in the extraction efficiency with respect to the free ligand, although both the *D* and *S* values of ligands **18** are lower than those of the upper rim functionalized calix[4]arene **15c** ($D_{Am} > 100$, $c_L = 10^{-3}$ M, NPHE, 1 M HNO_3).[23] This difference should, however, not solely be attributed to the differences in preorganization of the chelating groups by either lower or upper rim functionalization. In the latter case the influence of the *N*-phenyl rings on the coordination behavior of the amide oxygen might be significant. Striking is the absence of an extraction maximum between 1–2 M HNO_3 for upper rim functionalized calixarenes **15**, but instead there is a steady increase in extraction up to 4 M HNO_3. The tight positioning of the CMPO groups in **18a** generally has a disadvantageous



	R^1	R^2	R^3	R^4
16a	CH_3	CH_3	CH_3	C_3H_7
16b	CH_3	C_3H_7	CH_3	C_3H_7
16c	CH_3	CH_3	C_3H_7	C_3H_7
16d	CH_3	C_3H_7	C_3H_7	C_3H_7
16e	CH_3	CH_3	CH_3	CH_3
16f	C_3H_7	C_3H_7	C_3H_7	C_3H_7

17

18a n = 2, R = t-butyl
18b n = 3, R = t-butyl
18c n = 4, R = t-butyl
19a n = 2, R = n-adamantyl
19b n = 3, R = n-adamantyl
19c n = 4, R = n-adamantyl

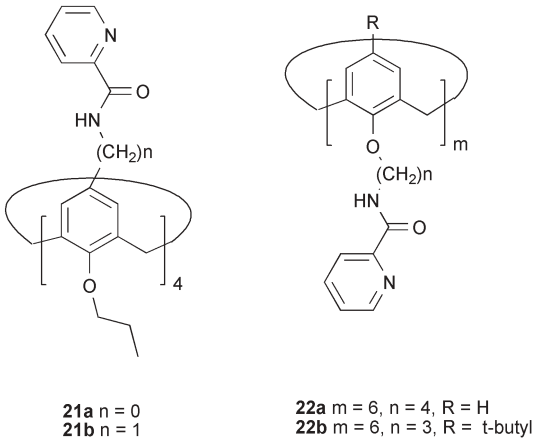
20a n = 0
20b n = 1

Chart 8

effect on the actinide and lanthanide extraction. Some degree of flexibility of the CMPO groups is needed for a good metal–ligand interaction. This is reflected by an increase in the metal extraction in the case of the more flexible **18c** ($D_{Am} \sim 60$, $c_L = 10^{-3}$ M, NPHE, 3 M HNO_3).

Distribution of the ligand–metal complex into the organic layer can often be improved by increasing the solubility of the ligand by attachment of large lipophilic groups to the ligand. For instance, the Eu(III) extraction can be improved when elongating the alkyl chain from $R^1 = C_5H_{11}$ in **15c** to $R^1 = C_{14}H_{29}$ in **15d**. However, an additional lengthening to $R^1 = C_{18}H_{37}$ as in **15a** accounts for a decrease in the Eu(III) extraction, most probably because such long alkyl chains can give rise to additional solubility effects as 'intramolecular crystallization' or aggregation at the water–organic solvent interface. The adamantyl groups in the calix[4]arenes **19** and **20** have been used to enhance the lipophilicity of the complexes.[28] This, however, did not result in improvement of the *D* values as compared to the upper rim CMPO calix[4]arenes **15**. As with **18c**, ligand **19c**, having the longest $-(CH_2)_n-$ spacer, has the highest extraction efficiency ($D_{Am} = 2.4$). In contrast to *tert*-butyl derivatives **18** a somewhat lower extraction was obtained with the upper rim CMPO-ligand **20b** ($D_{Am} = 1.9$, both $c_L = 10^{-3}$ M, CH_2Cl_2, 3 M HNO_3). A direct connection of the adamantyl group to the CMPO moiety as in **20a** results in a lowering of the D_{Am} by a factor of 100 compared to **20b**. Evidently not only the lipophilicity has changed, apparently, the bulky adamantyl groups seem to leave little room for efficient metal coordination. This suggests that the amide carbonyl oxygen is not only functioning as an internal buffer,[29] but plays a significant role in the binding. Improvements in the *D* values by such means as lipophilicity increments often come along with a change of the preorganization properties of the calixarene platform, owing to its flexibility. Organic groups that substitute the rims can influence the calixarene conformation, interfere with the metal coordination or interact with the solvent, in such a way that destabilization of the complex results. These factors complicate the predictions of the outcome such structural changes may have and makes it difficult to attribute the effect solely to the increased lipophilicity of the platform.

