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Use of Soft Heterocyclic N-Donor Ligands To Separate Actinides and Lanthanides

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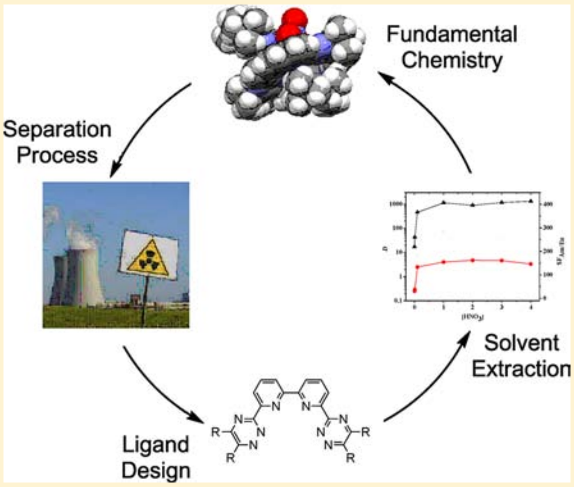
Supporting Information

ABSTRACT: The removal of the most long-lived radiotoxic elements from used nuclear fuel, minor actinides, is foreseen as an essential step toward increasing the public acceptance of nuclear energy as a key component of a low-carbon energy future. Once removed from the remaining used fuel, these elements can be used as fuel in their own right in fast reactors or converted into shorter-lived or stable elements by transmutation prior to geological disposal. The SANEX process is proposed to carry out this selective separation by solvent extraction. Recent efforts to develop reagents capable of separating the radioactive minor actinides from lanthanides as part of a future strategy for the management and reprocessing of used nuclear fuel are reviewed. The current strategies for the reprocessing of PUREX raffinate are summarized, and some guiding principles for the design of actinide-selective reagents are defined. The development and testing of different classes of solvent extraction reagent are then summarized, covering some of the earliest ligand designs right through to the current reagents of choice, bis(1,2,4-triazine) ligands. Finally, we summarize research aimed at developing a fundamental understanding of the underlying reasons for the excellent extraction capabilities and high actinide/lanthanide selectivities shown by this class of ligands and our recent efforts to immobilize these reagents onto solid phases.



1. INTRODUCTION

1.1. Background. One of the most important scientific, technological, and social challenges that faces humanity today is to render nuclear waste to be as safe as possible. As many countries consider expanding their civil nuclear power programs to meet their energy needs,[1] it becomes increasingly important to develop processes that reduce the radioactivity of nuclear waste. In order to obtain energy from fissile nuclei such as ^{237}U and ^{239}Pu, the nuclei are irradiated with neutrons such that the branch chain reaction leads to the required energy but fission products such as the lanthanides (Ln or rare earths) and minor actinides (An) are also produced. As shown in Figure 1, thermal fission of ^{235}U produces many fission products including those ranging in mass number from 75 (As) to 160 (Tb) following the removal of fuel rods from a nuclear reactor core. Currently, the PUREX (Plutonium and URanium EXtraction) process is used worldwide to remove Pu and U from the spent fuel, so that it can then be recycled and reused as mixed oxide (MOX) fuel.[2] The remainder of the waste contains the minor actinides that account for much of the long-term radiotoxicity of used nuclear fuel.

The processed nuclear fuel could be stored in a deep geological depository but the fuel will remain radioactive for millions of years, and storage of radioactive spent fuel is not favored by the public. An alternative method has been studied whereby the spent fuel can be treated so as to render it safe and more suitable for geological storage. The problems of the radioactive nature of the spent fuel arise from the long-lived (>10^3−10^6 years) radioactive elements in spent nuclear fuels. Figure 2 shows the rate of decay of spent nuclear fuel with time. It is evident that removal of U and Pu reduces the radiotoxicity considerably but additional removal of the minor actinides would allow the remaining waste to reach the level of natural U within 300 years, as opposed to 9000 years. The principal long-term loadings thus arise from isotopes of the minor actinides americium (Am) and curium (Cm), even though these elements (together with neptunium) comprise only 0.1% by mass of the waste (Figure 3). Recent studies have shown, however, that they can be removed by partitioning of the minor actinides from fission products such as the rare earths in a solvent extraction process. The separation of the minor actinides from the lanthanides is a necessary step because the ratio of An/Ln is ca. 1:40 and the effective neutron capture radii of the lanthanides are much greater than those of the minor actinides. Once separated and concentrated as oxides, irradiation by high-energy neutrons can transmute the long-

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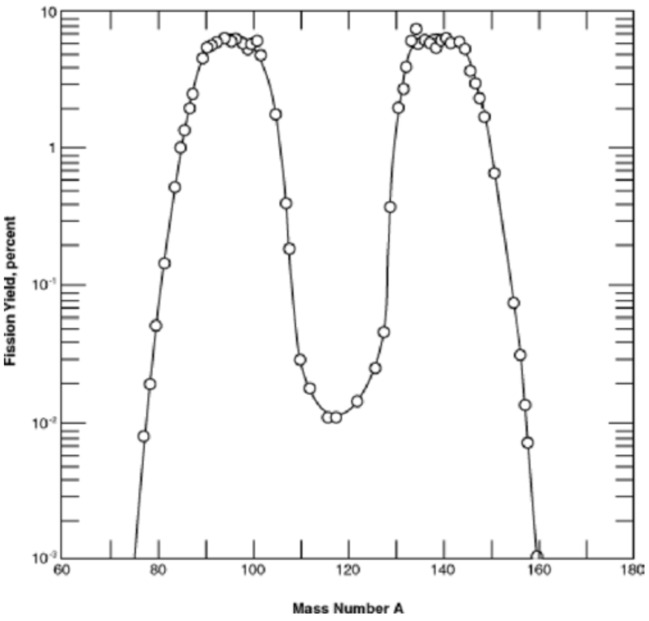


Figure 1. Fission yield curve for the thermal neutron fission of ^{235}U after ca. 100 days of cooling. The curve on the left corresponds to the transition metals, and the curve on the right corresponds to the lanthanides. This curve does not include volatile elements and the minor actinides.

lived isotopes of Am and Cm to short-lived or stable ones.[3] The combined processes of partitioning and transmutation (P and T) aim to significantly reduce the storage time needed for radioactive spent fuel and have thus been the subjects of much detailed research. Here we discuss some of the principal developments that have taken place with respect to partitioning in relation to the development of fundamental research, which leads to viable processes for P and T.

Historically, two main sequential processes have been studied for removal of the minor actinides from PUREX waste solutions. In the first step, both An^{III} and Ln^{III} are coextracted from the remaining waste, followed by the separation of An^{III} from Ln^{III}.[4] Reagents suitable for use in the first step have been developed and are typically based on bidentate chelating hard O-donor ligands. For example, in the United States, the TRUEX (TRansUranic EXtraction) process[5] using [(*N*,*N*-diisobutylcarbamoyl)methyl](octyl)phenylphosphine oxide (CMPO) as the extractant has been extensively studied for An^{III}/Ln^{III} coextraction from high-level waste. In France and Japan, bidentate diamide and diglycolamide ligands have been developed for the An^{III}/Ln^{III} coextraction step (the DIAMEX process).[6] The current reference molecules are *N*,*N*′-dimethyl-*N*,*N*′-dioctyl[(hexyloxy)ethyl]malonamide (DMDOHEMA), and *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA). Ligands composed of soft N- and S-donor atoms have been the focus of research to carry out the more challenging An^{III}/Ln^{III} separation in the second step. In Europe, the SANEX (Selective ActiNide EXtraction) process has been proposed to perform this separation using hydrophobic N-donor ligands,[7] while in the United States, the TALSPEAK process aims to separate An^{III} from Ln^{III} by selective back-extraction (or stripping) of An^{III} following an initial TRUEX separation step.[8]

1.2. Ligand Design.

Previously, prior to the 1980s, the partitioning of An^{III} from Ln^{III} had been regarded as being very difficult, if not impossible, to achieve. Both Am^{III} and Cm^{III} have chemical properties similar to those of each other and also La^{III} and the lanthanides Ce^{III} to Lu^{III}.[9] The predominant cationic charge for all is M^{III}; the ionic radii (ca. 0.1 nm)[10] are similar; the type of bonding in the complexes is essentially ionic; the coordination numbers are not rigid, and there is flexibility in the arrangement of the ligands around the metal cations. In order to devise a molecule able to separate Am^{III} from Eu^{III}, therefore, there appeared to be little in the way of differences in the chemistry between the two elements to help in the design of the molecule. However, the interactions between Am^{III} and soft N-donor heterocycles could be considered to be more covalent than those with Eu^{III}, and it is believed there is a greater covalent interaction between these ligands and the 5f orbitals of the actinides than with the 4f orbitals of the lanthanides. The exact origin of this covalency effect is still the subject of ongoing debate and is rather poorly understood.[11] Experiment has moved far in advance of theory in this area, and deeper theoretical studies are needed to further our understanding. The 4f orbitals of the lanthanides are embedded in the core of the atom and play less of a role in metal−ligand bonding.

Any reagent chosen for use in a SANEX process must fulfill several challenging criteria.[12] Obviously, the reagent should show a good level of selectivity toward the actinides so that the separation process can be composed of as few stages as possible. The solubility of both the reagent and its extracted

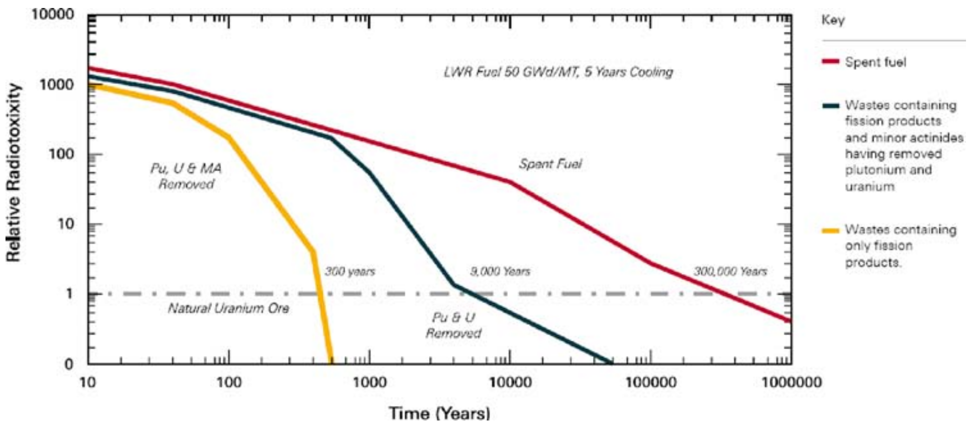
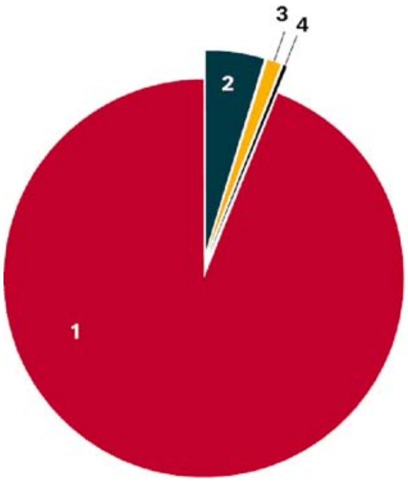


Figure 2. Relative radioactive decay of spent nuclear fuel as a function of time. Reproduced with permission from The Royal Society Science Policy Centre Report 10/11, Oct 2011; ISBN 978-0-85403-891-6.



Spent fuel contains approximately:

1 94% by mass of uranium (U) with an enrichment level at or slightly above that of natural uranium;

2 4-5% of fission products, including strontium (Sr), caesium (Cs), iodine (I) and technetium (Tc).

3 1% plutonium (Pu)

4 0.1% other minor actinides, such as neptunium (Np), americium (Am) and curium (Cm)

Key

1 Uranium	-94%
U-235	-0.7%
U-238	-93%

2 Fission Products	-4-5%
Sr-90	0.1%
Cs-137	0.2%
I-129	0.03%
Tc-99	0.1%

3 Plutonium	-1%
Pu-238	0.04%
Pu-239	0.7%
Pu-240	0.3%
Pu-241	0.2%
Pu-242	0.1%

4 Minor Actinides	-0.1%
Np-237	0.07%
Am-241	0.03%
Cm-244	0.01%

Figure 3. Approximate composition of spent nuclear fuel. Reproduced with permission from The Royal Society Science Policy Centre Report 10/11, Oct 2011; ISBN 978-0-85403-891-6.

complexes in the organic phase should be high to minimize the possibility of third-phase formation or precipitation. The reagent must show a sufficiently high level of resistance toward acid hydrolysis and radiolysis, and any degradation products formed must not interfere with the separation process to any significant degree. The reagent should be able to extract from nitric acid solutions of low pH ($\leq$4 M HNO_3) that are produced in the PUREX process. If possible, the reagent should only be composed of the elements C, H, N, and O so that any spent solid residues or solvent streams may be incinerated without producing corrosive products at the end of their useful life. Finally, to permit large-scale production, the synthesis of the reagent should be as cost-effective and practical as possible.

Considerable effort has been devoted to the design, synthesis, and evaluation of soft N- and S-donor ligands in order to carry out this challenging separation in recent decades.[13] We have recently reviewed in detail the development of soft N- and S-donor ligands in Europe for the partitioning of actinides from lanthanides in a future SANEX process.[14] Herein we provide an overview of the use of soft N-donor ligands for separating actinides from lanthanides and some guiding principles for the design of ligands suitable for this purpose.

1.3. Early N-Donor Ligand Designs.

Since the 1980s, a range of tridentate N-donor ligands based on 2,2′:6′,2″-terpyridine were evaluated as selective An^{III} extractants. Selected examples of these ligands are gathered in Figure 4. In initial solvent extraction tests, 2,2′:6′,2″-terpyridine **1** itself showed promising selectivity ($SF_{Am/Eu}$ = 7.2) in the extraction of Am^{III} and Eu^{III} from dilute (0.1 M) nitric acid solutions into hydrogenated tetrapropene (TPH) in the presence of 2-bromodecanoic acid.[15] Unfortunately, no extraction was observed in the absence of the synergist or from more concentrated (>0.1 M HNO_3) nitric acid solutions. More hydrophobic 2,2′:6′,2″-terpyridine derivatives **2**−**6** were even less promising and afforded lower Am^{III} distribution ratios than 2,2′:6′,2″-terpyridine **1** at comparable acidities.[16] This was attributed to an increase in the basicities of ligands **2**−**6** caused by alkyl substitution so that protonation of the ligands occurred rather than metal-ion coordination. Owing to these difficulties, this family of ligands was not developed further toward a separation process.

To overcome the high basicity of 2,2′:6′,2″-terpyridine and its derivatives, 2,4,6-tri-2-pyridyl-1,3,5-triazine (TPTZ) **7** was developed. The central 1,3,5-triazine ring of **7** was designed to lower the basicity of 2,2′:6′,2″-terpyridine **1** and enable extraction from more concentrated nitric acid solutions. Slightly higher *D* values and higher selectivities ($SF_{Am/Eu}$ > 10) were found for **7** and its more hydrophobic derivative **8** than **1** in initial extraction tests under the same conditions, although no significant extraction was observed from >0.1 M HNO_3. Nevertheless, in a laboratory-scale An^{III}/Ln^{III} group separation process demonstration using mixer settlers, 99.9% of Am^{III} was recovered from 0.125 M HNO_3 spiked with Am^{III}, Eu^{III}, and Ce^{III} tracers using TPTZ **7** as the extractant and dinonylnaphthalenesulfonic acid as the synergist.[17]

Following these results, the related 4-amino-2,6-di-2-pyridyl-1,3,5-triazine (ADPTZ) ligands **9**−**13** were synthesized and studied. Although ADPTZ **9** and its amido-functionalized derivatives **10**−**13** efficiently extracted Am^{III} from dilute nitric acid solutions in synergistic combination with 2-bromodecanoic acid, the extraction decreased at higher (>0.1 M HNO_3) acidities.[18] After a process flowsheet had been designed, the most promising ligand **13** was employed in a 32-stage spiked test in laboratory-scale mixer settlers at the CEA, with good results (>99.9% Am^{III} and Cm^{III} recovered and separated from the lanthanides),[19] although the need to buffer the feed solution with glycolic acid/sodium glycolate was an obvious disadvantage.

Another family of ligands to show encouraging results is that based on 2,6-bis(benzoxazol-2-yl)pyridine **14**. Tridentate ligands **14**−**24** containing benzoxazole, benzimidazole, and benzothiazole moieties were synthesized and evaluated in Am^{III}/Eu^{III} solvent extraction experiments.[20] The most promising ligands of this family were dodecyl-substituted **16** (BODO) and its branched derivative **24**. These ligands showed superior selectivities compared to those based on 2,2′:6′,2″-terpyridine **1** or TPTZ **7** ($SF_{Am/Eu} \leq 79$), but once again the ligands could not extract from nitric acid solutions of pH relevant to a separation process.[21]

The related tridentate pyridine ligands **25**−**38** containing lateral five-membered heterocyclic rings were also studied. The bis(oxadiazolyl)pyridine ligands **28**−**31** and **33**−**38** did not show encouraging results and only weakly extracted Am^{III} as monosolvates from dilute nitric acid solutions into toluene, chlorobenzene, or *tert*-butylbenzene with modest selectivities ($1.5 \leq SF_{Am/Eu} \leq 19.6$).[22] In contrast, the bis(1,2,4-triazol-3-

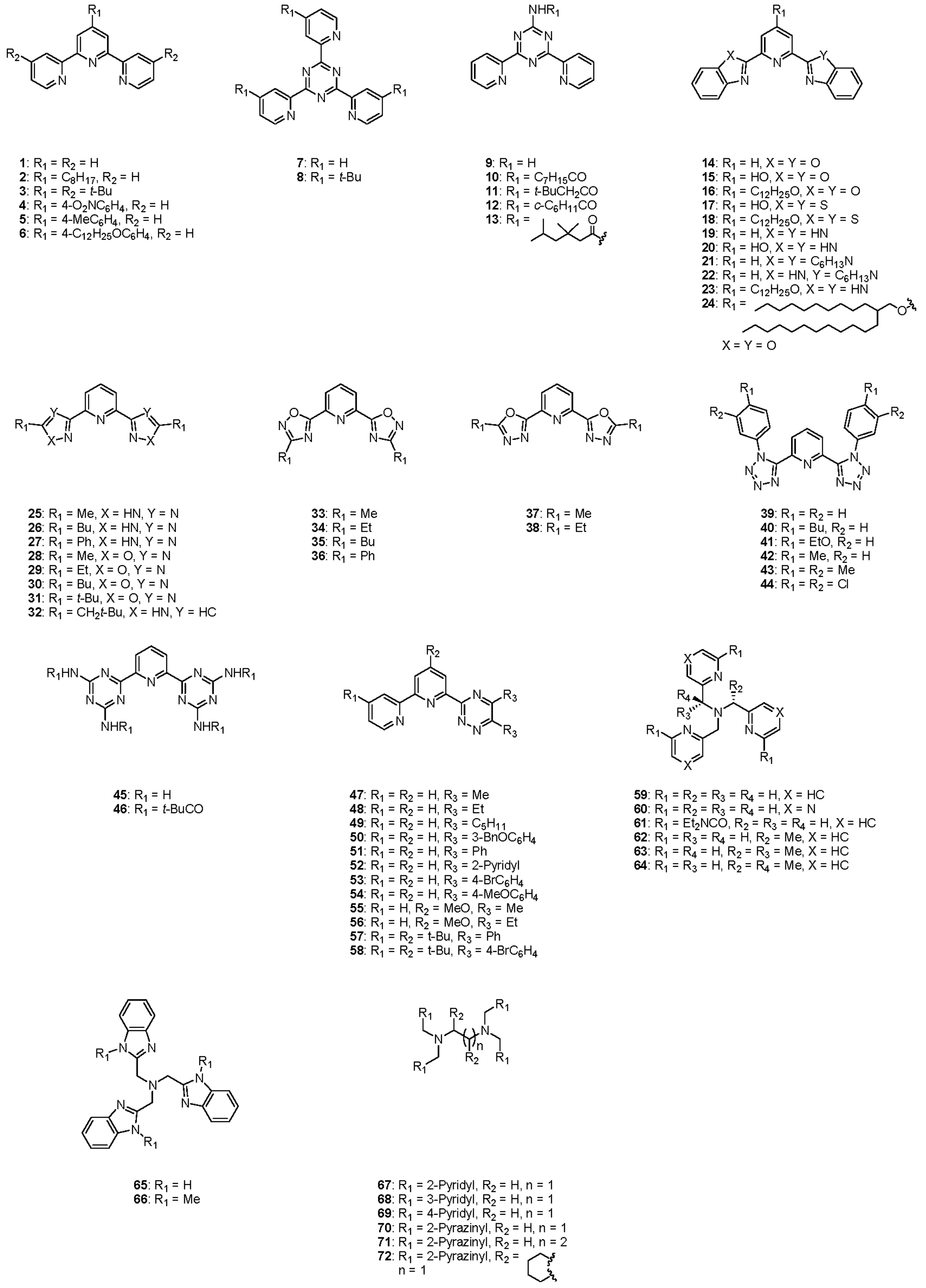


Figure 4. Structures of representative early N-donor ligand designs studied for the separation of actinides from lanthanides.

yl)pyridines **25**−**27** could extract Am^{III} very efficiently (D_{Am} approximately 200 for **25**) and selectively ($SF_{Am/Eu}$ = 55 for **25**) from dilute nitric acid into TPH under similar conditions in the presence of 2-bromohexanoic acid,[23] while 2,6-bis(5-(2,2-dimethylpropyl)-1*H*-pyrazol-3-yl)pyridine **32** also showed encouraging extraction results at low acidities ($SF_{Am/Eu}$ = ca. 100; $[HNO_3] < 1$ M).[24] Similarly, 2,6-bis(1-aryl-1*H*-tetrazol-5-yl)pyridines **39**−**44** were highly efficient and selective ($D_{Am} \leq 50$; $SF_{Am/Eu} \leq 100$) extractants of Am^{III} when dissolved in fluorinated diluents in combination with chlorinated cobalt dicarbollide.[25]

In a combinatorial chemistry study,[26] the 6-(1,2,4-triazin-3-yl)-2,2′-bipyridine (hemi-BTP) ligands **47**−**58** were identified as potential candidates for An/Ln separation. However, despite good selectivities being observed (e.g., $SF_{Am/Eu} \leq 30$ for **48**), the ligands resembled 2,2′:6′,2″-terpyridine **1** in their extraction properties and could only extract from weakly acidic nitric acid

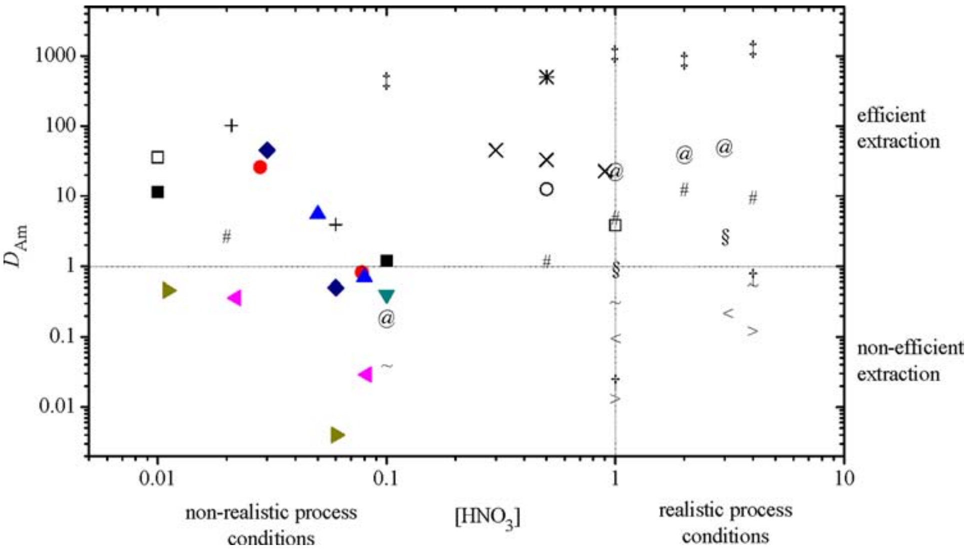


Figure 5. Distribution ratios for Am^{III} as a function of the nitric acid concentration for different classes of N-donor ligands. The graph is arbitrarily divided into regions based on the criteria of extraction efficiency and acidity. Ligands in the top right-hand part are able to extract Am^{III} efficiently ($D_{Am} \geq 1$) under realistic ($[HNO_3] \geq 1$) process conditions (key: ■ = **1**, ● = **7**, ▲ = **9**, ▼ = **10**, ◀ = **16**, ▶ = **60**, ◆ = **70**, + = **48**, × = **129**, * = **141**, ○ = **142**, □ = **149**, # = **151**, < = **160**, > = **153**, † = **154**, ‡ = **159**, ∼ = **155**, and @ = **156** in cyclohexanone; § = **156** in 1-octanol). See the Supporting Information for extraction conditions.

solutions in the presence of the synergist 2-bromodecanoic acid or chlorinated cobalt dicarbollide.[27]

Examples of nonplanar podand N-donor ligands include those based on tridentate tris(2-pyridylmethyl)amine **59** and hexadentate *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethane-1,2-diamine (TPEN) **67**. In solvent extraction tests, tris(2-pyridylmethyl)amine ligands **59**−**64** performed very similarly to many tridentate planar heterocyclic N-donor ligands discussed previously. The pyrazine ligand **60** showed better results than the pyridine ligand **59** in the extraction of Am^{III} into TPH containing 2-bromodecanoic acid,[28] while chiral ligands **62**−**64** efficiently extracted Am^{III} into nitrobenzene at pH > 4.7.[29] However, protonation of the ligands prevented extraction from solutions of lower pH.