The approximate overall composition of the extracted species in the extraction of actinides and lanthanides is usually probed by studying the log *D vs.* log c_L curves.[23] The metal–ligand stoichiometries that are found by slope analysis of the plots using CMPO-calix[4]arenes are between 1 and 2. The narrow rim ligands generally have lower stoichiometry numbers compared to those of the wide rim ligands. Thus a 1 : 1 cation/ligand stoichiometry is expected for the former and a 1 : 2 stoichiometry for the latter. The narrow rim CMPO ligands form rigid cages and highly symmetric metal complexes, according to nuclear magnetic relaxation dispersion (NMRD) studies of various lanthanide complexes.[30] In contrast, the wide rim CMPO derivatives are more flexible and tend to form polymeric species in solution which do not depend so much on the narrow rim alkyl substituents. Calixarenes **16e**, **16f**, and **17** favor the formation of oligomeric species in large assemblies. Such structures are sterically possible as has been proven by an X-ray crystal structure of



21a n = 0
21b n = 1

22a m = 6, n = 4, R = H
22b m = 6, n = 3, R = t-butyl

Chart 9

16f as $[Eu_5\mathbf{16f}_2(NO_3)_{15}]\cdot 2H_2O$ in which one of the Eu(III) cations is coordinated to two CMPO arms belonging to different calixarene units.[25]

The picolinamide group can coordinate in a mono-(carbonyl oxygen) and bidentate (nitrogen) fashion. Casnati *et al.*[31] have studied the preorganization of the picolinamide chelating group on calix[4,6, and 8]arenes. The solution conformations of the ligands based on the larger calixarenes (*i.e.* 6 and 8 monomers) in DMSO-d_6 solution at room temperature are not restricted to the cone formation. For example, ^{1}H NMR-studies revealed that ligand **22b** (Chart 9) exists in different conformations, with a preference for the 1,2,3-alternate form.

Despite the increased mobility of the larger macrocyclic rings, multicoordinate ligands based on calix[6]arene and calix[8]arene still give an increase in extraction efficiency and selectivity for Am(III) over Eu(III) with regard to the free ligand, whilst the total concentration of chelating groups in the extractions using the multicoordinate ligands is less. In contrast to the CMPO-substituted calix[4]arenes **15** and **18** there are only small differences in the extraction efficiencies between the upper and lower rim picolinamide functionalized calix[4]arenes. The differences are more pronounced within these two groups, higher D_{Am} values are obtained for the calix[4]arenes having longer $-(CH_2)_n-$ spacer lengths or lipophilic moieties. In the extraction experiments the lipophilic dicarbollide anion (Br_6-COSAN)[32] was used as a synergist in the otherwise very low metal distribution. For example, ligand **22b** gives a $D_{Am} = 6.1$ ($S_{Am/Eu} = 2.3$, $c_L = 10^{-2}$ M, NPHE, 10^{-3} M HNO_3), whereas it is over 300 when Br_6-COSAN (3×10^{-3} M) is added. Of the studied ligands the highest $S_{Am/Eu}$ obtained was 13.8 ($c_L = 5 \times 10^{-3}$ M, NPHE, 10^{-3} M HNO_3) for ligand **21a**, while the calix[8]arene based ligands are the strongest extractants of Am(III) and Eu(III). Unfortunately, all the studied picolinamide calixarenes suffer from protonation at higher acidities, making them less interesting for industrial usage.