Extraction results with hexadentate TPEN ligands were more promising. For example, TPEN **67** could selectively extract Am^{III} from ammonium nitrate solutions into nitrobenzene without the need for a synergist (D_{Am} = ∼100; $SF_{Am/Eu}$ = ∼100),[30] while similar results were obtained in 1-octanol in the presence of decanoic acid. Comparable results were observed with the softer ligand *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazinylmethyl)-ethane-1,2-diamine **70**. Interestingly, its more flexible derivative **71** showed better extraction capability but almost no selectivity ($SF_{Am/Eu} \leq 2.3$) under the same conditions, while the more rigid ligand **72** failed to extract either Am^{III} or Eu^{III}.[31]

Various fundamental studies have been carried out aimed at understanding the molecular basis of the observed separations (or lack thereof). In particular, the structures and stoichiometries of the formed metal complexes have been probed by various techniques, including X-ray crystallography, lanthanide NMR studies, electrospray ionization mass spectrometry (ESI-MS), and slope analysis of solvent extraction data. X-ray crystallographic studies show that many of the tridentate N-donor ligands discussed here only form 1:1 complexes with trivalent lanthanide nitrates in which the remainder of the metals inner coordination sphere occupied by nitrate ions and/or water molecules. This is true for 2,2′:6′,2″-terpyridine **1**,[16] TPTZ **7**,[32] ADPTZ **9**,[33] and BODO **16**.[20] Exceptions include the formation of 1:2 complexes of **1** with Ce^{III}, U^{III}, and Nd^{III} under anhydrous conditions, as observed by ^1H NMR spectroscopy in deuterated pyridine and X-ray crystallography,[34] and the formation of both 1:1 and 1:2 complexes of the hemi-BTPs with La^{III} and Y^{III}, as revealed by ^1H NMR titrations in deuterated acetonitrile.[27a] In addition, the podand ligand **59** and benzimidazoles **65** and **66** have been shown by ^1H NMR spectroscopy to form both 1:1 and 1:2 complexes with U^{III} and La^{III}.[35] It should be noted here that the extraction properties of the above ligands are best interpreted by a combination of techniques. For example, while X-ray crystallography provides useful structural information on metal complexes, it does not always reflect the actual species formed in solution under extraction conditions.

It is clear that many of the N-donor ligands discussed above suffer from two main drawbacks: their inability to efficiently extract Am^{III} from acidic nitric acid solutions (>1 M HNO_3) and the need to use a hydrophobic anion source (e.g., 2-bromocarboxylic acids or chlorinated cobalt dicarbollide) as a synergist. Figure 5 shows the distribution ratios for Am^{III} as a function of $[HNO_3]$ for several classes of N-donor ligand. It can be seen that many N-donor ligands discussed here, with few exceptions, are unable to extract Am^{III} from nitric acid efficiently under realistic (≥1 M HNO_3) process conditions. These drawbacks are probably related to the high basicities of these ligands and/or the preferential formation of 1:1 complexes with An^{III}. Several of these ligands formed only 1:1 complexes in solution with Ln^{III}.[15b,22,27a,35b] Such complexes would not be very hydrophobic because the coordination sphere of the metal is not completely enclosed. Ultimately, these drawbacks render many of these ligands unsuitable for use in an industrial-scale SANEX separation process.

1.4. Mixed N- and O-Donor Ligands.

As mentioned previously, extensive work has shown that bidentate ligands containing hard O-donor atoms (e.g., CMPO, DMDOHEMA, TODGA) are able to coextract trivalent actinides and lanthanides from high-level liquid waste solutions in a highly

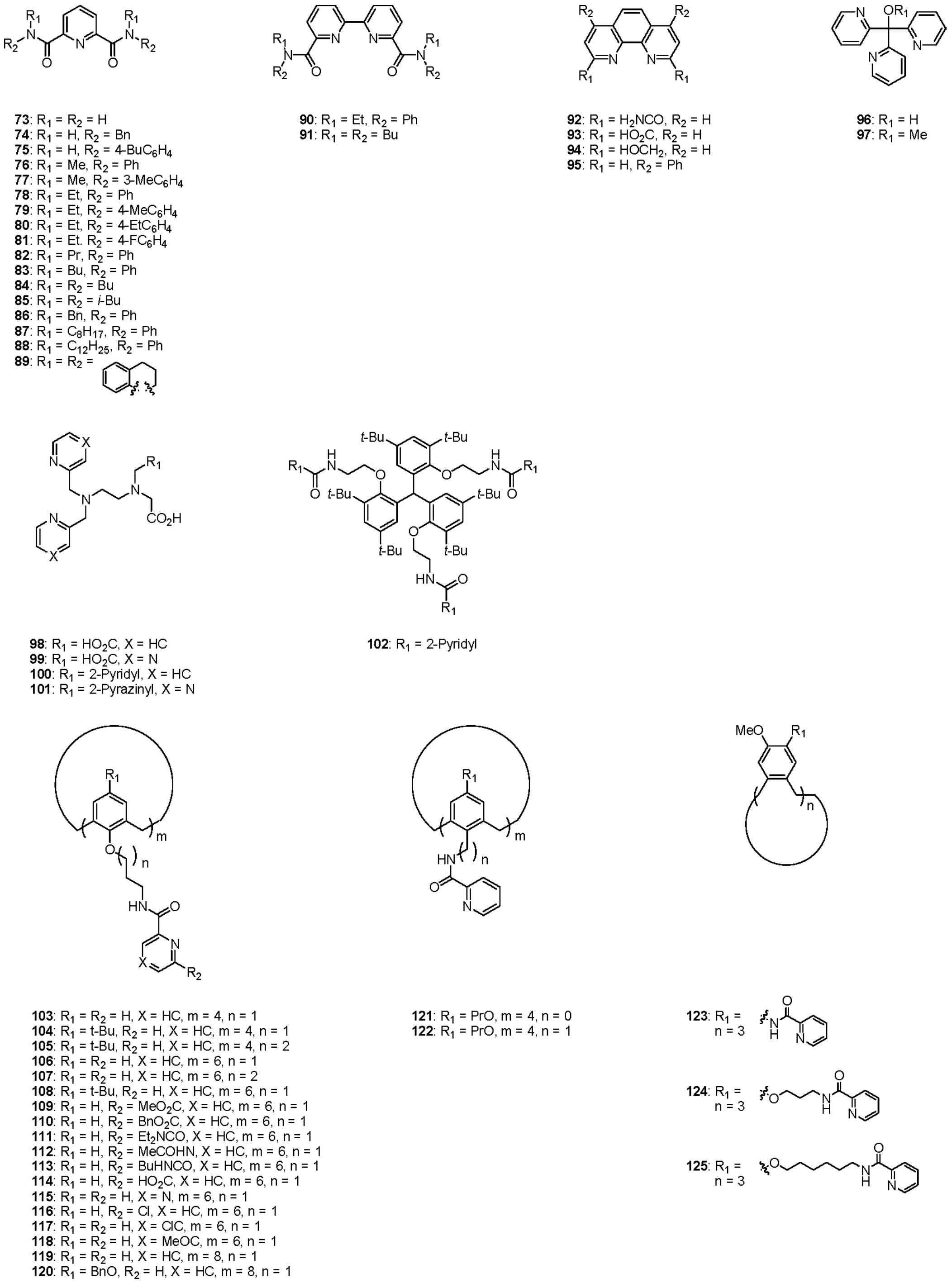


Figure 6. Structures of representative mixed N- and O-donor ligands studied for the separation of actinides from lanthanides.

efficient manner. To achieve an actinide-selective extraction, it was reasoned that ligands containing soft N-donor atoms in combination with hard O-donor atoms would be able to extract the actinides selectively, while still retaining the extraction efficiency characteristic of the hard O-donor ligands. Mixed N- and O-donor ligands have thus been extensively studied as potential ligands for selective actinide extraction. Representative examples of these ligands are gathered in Figure 6.

Early studies showed that bidentate dialkylamides derived from picolinic acid only weakly extracted Am^{III} from solutions of low acidity.[36] More recently, terdentate dipicolinamide derivatives **73–89** containing two amide groups have been investigated. An efficient extraction of U, Am, and Eu into polar fluorinated diluents (e.g., phenyltrifluoromethyl sulfone and 3-trifluoromethylnitrobenzene) was observed in many cases, especially from highly acidic (2–6 M HNO_3) solutions.[37] Furthermore, the extractions were mildly selective for Am over Eu ($SF_{Am/Eu} \leq 6$), showing a reversal of the modest selectivity for Eu over Am found for many of the O-donor ligands. Recent structure–activity relationships showed that substituents on the aromatic rings of the amido groups influence the distribution ratios of the extracted metals and the Am/Eu separation factor, with a linear correlation being observed between the extraction ability and the σ constants of the substituents.[38]

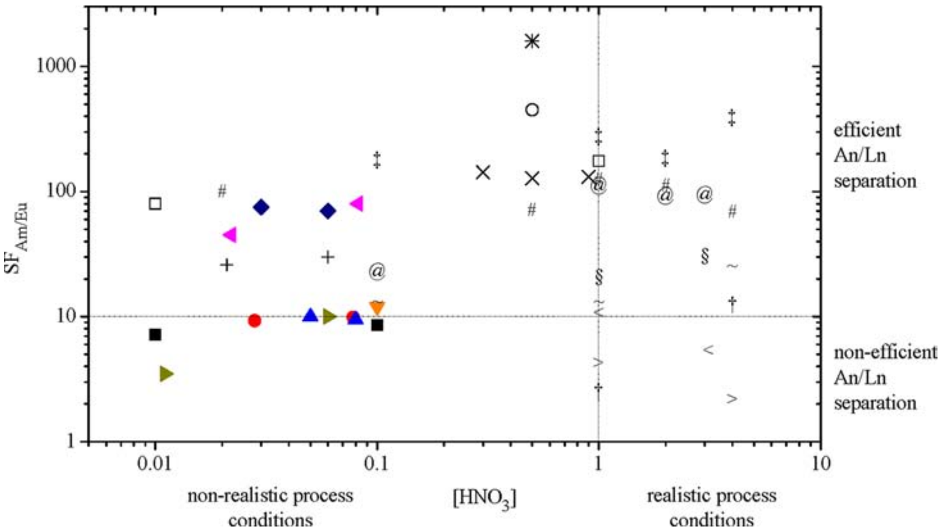


Figure 7. Separation factors of Am^{III} over Eu^{III} as a function of the nitric acid concentration for different classes of N-donor ligand. The graph is arbitrarily divided into regions based on the criteria of extraction selectivity and acidity. Ligands in the top right-hand part are able to separate Am^{III} from Eu^{III} efficiently ($SF_{Am/Eu} \geq 10$) under realistic ($[HNO_3] \geq 1$) process conditions (key: ■ = **1**, ● = **7**, ▲ = **9**, ▼ = **10**, ◀ = **16**, ▶ = **60**, ◆ = **70**, + = **48**, × = **129**, * = **141**, ○ = **142**, □ = **149**, # = **151**, < = **160**, > = **153**, † = **154**, ‡ = **159**, ~ = **155**, and @ = **156** in cyclohexanone; § = **156** in 1-octanol). See the Supporting Information for extraction conditions.

The modest selectivity for Am^{III} over Eu^{III} shown by the terdentate dipicolinamides can be enhanced by the addition of a second pyridine ring, giving rise to the quadridentate 2,2′-bipyridine-6,6′-dicarboxamides **90** and **91**. These ligands were found to be significantly more selective for Am over Eu ($SF_{Am/Eu} \leq 30$) than their terdentate counterparts when used in synergistic combination with the lipophilic anion source chlorinated cobalt dicarbollide in fluorinated diluents.[39] The efficiency of extraction of some fission products was also significantly enhanced, particularly in the case of Cd. Although the more preorganized quadridentate N- and O-donor ligands 2,9-bis(hydroxymethyl)-1,10-phenanthroline **94**[40] and 1,10-phenanthroline-2,9-dicarboxamide **92**[41] have been shown to have large stability constants for their lanthanide complexes, their solvent extraction properties have not yet been reported. The TPEN derivatives **98**−**101** constitute rare examples of water-soluble N- and O-donor complexing agents used for the selective stripping of Am from a loaded organic phase.[42]

In the search for greater levels of An/Ln selectivity, a more recent approach has involved the incorporation of known An/Ln chelating groups onto preorganized macrocyclic platforms (e.g., calixarenes, resorcarenes, and tripodal scaffolds) to create multicoordinate ligands.[43] Calixarenes, in particular, have been extensively employed as molecular scaffolds for the synthesis of multidentate ligands.[44] It has been previously shown that calixarenes bearing CMPO and other O-donor binding groups are efficient coextractants of both Am^{III} and Eu^{III}.[45] Analogous systems containing both O- and N-donor atoms were subsequently investigated. A series of multidentate calix[4]-arenes, calix[6]arenes, and calix[8]arenes bearing picolinamide groups **103**−**122** was synthesized and studied for the ability to separate Am^{III} and Eu^{III}.[46] The ligands were found to be more efficient than an analogous bidentate model compound, illustrating the cooperative effect of multiple binding sites. The calix[8]arenes **119** and **120** were the most efficient extractants, while the upper-rim-substituted calix[4]arene **121** was the most selective ($SF_{Am/Eu}$ = 13.8). Unfortunately, efficient extractions only took place at [HNO_3] < 0.01 M in the presence of the synergist brominated cobalt dicarbollide. Ligand **102** containing picolinamide groups attached to a triphenoxymethane platform showed broadly similar extraction results.[47]

In an effort to reduce the basicity of the pyridine N atom, the effect of substituents on the pyridine rings of calix[6]arene picolinamides on their extraction properties was studied. A more efficient extraction was observed from dilute ($HNO_3 \leq$ 0.1 M) nitric acid solutions when the pyridine ring was replaced by a less basic pyrazine ring (ligand **115**) or when it contained a 4-chloro substituent (ligand **117**).[48] Additional ester or amide groups in the 6 positions of the pyridine rings (ligands **109**−**111** and **113**) further increased the extraction efficiency, even at higher acidities (HNO_3 = 2−3 M).[49] However, a synergist was still required for these extractions. The stoichiometries of the extracted species ranged from 1:2 (for unsubstituted calix[4]-arenes and calix[6]arenes) to 2:1 (for calix[6]arenes with additional carboxy binding sites). The role of the anionic cobalt dicarbollide synergist appears to be the formation of a supramolecular hydrophobic ternary lanthanide/calixarene/dicarbollide complex at the phase interface, as established by ESI-MS, ^{1}H NMR, and ^{11}B NMR spectroscopy.[50]

Mixed N- and O-donor ligands constitute a promising class of ligands for the extraction of Am^{III} and Eu^{III} from high-level nuclear waste solutions. Compared to the O-donor ligands, which show a slight selectivity for Ln over An, the addition of soft N-donor atoms switches this selectivity in many cases. However, in most cases, the selectivity of the ligands for An over Ln is not sufficiently high enough for use in an efficient and robust An/Ln separation process. Another drawback of some of these ligands is their inability to extract from solutions of acidity >1 M HNO_3, even in the presence of synergists. This may be due to competing protonation of the N-donor atoms, which was also found for many previous N-donor ligand designs. The addition of amide groups to the 2 and 6 positions of the pyridine rings increases the extraction ability of mixed N- and O-donor ligands by reducing the basicity of the pyridine N atom, enabling highly efficient coextractions of An and Ln from nitric acid solutions in many cases.

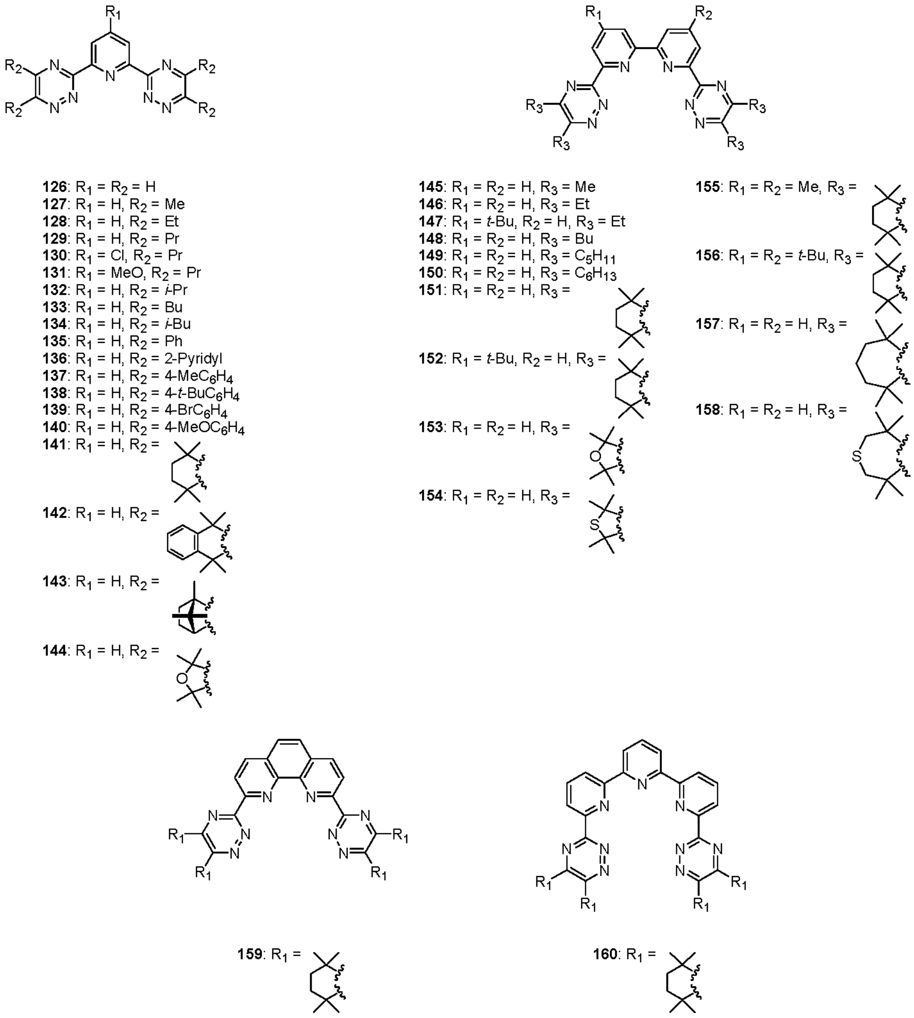


Figure 8. Structures of representative bis(1,2,4-triazine) N-donor ligands studied for the separation of actinides from lanthanides.

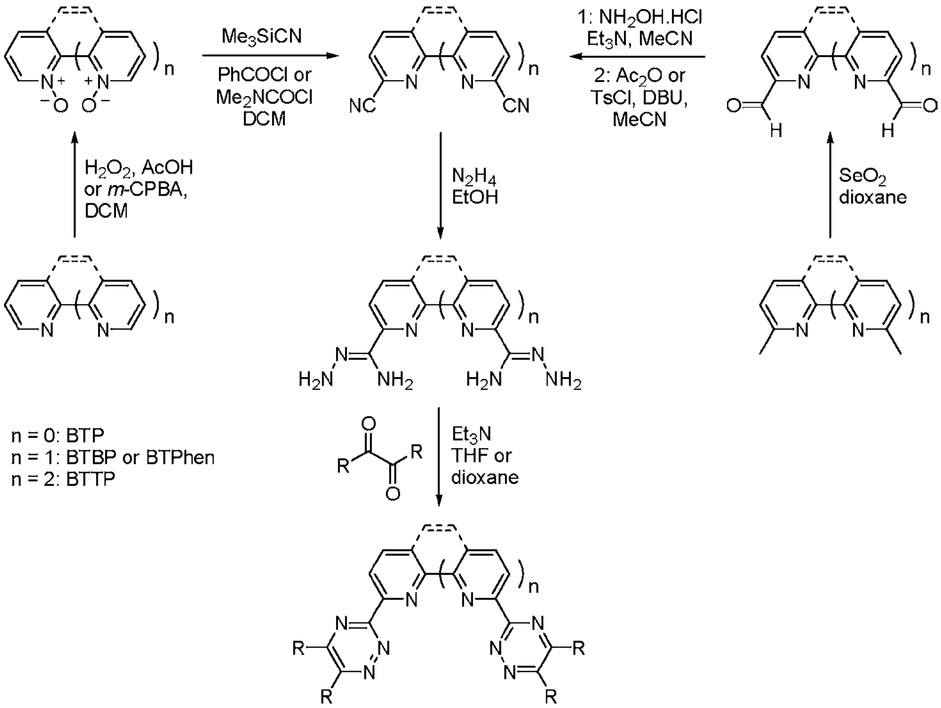
1.5. Bis(1,2,4-triazine) Ligands. Bis(1,2,4-triazine) oligopyridine ligands are currently the European benchmark N-donor ligands for the separation of trivalent actinides from trivalent lanthanides. It will be seen that the solvent extraction performance of this class of ligands sets them apart from previous N-donor ligand designs. Examples of bis(1,2,4-triazine) ligands are shown in Figure 8. A summary of the general routes for synthesizing bis(1,2,4-triazine) ligands is presented in Scheme 1.[51] These ligands are synthesized in two steps from a dinitrile intermediate. The addition of hydrazine to this intermediate affords dicarbohydrazonamides, which are treated with α-diketones to furnish the ligands. The dinitriles can be obtained either by oxidation of the parent oligopyridine, followed by a Reissert–Henze cyanation reaction, or by oxidation of a dimethyloligopyridine, followed by a one-pot dioxime formation/dehydration of the resulting dialdehyde (Scheme 1).

The simplest member of this ligand class, the 2,6-bis(1,2,4-triazin-3-yl)pyridine (BTP) ligands have been known for some time,[52] but it was not until 1999 that their solvent extraction results were reported by Kolarik. In sharp contrast to many previous N-donor ligands (cf. Figure 5), BTPs could extract Am^{III} directly from nitric acid solutions of high acidity ($D_{Am} \leq 61$ from 1 M HNO_3) with excellent selectivity ($SF_{Am/Eu} \leq 150$) without the need for a lipophilic anion source as a synergist.[23] Slope analysis of solvent extraction data showed that Am^{III} was extracted by BTPs **129** and **132** as their $ML_3(NO_3)_3$ complexes.[53] Thus, for the first time, an N-donor ligand fulfilled two of the key requirements of a SANEX separation process: the ability to extract actinide(III) nitrates directly from nitric acid solutions of low pH without the need for added synergists and with high selectivities over the lanthanides. Figure 7 shows the Am^{III}/Eu^{III} separation factors as a function of the acidity for several classes of N-donor ligand (Figure 7). Bis(1,2,4-triazine) ligands are unique among N-donor ligands in being able to separate An from Ln under realistic process conditions with very high selectivities.

Laboratory-scale countercurrent hot tests were subsequently implemented using BTPs **129** and **132** as the extractants. However, lower than expected An^{III} recovery yields were obtained, and subsequent studies revealed that chemical degradation of the extractants had occurred during the hot tests.[54] The proposed degradation mechanism, revealed by gas chromatography and atmospheric pressure chemical ionization mass spectrometry studies, involved chemical attack at the labile benzylic positions of **129** and **132** by free-radical species (indirect radiolysis), leading to oxidation and subsequent cleavage of the alkyl side chains. In addition, some BTPs were also unstable to hydrolysis in contact with HNO_3 in the absence of radionuclides.