3.1.2 Cavitands. Cavitands are macrocyclic platforms structurally related to calixarenes. The major difference is the intramolecular rigidification of the macrocycle by the upper rim phenyl–phenyl ethylene glycol bridges preventing the

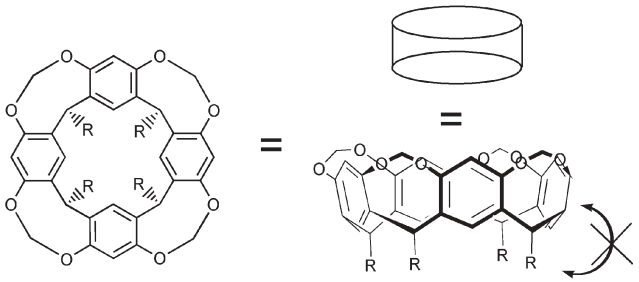


Chart 10 Representation of the structure of a cavitand. Left: top view, right: side view.

phenyl rings from rotating (Chart 10). Consequently, changes in its rigidity induced by substituents are very small in contrast to the adjustable rigidity of the calixarene platform.

As compared to the calixarenes the increase in Am(III) extraction obtained by the CMPO-cavitands is much smaller. At low acidity the D_{Am} values of cavitands **24a** and **24b** (Chart 11) are approximately the same ($D_{Am} \approx 30$, $S_{Am/Eu} \approx 2$, $c_L = 10^{-3}$ M, NPHE, 10^{-3} M HNO_3). In contrast to free CMPO and CMPO-functionalized calixarenes **15** and **18** the D_{Am} of **24a** decreases upon an increase in acidity.[33] This is not the case for cavitand **24b**, having longer $-(CH_2)_n-$ chains; its D_{Am} is higher at concentrations $\geqslant 0.1$ M HNO_3. The rigidity of the cavitand platform does not allow for a good metal–ligand interaction in the 1,3-substituted CMPO-cavitand **25a**, which is a much weaker extractant (5.5 times lower D_{Eu}) than the 1,2-derivative **25b**.[34] The coordination stoichiometry of the tetrasubstituted cavitand **24a** with Eu^{3+} is either in a 1 : 1 or 1 : 2 (metal : ligand) fashion, dependent on the ligand concentration.[34] IR-measurements show that in the 1 : 1 complex the carbonyl oxygens are also binding to the metal as concluded by a shift of the $\upsilon_{C=O}$ stretching vibration to a lower value upon complexation. In the 2 : 1 complex, however, the CMPO moieties coordinate mainly with the stronger donating phosphoryl oxygens, allowing another ligand to participate. Confining chelating groups in close proximity on a platform can also enhance the intramolecular interaction between the chelating groups. The extraction of Eu(III) is considerably improved by *N*-propylation of the amide. Beside the increased basicity and lipophilicity of **24c**, the increase in extraction was also attributed to the absence of intramolecular hydrogen bonding between the CMPO moieties, which makes rearrangements of the chelating groups and breaking of hydrogen bonds as for **24a,b** before complex formation, unnecessary.

There are no studies to improve the extraction efficiency by the introduction of lipophilic groups. However, the distribution factors of *N*-acylthiourea-cavitands, which otherwise do not extract Am(III) and Eu(III) at all, and CMPO-cavitands are greatly improved by the addition of Br_6-COSAN as a synergist.[33]

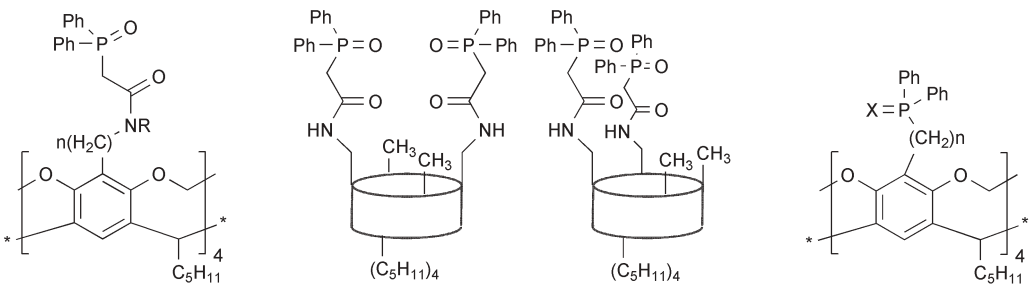
Cavitands functionalized with monodentate coordinating groups have also been studied by our group.[35] Phosphane sulfides were chosen because of their higher stability compared to dithiophosphinic acids. The lower complexation strength of the former would be compensated by preorganization of the moieties. However, only low extraction efficiencies and selectivities were obtained for phosphane sulfide cavitand **26a** ($D_{Am} = 0.032$, $S_{Am/Eu} = 1.7$, 10^{-3} M HNO_3) and no extraction was observed for **26b** ($D < 10^{-3}$). Also phosphine oxide moieties were used as monodentate coordinating groups.[34] Surprisingly, the influence of the $-(CH_2)_n-$ spacer length on the extraction efficiency was reversed in the case of phosphine oxide cavitand **27a**, having the shortest spacer; the amount of extracted metal ion is less compared to **27b**. Apparently, the smaller oxygen *vs*. sulfur is not sufficiently reachable to form a strong metal bond in the tight preorganization of **27a**. The above "spacer length" effect is an example of the necessity of a proper combination of a platform (including spacer) and a chelating group in order to obtain a good multicoordinate ligand. In other words, each coordinating group demands custom preorganization.

3.2 C_3-Symmetric platforms

Only three CMPO moieties are necessary for the coordination of a metal ion. The following sections outline platforms which serve as a base for three arm constructs in multicoordinate An(III) ligands.

3.2.1 Trityls

The triphenoxymethane platform (**28**, Chart 12) also referred to as the trityl platform can be conformationally locked, such that the three hydroxyl groups point in the same direction, by



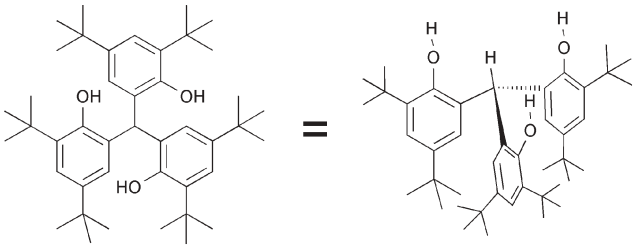
24a n = 1, R = H
24b n = 3, R = H
24c n = 1, R = propyl

25a

25b

26a n = 1, X = S
26b n = 4, X = S
27a n = 1, X = O
27b n = 4, X = O

Chart 11



28 28

Chart 12

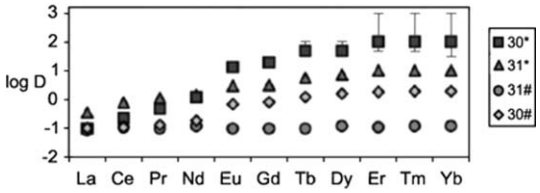


Fig. 1 Extraction of Ln(III) into CH_2Cl_2 solution at 1 M HNO_3 with ligand **31**; $c_L = 3 \times 10^{-3}$ M (**31***) or $c_L = 3 \times 10^{-4}$ M (**31#**), and with ligand **30**; $c_L = 3 \times 10^{-3}$ M (**30***) or $c_L = 3 \times 10^{-4}$ M (**30#**).

substituting the *m*-position of the benzene ring with a (sterically) bulky group.[36]