To improve the hydrolytic and radiolytic stability of these ligands, BTPs **141** (CyMe$_4$-BTP) and **142** (BzCyMe$_4$-BTP), in

Scheme 1. General Scheme for the Synthesis of Bis(1,2,4-triazine) N-Donor Ligands



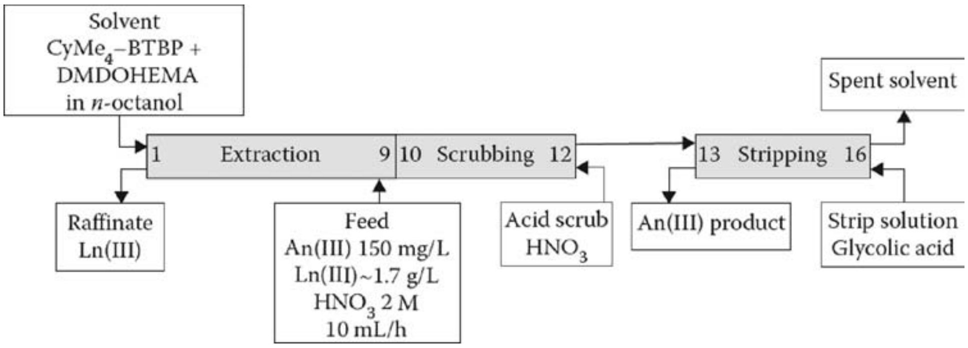


Figure 9. Process flowsheet for the SANEX hot test performed on a genuine DIAMEX solution using CyMe$_4$-BTBP **151** and DMDOHEMA in 1-octanol. Courtesy of Magnusson, D.; Christiansen, B.; Glatz, J. P.; Malmbeck, R.; Modolo, G.; Serrano Purroy, D.; Sorel, C. ATALANTE 2008: Nuclear Fuel Cycles for a Sustainable Future, May 2008, Montpellier, France, 2008. See ref 62 for details.

which the benzylic H atoms have been replaced with methyl groups, were designed and synthesized. In solvent extraction tests, **141** and **142** were more efficient and selective than **129** and **132**.[55] For 0.01 M solutions of CyMe$_4$-BTP **141** in 1-octanol in the presence of DMDOHEMA, D_{Am} = 500 and $\mathrm{SF}_{\mathrm{Am/Eu}}$ = 5000 after 15 min of contact with 0.5 M HNO_3. For BzCyMe$_4$-BTP **142**, D_{Am} = 10 and $\mathrm{SF}_{\mathrm{Am/Eu}}$ = 500 under the same conditions. More importantly, both **141** and **142** were resistant toward hydrolysis (boiling 3 M HNO_3 for 24 h), while no degradation of **142** occurred upon exposure to 100 kGy of γ radiation (**141** was degraded by ca. 80%). More recently, BTP **143** derived from camphor showed good resistance toward nitric acid, despite the presence of two benzylic H atoms.[56] Unfortunately, back-extraction of An$^{\mathrm{III}}$ from the ligands **141** and **142** could not be achieved, limiting the application of these ligands in demonstration tests.[54]

One of the breakthroughs in the development of reagents for selective An$^{\mathrm{III}}$ partitioning came when the 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP) ligands were developed in our laboratories and subsequently tested.[57] In solvent extraction experiments, BTBPs were just as selective for Am$^{\mathrm{III}}$ over Eu$^{\mathrm{III}}$ as the BTPs, but more importantly, the extracted metal ions could be back-extracted (stripped) from the loaded organic phase, enabling the ligand to be reused in a process. The distribution ratios were also lower than those of the BTPs (typically, $D_{\mathrm{Am}} \leq 20$ for C5-BTBP **149**).[58] Although the extraction kinetics were somewhat slower than those of many of the BTPs, this could be accelerated by using diamides (e.g., DMDOHEMA, TODGA) as phase-transfer agents or by using cyclohexanone as the diluent.[59] In addition, the use of synergists was not necessary, and the ligands could extract Am$^{\mathrm{III}}$ even from 4 M nitric acid solutions.

The current European reference ligand for the SANEX process is CyMe$_4$-BTBP **151**. This ligand was designed to combine the favorable extraction and back-extraction properties of the BTBPs with the enhanced chemical stability of CyMe$_4$-BTP **141**. The ligand **151** showed excellent selectivities for Am$^{\mathrm{III}}$ and Cm$^{\mathrm{III}}$ over the entire lanthanide series (e.g., $\mathrm{SF}_{\mathrm{Am/Eu}}$ approx 140) and good extraction kinetics when dissolved in octanol containing DMDOHEMA as the phase-transfer agent.[60] Back-extraction of first the lanthanides (with 0.5 M HNO_3), followed by the actinides (with 0.5 M glycolic acid), was successfully achieved. Furthermore, there was no decomposition of **151** when it was exposed to 1 M HNO_3 for over 2 months. The synthesis of the aliphatic diketone precursor to **151** and related ligands, which was once problematic, has recently been improved, and the ligand is now commercially available.[61]

Given its excellent extraction properties, $CyMe_4$-BTBP **151** was employed in a SANEX hot demonstration test using centrifugal contactors at the Institute for Transuranium Elements in Karlsruhe in 2008.[62] The process flowsheet is shown in Figure 9 and comprised 16 stages (9 for extraction, 3 for scrubbing, and 4 for stripping). Using a solution of $CyMe_4$-BTBP **151** and DMDOHEMA dissolved in 1-octanol, more than 99.9% of Am^{III} and Cm^{III} was separated from a genuine 2 M HNO_3 DIAMEX feed solution, leaving more than 99.9% of the lanthanides in the raffinate. Recent studies also show that solutions of **151** and TODGA can be used to separate trivalent actinides directly from PUREX raffinate (a one-cycle SANEX process) without the need for a preceding DIAMEX separation.[63] Furthermore, the feasibility of employing $CyMe_4$-BTBP **151** in a GANEX (Group ActiNide EXtraction) demonstration test was investigated, with encouraging results.[64] A solution composed of **151** and tributyl phosphate in cyclohexanone could selectively extract U, Np, Pu, and Am from 4 M HNO_3 solutions containing macro (>9000 ppm) concentrations of metal ions.

To be considered for use in an An/Ln partitioning process, the chosen ligand must show acceptable resistance toward radiolytic degradation. Several studies have thus been carried out in order to assess the resistance of BTBP ligands toward radiolysis. Unsurprisingly, alkyl-substituted BTBPs such as C5-BTBP **149**, like their BTP counterparts, were found to be chemically unstable when exposed to γ radiation.[65] However, $CyMe_4$-BTBP **151** was more resistant toward radiolysis. The extraction performance of solutions of **151** in hexanol or cyclohexanone was unchanged when exposed to low doses (<30 kGy) of γ radiation. In contrast, the extraction performance of solutions of C5-BTBP **149** decreased under the same conditions.[66] The stability of BTBPs also depended on the dose rate and the type of radiation. Extractions by BTBP **152** were unaffected at low dose rates, but at higher dose rates (approximately 1.2 kGy/h), the extraction efficiency and selectivity decreased.[67] In addition, the rate of degradation of **151** in 1-octanol was 40% higher when exposed to γ radiation (0.22 kGy/h) than to α radiation (1 kGy/h).[68]

Recently, several derivatives of $CyMe_4$-BTBP modified by additional alkyl substitution on the pyridine rings, or by modification of the aliphatic rings, have been reported. The nonsymmetrical *tert*-butyl-substituted BTBP **152** is reported to have a higher solubility than $CyMe_4$-BTBP **151**,[69] although the extraction kinetics are significantly slower than those of **151**. Surprisingly, symmetrical BTBPs **155** and **156**, which each have two additional alkyl groups, have lower solubilities than $CyMe_4$-BTBP **151** in extraction-relevant diluents.[70] The exact reasons for this are unclear, but it appears that the enhanced solubility of **152** is related to its higher entropy of dissolution. The extraction kinetics of **155** and **156** were significantly slower than those of **151**, although efficient and selective (D_{Am} > 10, $SF_{Am/Eu}$ > 90) extractions were observed both in cyclohexanone and in 1-octanol in the presence of a phase-transfer agent. Replacing the six-membered aliphatic rings of **151** with five-membered heterocyclic rings (in BTBPs **153** and **154**) decreased the ligands' solubilities and extraction performances substantially, rendering **153** and **154** unsuitable for process development.[71] Similarly, the related pentadentate ligand **160** was a much weaker extracting agent than $CyMe_4$-BTBP **151** and did not extract Am^{III} or Eu^{III} from nitric acid solutions to any significant extent.[72]

One of our more recent breakthroughs came when $CyMe_4$-BTPhen **159** was developed. This ligand can be considered as a more preorganized quadridentate ligand in which the 2,2′-bipyridine moiety of the BTBPs has been replaced with a 1,10-phenanthroline moiety. The effect of this simple modification on the ligand extraction properties was startling. The extractions by solutions of $CyMe_4$-BTPhen **159** in 1-octanol were about 2 orders of magnitude more efficient than those of $CyMe_4$-BTBP **151** ($D_{Am} \leq 1000$ for **159** and $D_{Am} \leq 10$ for **151**).[73] The selectivity of **159** was similar to that of **151**, but more importantly, the kinetics of extraction were significantly faster such that equilibrium was reached within 15 min in the absence of a phase-transfer agent. Although the distribution ratios were somewhat higher than those of the BTPs, back-extraction of the metal was, nevertheless, achieved using glycolic acid.[74] Furthermore, **159** was found to have a higher solubility than **151** in 1-octanol. These improved properties make **159** a suitable candidate for use in a highly efficient separation process. For example, the faster kinetics compared to **151** would permit higher flow rates to be used in a countercurrent separation process without the need for a phase-transfer agent (as is the case with $CyMe_4$-BTBP **151**).

Why do bis(1,2,4-triazine) ligands extract Am^{III} with very high selectivity over Eu^{III} under realistic SANEX process conditions, while other closely related N-donor ligands do not? Although the exact fundamental reasons are still not fully understood, one idea is that the two adjacent N atoms in the triazine rings play a key role. Structural studies show that it is always the N atom at position 2 in the triazine ring that coordinates to a metal and not the N atom at position 4. It is thought that the nucleophilicity (and hence the covalent contribution) of the ligating N atom at position 2 is increased by a molecular orbital interaction with the lone electron pair of the adjacent noncoordinating N atom at position 1. This interaction, known as the α effect, accounts for the increased reactivities of certain nucleophiles (e.g., hydrazine, hydroxylamine, hydroperoxide anion) that do not correlate with their basicities.[75] In bis(1,2,4-triazine) ligands, this effect would be expected to increase the covalent interaction between the ligand (specifically the 2N atom of the 1,2,4-triazine ring) and the soft actinides and, hence, the selectivity over the harder lanthanides. This effect is thought to be the reason why bis(1,2,4-triazine) ligands are so selective toward An^{III}.

This effect would also be expected to decrease the basicity of the triazine rings and may help to explain why bis(1,2,4-triazine) ligands can extract even from 4 M HNO_3 while other N-donor ligands cannot. Indeed, 1,2,4-triazine itself is a very weak base ($pK_a = -1.77$).[76] Furthermore, the electron-withdrawing effect of the lateral 1,2,4-triazine rings of bis(1,2,4-triazine) ligands would also lower the basicities of adjacent pyridine or phenanthroline rings, thereby increasing the resistance of the ligands toward competing protonation. It appears that the α effect plays a dual role in increasing the thermodynamic stabilities of the extracted actinide complexes of bis(1,2,4-triazine) ligands and decreasing the basicities of the free ligands, enabling highly selective extractions to take place from nitric acid solutions under realistic SANEX process conditions. As Figures 5 and 7 show, bis(1,2,4-triazine) ligands are currently the only N-donor ligands to our knowledge that can efficiently and selectively extract An^{III} over Ln^{III} under the challenging conditions of a SANEX process.