Scott *et al.* attempted to mimic the 3 : 1 CMPO : metal stoichiometry[36] by preorganizing CMPO groups on the trityl platform. From an X-ray crystal structure of trityl **29** (Chart 13) it is clear that the CMPO-groups are oriented all up for cooperative binding. Am(III) extraction experiments have not been performed using ligand **29**. However, Eu(III) extractions gave a D_{Eu} of only 0.031 ($c_L = 10^{-3}$ M, 1 M HNO_3, CH_2Cl_2). A structurally modified trityl derivative was immobilized on Tentagel resin to serve as a scaffold for the generation of libraries. The CMPO-derivative of this immobilized scaffold extracted Am(III) with a slight preference over Eu(III).[37]

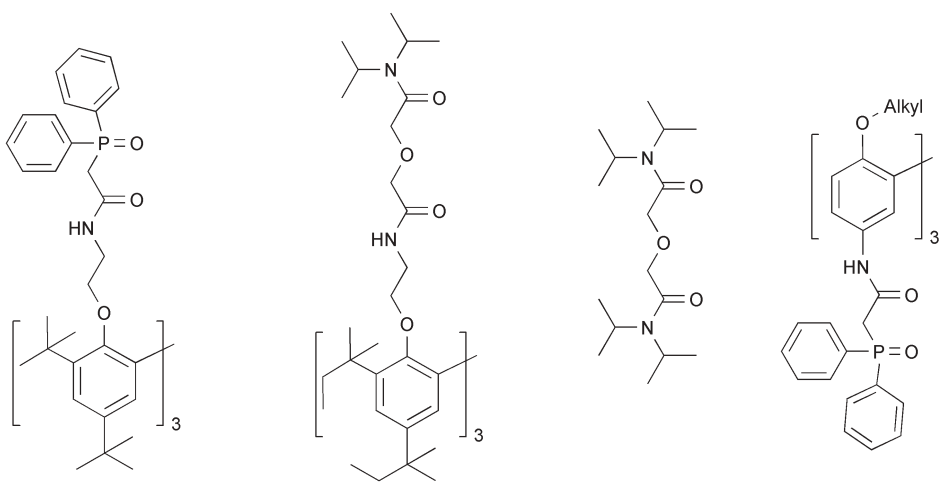
Ligand **30** consists of a slightly more lipophilic trityl platform with DGA (diglycolamide) chelating groups preorganized onto it.[38] X-Ray crystal structures of **30** and **31** with Yb(III) show that the DGA chelating groups maintain the same coordination environment. Whether preorganized or not, the metal–oxygen bond distances are virtually the same. Ligand **30** has a selectivity for Eu(III) over Am(III) ($D_{Am} >$ 100, average $S_{Eu/Am} = 6.16$, $c_L = 10^{-3}$ M, 3 M HNO_3, CH_2Cl_2) which is slightly higher than for simple DGA chelators (*i.e.* $S_{Eu/Am} = 3.43$ in DCE (1,2-dichloroethane) and 0.81 in $CHCl_3$). The multicoordinate ligand **30** has an increased ion size selectivity as compared to the "free" DGA **31**. From Fig. 1 it is clear that the affinity for the heavier lanthanides is preferred over that of the lighter lanthanides.

The organic phase has a pronounced effect on the extraction properties of the ligand. For the above described example in 1-octanol the selectivity shifts towards Eu(III). The solvent effect is much less pronounced for the un-preorganized ligand **31**.

Böhmer *et al.*[39] used the trityl platform for the preorganization of CMPO groups at the 'opposite' site of the molecule directly on the phenyl rings, comparable with most wide rim CMPO calix[4]arenes. According to *ab initio* modeling studies trityl-CMPO derivative **32** should be well adapted to form stable 1 : 1 inclusion complexes like ligand **29**. The extraction efficiency of trityl **32** ($D \sim 18$, $c_L = 10^{-3}$ M, 1 M HNO_3, CH_2Cl_2) is less than that of the corresponding calixarene **15**; the $S_{Am/Eu}$ is about 2 over the whole range of nitric acid concentrations. Interestingly, **32** does not give an extraction maximum at 1–2 M HNO_3 as with **15**, nor an increase in D_{Am} upon increase of the HNO_3 concentration as observed for CMPO-calix[4]arene **18**, but a drastic lowering of the D_{Am} value is observed to a minimum at 4 M HNO_3.

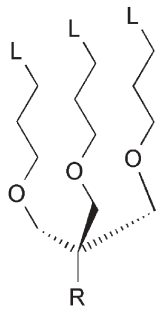
3.2.2 Tripodands. The conformationally most flexible C_3-symmetric platforms are the tripodands **33** (Chart 14), which consist of a central carbon atom, substituted with three identical arms that can be functionalized with chelating groups L and one substituent R which can function as a solubility modifier.

The high flexibility of the tripodal platforms does not abstain them from contributing to a positive effect on the



29 30 31 32

Chart 13



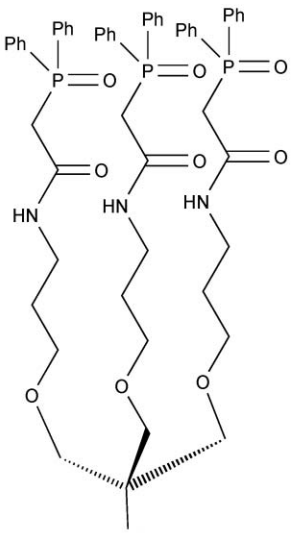
33

Chart 14

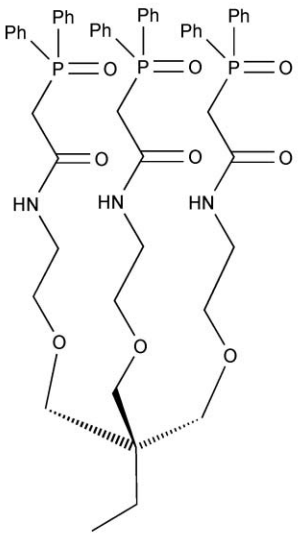
extraction efficiency of the chelating sites.[40] The extraction efficiencies of CMPO-functionalized tripodands **34** are higher in TCE (tetrachloroethane) with an average $D_{Am} \approx 0.6$ ($c_L = 10^{-3}$ M, 1 M HNO_3) than in 1-octanol (average $D_{Am} \approx 7.5 \times 10^{-3}$, $c_L = 10^{-3}$ M, 1.4 M HNO_3).[40] When in the latter case the [HNO_3] is raised to 2.9 M, there is a twofold increase in D_{Am}. Shortening of the $-(CH_2)_n-$ spacer by one carbon as in **35** resulted in a slight decrease of D_{Am}, whereas the $S_{Am/Eu}$ remains the same. There are only small differences in the extraction efficiencies of **34a**–**34c** (Chart 15), which differ in their lipophilicity. In contrast, the attachment of a COSAN moiety (**36**), which not only functions as a lipophilic group, but also as a counterion, increases the D_{Eu} and D_{Am} considerably at lower acidities [HNO_3] $\ll$ 1 M.

3.2.3 Silica/magnetic particles. The covalent attachment of chelating groups to (magnetic) silica particles aids in the extraction of Am(III). The ordering and mutual distances of the chelating groups on the surface of these particles is not precisely known. It is very likely that the chelating groups are situated next to each other, thus, in principle, these particles can be considered as a sort of platform on which the chelating groups are preorganized. The modification of these particles by the introduction of chelating group containing calixarenes,[41] tripodands,[40] dendrimers[42] or tetraazamacrocycles[43] gives rise to an even higher extraction efficiency. The advantage of these functionalized particles is that they can easily be removed either by filtration or by applying a magnetic field.