Bis(1,2,4-triazine) ligands have also been extensively studied from a fundamental point of view in order to shed more light on the origins of their excellent extraction properties. In the case of the BTPs, several examples of lanthanide 1:3 complexes of formula $[M(BTP)_3](NO_3)_3$ have been isolated and structurally characterized by X-ray diffraction.[77] An example with $CyMe_4$-BTP **141** is shown in Figure 10. In these complexes, it can be seen that the metal ion is 9-coordinate and is completely enclosed by three ligands in a C_3-symmetric arrangement, while the nitrate ions are displaced to the metals outer coordination sphere. These 1:3 species are considerably more hydrophobic than the 1:1 complexes formed by many related tridentate N-donor ligands, and their formation is in agreement with the superior extraction performance of BTP ligands. Numerous studies also show that 1:3 lanthanide and actinide BTP complexes are formed in solution. Under extraction-relevant conditions (acidic H_2O/MeOH) and in 1-octanol, BTPs formed Ln^{III} 1:3 complexes as shown by ESI-MS and time-resolved laser fluorescence spectroscopy measurements.[78] In addition, BTPs formed 1:3 complexes with Am^{III}, Cm^{III}, and Pu^{III} that were more thermodynamically stable than the 1:3 complexes formed with Eu^{III}.[79]

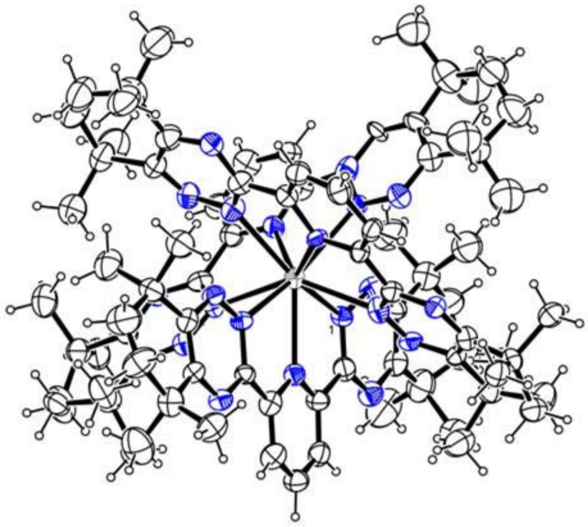


Figure 10. X-ray crystal structure of $[Y(\textbf{141})_3]\cdot[Y(NO_3)_5]\cdot NO_3$. Counterions and solvent molecules are omitted for clarity. Y−N bond distances range from 2.426(8) to 2.522(8) Å. See ref 55 for details.

With quadridentate BTBP and BTPhen ligands, the dominant M/L complex stoichiometry is 1:2, although 1:1 complexes (which are likely precursors to 1:2 complexes) have also been observed both in solution and in the solid state. Several X-ray structures of 1:1 complexes of BTBPs with $Ln(NO_3)_3$ were reported.[80] One example with BTBP **146** is shown in Figure 11. The ligand coordinates in a planar tetradentate fashion to the metal, which is 9-coordinate. The remaining coordination sites are occupied by nitrate ions and water molecules. Although 1:2 complexes of the BTBPs with Ln^{III}/An^{III} have been observed in solution for some time,[81] it was not until recently that the first example of a 1:2 Ln^{III} BTBP complex was characterized by X-ray diffraction (Figure 12).[82] The two $CyMe_4$-BTBP ligands **151** in this complex coordinate in an orthogonal fashion to Eu^{III}, which is 10-coordinate. In addition, there is a single bidentate nitrate ion in the inner coordination sphere of the metal. Thus, the complex is hydrophobic, but the metal is not completely enclosed (as is the case with the BTP 1:3 complexes). An almost identical 1:2 structure was formed between $CyMe_4$-BTPhen **159** and Eu^{III}, as shown in Figure 13,[83] suggesting that the enhanced extraction performance of **159** compared to the BTBPs was not due to structural differences in their An^{III} complexes.

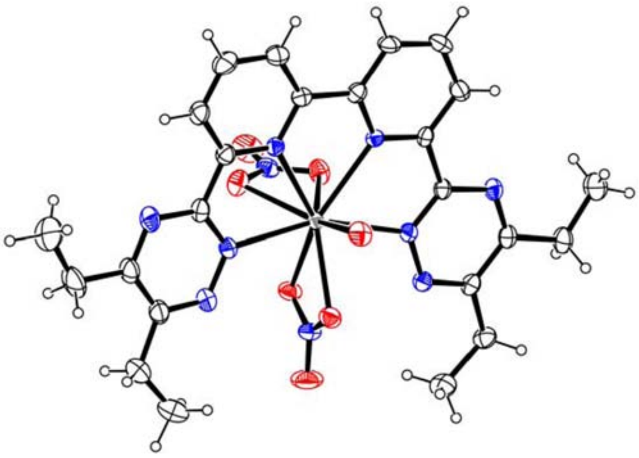


Figure 11. X-ray crystal structure of $[Lu(\textbf{146})(NO_3)_2(H_2O)]\cdot NO_3$. Counterions and solvent molecules are omitted for clarity. Lu−N bond distances range from 2.433(7) to 2.457(7) Å. See ref 80 for details.

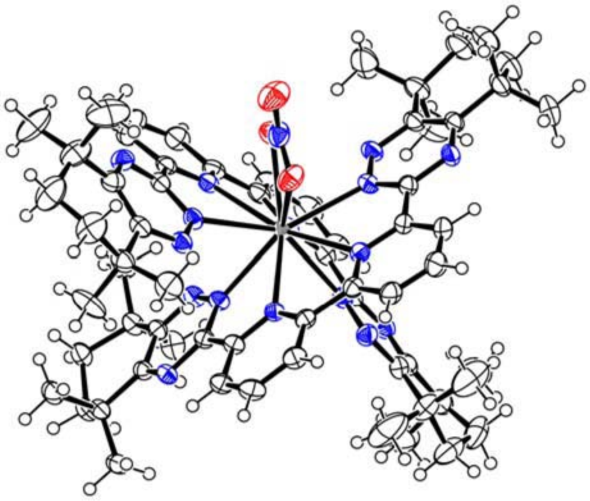


Figure 12. X-ray crystal structure of $[Eu(\textbf{151})_2(NO_3)]\cdot[Eu(NO_3)_5]$. Counterions and solvent molecules are omitted for clarity. Eu−N bond distances range from 2.539(3) to 2.599(3) Å. See ref 82 for details.

Quantum mechanics calculations and molecular dynamics simulations at the oil/water interface suggest that bis(1,2,4-triazine) ligands are only weakly surface-active in their neutral forms but are highly surface-active in their protonated forms and when complexed to a single Ln^{III}/An^{III} ion.[84] This suggests that complexation and extraction occur at the phase interface via the protonated ligands. This also helps to explain why the

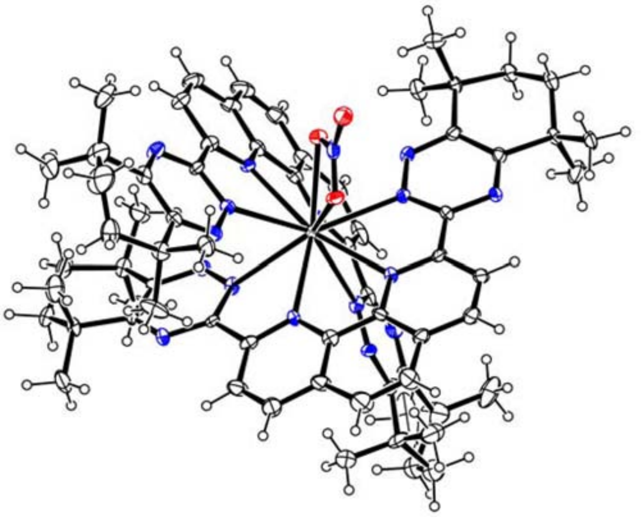


Figure 13. X-ray crystal structure of [Eu(**159**)$_2$(NO$_3$)]·[Eu(NO$_3$)$_5$]. Counterions and solvent molecules are omitted for clarity. Eu−N bond distances range from 2.546(6) to 2.616(5) Å. See ref 73 for details.

extraction efficiency actually increases with aqueous phase acidity in many cases. The surface activity of a ligand is also related to the rate of metal-ion extraction. Surface tension measurements and kinetics studies showed that CyMe$_4$-BTPhen **159** had a higher concentration at the interface than CyMe$_4$-BTBP **151** in several diluents and the Eu^{III} extraction rate constants for **159** were larger than those for **151**.[73] These results go some way to explain why CyMe$_4$-BTPhen **159** has improved extraction kinetics compared to CyMe$_4$-BTBP **151**. The higher concentration of **159** at the interface is likely due to the inherent dipole moment present in **159** caused by locking the central N-donor atoms into the chelating cis conformation. In contrast, **151** lacks this dipole moment because the ligand exists in its more favored trans−trans−trans conformation in solution, where all of the C−N bond dipoles cancel each other out.

1.6. Solid-Supported Ligands.

Numerous examples of ligands for selective actinide extraction on solid supports have been reported. However, the majority of these examples make use of ligands that form complexes via O-, P-, and S-donor atoms. Ligands are typically coated onto or impregnated into the solid supports, which include polymer resins and membranes, metal oxide microparticles, clays, carbon nanotubes, amorphous carbon, magnetic nanoparticles (MNPs), and SiO$_2$-stabilized polymers. More rarely, ligands are covalently attached to the solid supports. Solid-supported ligands can be particularly effective at extracting metals at low concentrations and have applications in the preconcentration or analysis of dilute samples. In light of the recent Fukushima nuclear incident, interest in such methods has significantly increased. Additionally, solid-supported ligands can be used as adsorbents in extraction chromatography, a purification method that reduces or eliminates the need for organic solvents. Such solid-supported ligands have been recently reviewed.[85]

Solid-supported soft heterocyclic N-donor ligands have also been reported for use in heterogeneous catalysis or transition-metal extraction, such as 2,2′-bipyridine (BIPY) or 2,2′:6′,2″-terpyridine **1** on silica,[86] or incorporated into a polymer,[87] TPTZ **7** on activated carbon,[88] and BTP ligands adsorbed onto composite polymer/silica materials.[89]

To date, the only published examples of solid-supported soft heterocyclic N-donor ligands for minor actinide extraction have made use of alkyl-BTP systems.[90] These ligands have been impregnated into styrene−divinylbenzene copolymer resins supported on 40−60 μm porous silica particles (SiO$_2$−P) by a vacuum sucking method. The resulting loaded resins were shown to be resistant to γ irradiation and to degradation in concentrated HNO$_3$, and only a small amount of leaching of the ligands into 3 M HNO$_3$ solutions was observed. The extent of leaching could be further reduced by using branched-chain alkyl groups attached to the triazine rings.[89] The ligand-loaded resins were used for extraction chromatography in a process termed MAREC (Minor Actinides Recovery from High Level Liquid Waste by Extraction Chromatography)[91] and suggested for use in an ion-exchange process known as ERIX (Electrolytic Reduction and Ion EXchange).[89]

BTP **134**/SiO$_2$−P was used to separate heavier lanthanides from lighter lanthanides in a 1.0−5.5 M HNO$_3$ solution at 25 °C.[92] The presence of competing chelating agents (e.g., DTPA) reduced the extraction efficiency for all lanthanides tested from a 0.01 M HNO$_3$ solution; however, smaller organic acids (e.g., formic acid, citric acid) were found to decrease the absorption of the lighter lanthanides selectively. Complete separation of lanthanides could be achieved by column chromatography with virtually 100% recovery of all elements.[92] The same system could be used for minor actinide partitioning. Similarly, BTP-loaded resins extract Dy^{III} selectively from mixtures of lanthanides in 2.0−4.0 M HNO$_3$ at 50 °C.[93]

Resins impregnated with BTPs **133** and **134** displayed high affinities for Am^{III} and Cm^{III} over lanthanides in NaNO$_3$ and HNO$_3$ solutions, and complete separation of Am^{IV} from Ln^{III} was achieved by column chromatography using the same resins.[94] Likewise, Am^{III} was found to exhibit strong adsorption onto BTP **128**/SiO$_2$−P and BTP **129**/SiO$_2$−P compared to lanthanides in a 4.0 M NaNO$_3$ solution, with high selectivity for Am^{III} (SF$_{Am/Ln}$ = 100).[95]

The described BTP-impregnated resins have been used successfully to achieve complete separation of the minor actinides from simulated PUREX raffinate through a double-column system, whereby the minor actinides and lanthanides were first separated from fission products using a CMPO-impregnated resin, and the minor actinides were then extracted and separated from the lanthanides by a BTP/SiO$_2$−P packed column, with elution using a 0.5 M HNO$_3$ solution.[96]

Our work at the University of Reading is currently focused on attaching BTPhen ligands to solid supports and their applications in wastewater treatment and soil remediation. We are impregnating various BTPhen ligands into silica microparticles and polymer resins. We are also developing a method to covalently attach BTPhen ligands, for example, to silica- or zirconia-coated MNPs (Figure 14) with the aim of allowing magnetic recovery of the loaded particles from soil or wastewater samples. Regioselective bromination of BTPhen ligands is being performed, and Pd-catalyzed cross-coupling reactions will provide access to a variety of functional groups that could be linked to MNPs bearing amino or iodo surface groups. The resulting impregnated resins and BTPhen-MNPs will be assessed for their ability to extract lanthanides by extraction chromatography or magnetic separation, respectively, and their minor actinide absorption activity will be investigated. The high surface areas of these MNPs render them effective for the removal of pollutants from aqueous or nonaqueous media.