The extraction efficiency for solid-phase bound particles is characterized by a modified distribution ratio K_D, which is defined as $K_D = ((c_{L,0} - c_L)/c_L) \times V_L/m_S$, where $c_{L,0}$ is the starting concentration, m_S the total mass of the magnetic



34a $R^1 = C_2H_5$
34b $R^1 = NHC(O)C_8H_{19}$
34c $R^1 = NHC(O)C_{13}H_{27}$



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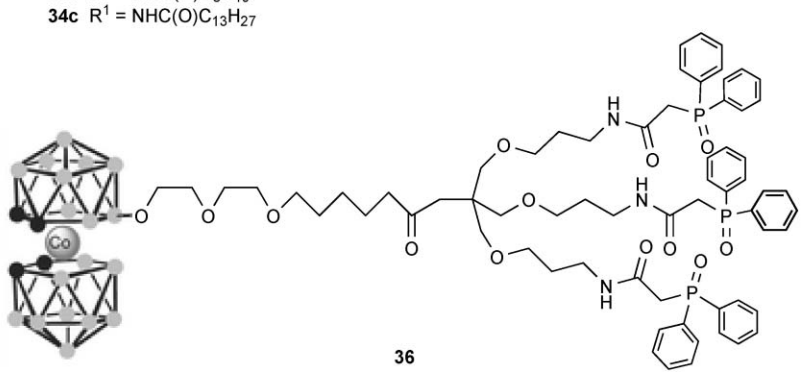
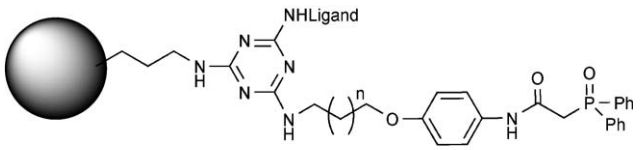


36

Chart 15



37a n = 1
37b n = 3

Chart 16

particles, V_L the volume of the radionuclide solution, and c_L the final activity of the radionuclide solution.

The extraction efficiency of CMPO groups directly attached to a magnetic particle is influenced by its $-(CH_2)_n-$ spacer length.[39] The K_D of particle **37b** (n = 3, Chart 16) being 26 at 3 M HNO_3 is ten times larger than that of **37a**. Presumably this is caused by the increased mobility of the CMPO groups on the surface making a cooperative binding of several groups to one cation possible. For systems where the ligating groups are preorganized onto a calixarene which itself is attached to a magnetic particle (attached *via* the lower rim) this is reversed; a shorter $-(CH_2)_n-$ spacer length gives rise to a higher K_D. It is not entirely clear what causes this. Changes in complex stoichiometry or even polymeric species could be involved or it could be just the result of a simple change in rigidity of the macrocyclic ring as longer spacers allow for more flexibility. The selectivity changes of the above discussed particles show no definite trend; it ranges between $S_{Am/Eu}$ = 1.6–2.8. Magnetic particles functionalized with tripodand ligands analogous to **34** have a K_D of lower than 1 at 3 M HNO_3 and this increases to 1359 at 0.01 M HNO_3.[40] Much more interesting is the selectivity as a function of the acidity, in 1 M HNO_3 $S_{Am/Eu}$ = 1.4 *via* $S_{Am/Eu}$ = 0.27 at 0.1 M HNO_3 to 1.1 in 0.01 M HNO_3. Usually, selectivities for CMPO-derivatives are continuous over a pH-range, so it should be questioned whether the metal is coordinated only by the CMPO moieties or also elsewhere.

Very high densities of chelating groups are obtained when dendrimers are used as a platform. Up to 64 either CMPO **38a**, PICO **38b** or DGA **38c** (Chart 17) chelating groups were attached to a 5th generation dendrimer (shown for the 4th generation) and subsequently coated on magnetic particles.[40] The dendrimers with the CMPO groups have a $S_{Am/Eu} \approx 2$, while those with the PICO moieties have a higher selectivity ($S_{Am/Eu}$ up to 3.5), although these lose their extraction power upon increasing the acidity. The DGA functionalized dendrimers show the highest increase in extraction and have a selectivity for Eu(III) ($S_{Am/Eu} \approx 0.3$). The gain in extraction efficiency using a dendrimer spacer between the chelator and the particle is not necessarily linearly increasing when using higher generations of dendrimers. For the PICO-functionalized dendrimers the K_D value decreases on going from the 3rd to the 4th generation dendrimer. This is attributed to steric disturbances of the radionuclide complexation due to the high chelator density on the surface. This phenomenon is also observed for the 3rd generation CMPO-functionalized dendrimers. When the surface concentration is higher, lower K_D values are obtained. The DGA derivatives do not show this behavior, which means that it is dependent on the chelating group. This underlines the fact that in a multicoordinate ligand the platform and the chelator depend mutually on one another and only a good match gives good results as described for the cavitands **26** and **27** (*vide supra*).

4. Conclusions and outlook

The separation of An(III) from Ln(III) cations remains a challenging problem. However, the preorganization of chelating groups onto a platform or suitable particles is an efficient way of improving the metal ion extraction efficiency and selectivity. As a result of preorganization a larger number of coordinating atoms is present in the coordination sphere of the metal ion. A larger number usually results in a higher extraction efficiency, although, oversaturation and steric interferences between the chelating groups may give an adverse effect as *e.g.* in the case of dendrimers. Since the processes that take place during the extraction of metal ions from aqueous nuclear waste solutions are very complex, the precise structures of the extracted species are often not known. This makes it difficult to give a theoretical explanation of the observed extraction results and makes the design and synthesis of better multicoordinate ligands essentially a matter of trial and error. For instance, the preorganization of three CMPO groups onto a trityl or tripodal platform to match the Am(III) coordination stoichiometry did not result in a significant extraction improvement as compared to the calixarenes. The extra CMPO group in the calix[4]arenes is of use at high [HNO_3] when protonation of the coordinating atoms is significant. This could be one of the reasons why the upper rim CMPO-functionalized calix[4]arenes give higher $S_{Am/Eu}$ (>10) values. Furthermore, the formation of complexes having different stoichiometries, the formation of oligomeric species or aggregrates, are responsible for extraction properties observed that differ from what might be expected on structural

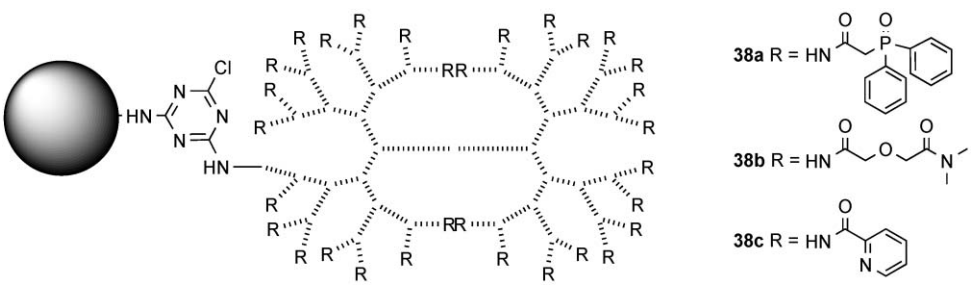


Chart 17

considerations. Nevertheless, some general observations can be made: the elongation of the $-(CH_2)_n-$ spacer between platform and chelating group and the attachment of lipophilic groups or solid particles give rise to an increase in D_{Am}. Designing multicoordinate ligands with an improved Am(III) selectivity is a more difficult and challenging task. In this respect there are no distinguishable trends that can be observed. High Am(III) selectivities are more easily obtained by using ligands that coordinate with softer donors like nitrogen or sulfur. Unfortunately, this type of ligands face problems such as protonation and oxidative degradation at higher [HNO_3], resulting in lower D_{Am} values. The preorganization of picolinamide groups onto calixarenes did result in a higher D_{Am}, although still suffered considerably from protonation.

It is clear that the structural confinement of the platform influences the preorganization. Only an optimal balance between the conformation of a platform and the chelating groups leads to a satisfactory multicoordinate ligand, which relies on fine tuning between these two variables. A thorough knowledge of the complexation mechanisms is needed to be able to deliberately design an efficient multicoordinate ligand.

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