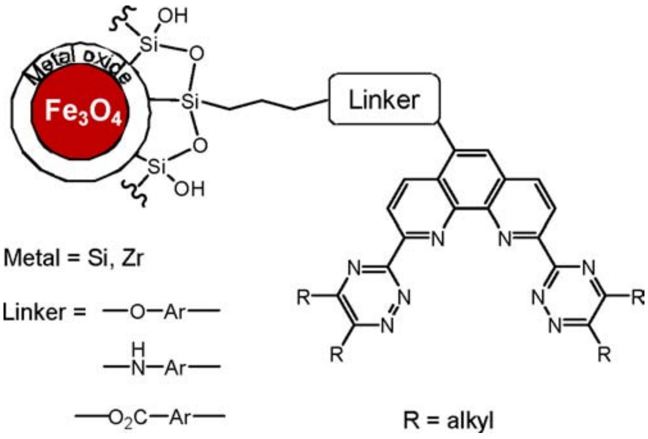


Figure 14. Diagram of BTPhen ligands covalently attached to MNPs via an alkoxysilane linker.

■ CONCLUSIONS

Partitioning and transmutation represents an attractive combination for the reduction in the levels of radioactivity in waste nuclear fuels. New reagents have been developed in recent decades that lead to the efficient removal of Am^{III} and Cm^{III} from the fuels. Bis(1,2,4-triazine) ligands stand out as the preeminent family of ligands for use in an actinide/lanthanide separation process and satisfy many of the criteria required for use in an industrial SANEX process. Among these, BTBP and BTPhen ligands, which were prepared for the first time in our laboratories, show the best properties. Although considerable advances have been made in understanding the fundamental reasons for the properties of these reagents at the molecular level, theory still lags behind. A future chemical engineering challenge is to design flowsheets that use these highly efficient reagents in solvent extraction processes on a pilot scale and, ultimately, on an industrial scale. There is currently great international interest in these developments and great societal pressure to close the fuel cycle and render nuclear energy to be as safe and sustainable as possible for future generations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Solvent extraction conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Fuel Cycle Stewardship in a Nuclear Renaissance*; The Royal Society Science Policy Centre Report 10/11; The Royal Society: London, 2011; ISBN 978-0-85403-891-6.

(2) (a) Baumgärtner, F. *Kerntechnik* **1978**, *20*, 74. (b) Baumgärtner, F.; Ertel, D. *J. Radiat. Chem.* **1980**, *58*, 11. (c) McKibben, J. M. *Radiochim. Acta* **1984**, *36*, 3. (d) Sood, D. D.; Patil, S. K. *J. Radioanal. Nucl. Chem.* **1996**, *203*, 547. (e) Musikas, C.; Schultz, W.; Liljenzin, J.-O. In *Solvent Extraction Principles and Practice*, 2nd ed.; Rydberg, J., Cox, M., Musikas, C., Choppin, G., Eds.; Marcel Dekker, Inc.: New York, 2004; pp 507−557. (f) Nash, K. L.; Madic, C.; Mathur, J.; Lacquement, J. In *The Chemistry of the Actinide and Transactinide Elements*; Katz, J. J., Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Vol. *1*; pp 2622−2798.

(3) (a) *Actinide and fission product partitioning and transmutation status and assessment report*; OECD/NEA: Paris, 1999. (b) Magill, J.; Berthou, V.; Haas, D.; Galy, J.; Schenkel, R.; Wiese, H.-W.; Heusener, G.; Tommasi, J.; Youinou, G. *Nucl. Energy* **2003**, *42*, 263. (c) Salvatores, M. *Nucl. Eng. Des.* **2005**, *235*, 805. (d) Salvatores, M.; Palmiotti, G. *Prog. Part. Nucl. Phys.* **2011**, *66*, 144.

(4) (a) Nash, K. L. *Solvent Extr. Ion Exch.* **1993**, *11*, 729. (b) Mathur, J. N.; Murali, M. S.; Nash, K. L. *Solvent Extr. Ion Exch.* **2001**, *19*, 357. (c) Lumetta, G. J.; Gelis, A. V.; Vandegrift, G. F. *Solvent Extr. Ion Exch.* **2010**, *28*, 287. (d) Hill, C. In *Ion Exchange and Solvent Extraction: A Series of Advances*; Moyer, B. A., Ed.; CRC Press: Boca Raton, FL, 2010; Vol. *19*; pp 119−193.

(5) Horwitz, E. P.; Kalina, D. G.; Diamond, H.; Vandegrift, G. F.; Schulz, W. W. *Solvent Extr. Ion Exch.* **1985**, *3*, 75.

(6) (a) Serrano-Purroy, D.; Baron, P.; Christiansen, B.; Malmbeck, R.; Sorel, C.; Glatz, J.-P. *Radiochim. Acta* **2005**, *93*, 351. (b) Modolo, G.; Asp, H.; Schreinemachers, C.; Vijgen, H. *Solvent Extr. Ion Exch.* **2007**, *25*, 703. (c) Magnusson, D.; Christiansen, B.; Glatz, J.-P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel, C. *Solvent Extr. Ion Exch.* **2009**, *27*, 26.

(7) (a) Madic, C.; Hudson, M. J.; Liljenzin, J.-O.; Glatz, J.-P.; Nannicini, R.; Facchini, A.; Kolarik, Z.; Odoj, R. *Prog. Nucl. Energy* **2002**, *40*, 523. (b) Madic, C.; Boullis, B.; Baron, P.; Testard, F.; Hudson, M. J.; Liljenzin, J.-O.; Christiansen, B.; Ferrando, M.; Facchini, A.; Geist, A.; Modolo, G.; Espartero, A. G.; De Mendoza, J. *J. Alloys Compd.* **2007**, *444−445*, 23.

(8) (a) Nilsson, M.; Nash, K. L. *Solvent Extr. Ion Exch.* **2007**, *25*, 665. (b) Nilsson, M.; Nash, K. L. *Solvent Extr. Ion Exch.* **2009**, *27*, 354.

(9) (a) Cotton, S. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, U.K., 2004; Vol. 3; pp 93−188. (b) Burns, C. J.; Neu, M. P.; Boukhalfa, H.; Gutowski, K. E.; Bridges, N. J.; Rogers, R. D. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, U.K., 2004; Vol. 3; pp 189−332. (c) Katz, J. J.; Morss, L. R.; Edelstein, N. M.; Fuger, J. In *The Chemistry of the Actinide and Transactinide Elements*; Katz, J. J., Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Vol. *1*; pp 1−17.

(10) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(11) (a) Choppin, G. R. *J. Alloys Compd.* **1995**, *223*, 174. (b) Alexander, V. *Chem. Rev.* **1995**, *95*, 273. (c) Choppin, G. R. *J. Alloys Compd.* **2002**, *344*, 55. (d) Gaunt, A. J.; Neu, M. P. *C. R. Chim.* **2010**, *13*, 821.

(12) Hudson, M. J. *Czech. J. Phys.* **2003**, *53*, A305.

(13) (a) Ekberg, C.; Fermvik, A.; Retegan, T.; Skarnemark, G.; Foreman, M. R. S.; Hudson, M. J.; Englund, S.; Nilsson, M. *Radiochim. Acta* **2008**, *96*, 225. (b) Kolarik, Z. *Chem. Rev.* **2008**, *108*, 4208. (c) Mincher, B. J.; Modolo, G.; Mezyk, S. P. *Solvent Extr. Ion Exch.* **2010**, *28*, 415.

(14) Lewis, F. W.; Hudson, M. J.; Harwood, L. M. *Synlett* **2011**, 2609.

(15) (a) Cordier, P. Y.; Hill, C.; Baron, P.; Madic, C.; Hudson, M. J.; Liljenzin, J.-O. *J. Alloys Compd.* **1998**, *271−273*, 738. (b) Hagström, I.; Spjuth, L.; Enarsson, Å.; Liljenzin, J.-O.; Skålberg, M.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Cordier, P. Y.; Hill, C.; Francois, N. *Solvent Extr. Ion Exch.* **1999**, *17*, 221.

(16) Drew, M. G. B.; Iveson, P. B.; Hudson, M. J.; Liljenzin, J.-O.; Spjuth, L.; Cordier, P. Y.; Enarsson, Å.; Hill, C.; Madic, C. *J. Chem. Soc., Dalton Trans.* **2000**, 821.

(17) Vitart, X.; Musikas, C.; Pasquiou, J. Y.; Hoel, P. *J. Less-Common Met.* **1986**, *122*, 275.

(18) Boubals, N.; Drew, M. G. B.; Hill, C.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Russell, M. L.; Youngs, T. G. A. *J. Chem. Soc., Dalton Trans.* **2002**, 55.

(19) Madic, C.; Lecomte, M.; Baron, P.; Boullis, B. *C. R. Phys.* **2002**, *3*, 797.

(20) Drew, M. G. B.; Hill, C.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Vaillant, L.; Youngs, T. G. A. *New J. Chem.* **2004**, *28*, 462.

(21) (a) Andersson, S.; Ekberg, C.; Foreman, M. R. S.; Hudson, M. J.; Liljenzin, J.-O.; Nilsson, M.; Skarnemark, G.; Spahiu, K. *Solvent Extr. Ion Exch.* **2003**, *21*, 621. (b) Andersson, S.; Ekberg, C.; Liljenzin, J.-O.; Nilsson, M.; Skarnemark, G. *Radiochim. Acta* **2004**, *92*, 863.

(22) Weigl, M.; Müllich, U.; Geist, A.; Gompper, K.; Zevaco, T.; Stephan, H. *J. Radioanal. Nucl. Chem.* **2003**, *256*, 403.

(23) Kolarik, Z.; Müllich, U.; Gassner, F. *Solvent Extr. Ion Exch.* **1999**, *17*, 23.

(24) Bremer, A.; Ruff, C. M.; Girnt, D.; Müllich, U.; Rothe, J.; Roesky, P. W.; Panak, P. J.; Karpov, A.; Müller, T. J. J.; Denecke, M. A.; Geist, A. *Inorg. Chem.* **2012**, *51*, 5199.

(25) Smirnov, I. V.; Chirkov, A. V.; Babain, V. A.; Pokrovskaya, E. Yu.; Artamonova, T. A. *Radiochim. Acta* **2009**, *97*, 593.

(26) Hudson, M. J.; Foreman, M. R. St. J.; Hill, C.; Huet, N.; Madic, C. *Solvent Extr. Ion Exch.* **2003**, *21*, 637.

(27) (a) Hudson, M. J.; Drew, M. G. B.; Foreman, M. R. St. J.; Hill, C.; Huet, N.; Madic, C.; Youngs, T. G. A. *Dalton Trans.* **2003**, 1675. (b) Krejzler, J.; Narbutt, J.; Foreman, M. R. St. J.; Hudson, M. J.; Casensky, B.; Madic, C. *Czech. J. Phys.* **2006**, *56*, D459.

(28) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pécaut, J.; Cordier, P.-Y.; Madic, C. *Inorg. Chem.* **1998**, *37*, 6690.

(29) Ishimori, K.; Watanabe, M.; Kimura, T.; Yaita, T.; Yamada, T.; Kataoka, Y.; Shinoda, S.; Tsukube, H. *Chem. Lett.* **2005**, *34*, 1112.

(30) (a) Watanabe, M.; Mirvaliev, R.; Tachimori, S.; Takeshita, K.; Nakano, Y.; Morikawa, K.; Mori, R. *Chem. Lett.* **2002**, *31*, 1230. (b) Mirvaliev, R.; Watanabe, M.; Matsumura, T.; Tachimori, S.; Takeshita, K. *J. Nucl. Sci. Technol.* **2004**, *41*, 1122.

(31) Karmazin, L.; Mazzanti, M.; Gateau, C.; Hill, C.; Pécaut, J. *Chem. Commun.* **2002**, 2892.

(32) (a) Chan, G. Y. S.; Drew, M. G. B.; Hudson, M. J.; Isaacs, N. S.; Byers, P. *Polyhedron* **1996**, *15*, 3385. (b) Drew, M. G. B.; Hudson, M. J.; Iveson, P. B.; Madic, C. *Acta Crystallogr.* **2000**, *C56*, 434.

(33) Drew, M. G. B.; Hudson, M. J.; Iveson, P. B.; Madic, C.; Russell, M. L. *J. Chem. Soc., Dalton Trans.* **2000**, 2711.

(34) Berthet, J.-C.; Rivière, C.; Miquel, Y.; Nierlich, M.; Madic, C.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2002**, 1439.

(35) (a) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pécaut, J. *J. Chem. Soc., Dalton Trans.* **2000**, 4167. (b) Natrajan, L.; Pécaut, J.; Mazzanti, M.; LeBrun, C. *Inorg. Chem.* **2005**, *44*, 4756.

(36) Nigond, L.; Condamines, N.; Cordier, P. Y.; Livet, J.; Madic, C.; Cuillerdier, C.; Musikas, C.; Hudson, M. J. *Sep. Sci. Technol.* **1995**, *30*, 2075.

(37) (a) Babain, V. A.; Alyapyshev, M. Yu.; Smirnov, I. V.; Shadrin, A. Yu. *Radiochemistry* **2006**, *48*, 369. (b) Babain, V. A.; Alyapyshev, M. Yu.; Kiseleva, R. N. *Radiochim. Acta* **2007**, *95*, 217.

(38) Alyapyshev, M. Yu.; Babain, V. A.; Tkachenko, L. I.; Eliseev, I. I.; Didenko, A. V.; Petrov, M. L. *Solvent Extr. Ion Exch.* **2011**, *29*, 619.

(39) Alyapyshev, M.; Babain, V.; Borisova, N.; Eliseev, I.; Kirsanov, D.; Kostin, A.; Legin, A.; Reshetova, M.; Smirnova, Z. *Polyhedron* **2010**, *29*, 1998.

(40) Williams, N. J.; Ballance, D. G.; Reibenspies, J. H.; Hancock, R. D. *Inorg. Chim. Acta* **2010**, *363*, 3694.

(41) Merrill, D.; Hancock, R. D. *Radiochim. Acta* **2011**, *99*, 161.

(42) Heitzmann, M.; Gateau, C.; Chareyre, L.; Miguirditchian, M.; Charbonnel, M.-C.; Delangle, P. *New J. Chem.* **2010**, *34*, 108.

(43) For a review, see: Dam, H. H.; Reinhoudt, D. N.; Verboom, W. *Chem. Soc. Rev.* **2007**, *36*, 367.

(44) For a review, see: (a) Baldini, L.; Casnati, A.; Sansone, F.; Ungaro, R. *Chem. Soc. Rev.* **2007**, *36*, 254. (b) Dozol, J.-F.; Ludwig, R. *Ion Exchange and Solvent Extraction: A Series of Advances*; Moyer, B. A., Ed.; CRC Press: Boca Raton, FL, 2010; Vol. *19*; pp 195−318. (c) Mokhtari, B.; Pourabdollah, K.; Dallali, N. *J. Radioanal. Nucl. Chem.* **2011**, *287*, 921.

(45) For example, see: (a) Lambert, B.; Jacques, V.; Shivanyuk, A.; Matthews, S. E.; Tunayar, A.; Baaden, M.; Wipff, G.; Böhmer, V.; Desreux, J. F. *Inorg. Chem.* **2000**, *39*, 2033. (b) Atamas, L.; Klimchuk, O.; Rudzevich, V.; Pirozhenko, V.; Kalchenko, V.; Smirnov, I.; Babain, V.; Efremova, T.; Varnek, A.; Wipff, G.; Arnaud-Neu, F.; Roch, M.; Saadioui, M.; Böhmer, V. *J. Supramol. Chem.* **2002**, *2*, 421. (c) Schmidt, C.; Saadioui, M.; Böhmer, V.; Host, V.; Spirlet, M.-R.; Desreux, J. F.; Brisach, F.; Arnaud-Neu, F.; Dozol, J.-F. *Org. Biomol. Chem.* **2003**, *1*, 4089. (d) Wang, P.; Saadioui, M.; Schmidt, C.; Böhmer, V.; Host, V.; Desreux, J. F.; Dozol, J.-F. *Tetrahedron* **2004**, *60*, 2509.

(46) Casnati, A.; Della Ca', N.; Fontanella, M.; Sansone, F.; Ugozzoli, F.; Ungaro, R.; Liger, K.; Dozol, J.-F. *Eur. J. Org. Chem.* **2005**, 2338.

(47) Dam, H. H.; Reinhoudt, D. N.; Verboom, W. *New J. Chem.* **2007**, *31*, 1620.

(48) Galletta, M.; Baldini, L.; Sansone, F.; Ugozzoli, F.; Ungaro, R.; Casnati, A.; Mariani, M. *Dalton Trans.* **2010**, *39*, 2546.

(49) Macerata, E.; Sansone, F.; Baldini, L.; Ugozzoli, F.; Brisach, F.; Haddaoui, J.; Hubscher-Bruder, V.; Arnaud-Neu, F.; Mariani, M.; Ungaro, R.; Casnati, A. *Eur. J. Org. Chem.* **2010**, 2675.

(50) Macerata, E.; Castiglione, F.; Panzeri, W.; Mariani, M.; Sansone, F.; Casnati, A.; Mele, A. *New J. Chem.* **2010**, *34*, 2552.

(51) For a review on the synthesis of 1,2,4-triazines, see: Raw, S. A.; Taylor, R. J. K. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Elsevier: Amsterdam, The Netherlands, 2010; Vol. *100*, pp 75−100.

(52) Case, F. H. *J. Heterocycl. Chem.* **1971**, *8*, 1043.

(53) Kolarik, Z.; Müllich, U.; Gassner, F. *Solvent Extr. Ion Exch.* **1999**, *17*, 1155.

(54) (a) Madic, C.; Hudson, M. J.; Liljenzin, J.-O.; Glatz, J.-P.; Nannicini, R.; Facchini, A.; Kolarik, Z.; Odoj, R. *New Partitioning Techniques for Minor Actinides*; EUR19149EN; European Comission: Luxembourg, 2000. (b) Hill, C.; Guillaneux, D.; Berthon, L.; Madic, C. *J. Nucl. Sci. Technol.* **2002**, No. Suppl. 3, 309.

(55) Hudson, M. J.; Boucher, C. E.; Braekers, D.; Desreux, J. F.; Drew, M. G. B.; Foreman, M. R. St. J.; Harwood, L. M.; Hill, C.; Madic, C.; Marken, F.; Youngs, T. G. A. *New J. Chem.* **2006**, *30*, 1171.

(56) Trumm, S.; Geist, A.; Panak, P. J.; Fanghänel, T. *Solvent Extr. Ion Exch.* **2011**, *29*, 213.

(57) Drew, M. G. B.; Foreman, M. R. St. J.; Hill, C.; Hudson, M. J.; Madic, C. *Inorg. Chem. Commun.* **2005**, *8*, 239.

(58) (a) Foreman, M. R. St. J.; Hudson, M. J.; Geist, A.; Madic, C.; Weigl, M. *Solvent Extr. Ion Exch.* **2005**, *23*, 645. (b) Nilsson, M.; Andersson, S.; Drouet, F.; Ekberg, C.; Foreman, M.; Hudson, M.; Liljenzin, J.-O.; Magnusson, D.; Skarnemark, G. *Solvent Extr. Ion Exch.* **2006**, *24*, 299.

(59) (a) Nilsson, M.; Ekberg, C.; Foreman, M.; Hudson, M.; Liljenzin, J.-O.; Modolo, G.; Skarnemark, G. *Solvent Extr. Ion Exch.* **2006**, *24*, 823. (b) Retegan, T.; Ekberg, C.; Dubois, I.; Fermvik, A.; Skarnemark, G.; Wass, T. J. *Solvent Extr. Ion Exch.* **2007**, *25*, 417.

(60) Geist, A.; Hill, C.; Modolo, G.; Foreman, M. R. St. J.; Weigl, M.; Gompper, K.; Hudson, M. J.; Madic, C. *Solvent Extr. Ion Exch.* **2006**, *24*, 463.

(61) (a) Lewis, F. W.; Harwood, L. M.; Hudson, M. J. WO2011077081 A1 (2011). (b) CyMe$_4$-BTP **141**, CyMe$_4$-BTBP **151**, CyMe$_4$-BTPhen **159**, and precursors are produced by Technocomm, U.K. (www.technocomm.co.uk).

(62) Magnusson, D.; Christiansen, B.; Foreman, M. R. S.; Geist, A.; Glatz, J.-P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel, C. *Solvent Extr. Ion Exch.* **2009**, *27*, 97.

(63) Wilden, A.; Schreinemachers, C.; Sypula, M.; Modolo, G. *Solvent Extr. Ion Exch.* **2011**, *29*, 190.

(64) (a) Aneheim, E.; Ekberg, C.; Fermvik, A.; Foreman, M. R. St. J.; Retegan, T.; Skarnemark, G. *Solvent Extr. Ion Exch.* **2010**, *28*, 437. (b) Aneheim, E.; Ekberg, C.; Fermvik, A.; Foreman, M. R. St. J.; Grűner, B.; Hájková, Z.; Kvičalová, M. *Solvent Extr. Ion Exch.* **2011**, *29*, 157.

(65) Fermvik, A.; Berthon, L.; Ekberg, C.; Englund, S.; Retegan, T.; Zorz, N. *Dalton Trans.* **2009**, 6421.

(66) Retegan, T.; Ekberg, C.; Englund, S.; Fermvik, A.; Foreman, M. R. S.; Skarnemark, G. *Radiochim. Acta* **2007**, *95*, 637.
(67) Fermvik, A.; Ekberg, C.; Englund, S.; Foreman, M. R. St. J.; Modolo, G.; Retegan, T.; Skarnemark, G. *Radiochim. Acta* **2009**, *97*, 319.
(68) Magnusson, D.; Christiansen, B.; Malmbeck, R.; Glatz, J.-P. *Radiochim. Acta* **2009**, *97*, 497.
(69) Ekberg, C.; Aneheim, E.; Fermvik, A.; Foreman, M.; Löfström-Engdahl, E.; Retegan, T.; Spendlikova, I. *J. Chem. Eng. Data* **2010**, *55*, 5133.
(70) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Distler, P.; John, J.; Stamberg, K.; Núñez, A.; Galán, H.; Espartero, A. G. *Eur. J. Org. Chem.* **2012**, 1509.
(71) Harwood, L. M.; Lewis, F. W.; Hudson, M. J.; John, J.; Distler, P. *Solvent Extr. Ion Exch.* **2011**, *29*, 551.
(72) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B.; Modolo, G.; Sypula, M.; Desreux, J. F.; Bouslimani, N.; Vidick, G. *Dalton Trans.* **2010**, *39*, 5172.
(73) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B.; Desreux, J. F.; Vidick, G.; Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T.-H.; Simonin, J.-P. *J. Am. Chem. Soc.* **2011**, *133*, 13093.
(74) Unpublished results.
(75) (a) Jencks, W. P.; Carriuolo, J. *J. Am. Chem. Soc.* **1960**, *82*, 675. (b) Jencks, W. P.; Carriuolo, J. *J. Am. Chem. Soc.* **1960**, *82*, 1778. (c) Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16. (d) Fina, N. J.; Edwards, J. O. *Int. J. Chem. Kinet.* **1973**, *5*, 1. (e) Buncel, E.; Um, I.-H. *Tetrahedron* **2004**, *60*, 7801.
(76) Brinck, T.; Murray, J. S.; Politzer, P. *J. Org. Chem.* **1991**, *56*, 2934.
(77) (a) Drew, M. G. B.; Guillaneux, D.; Hudson, M. J.; Iveson, P. B.; Russell, M. L.; Madic, C. *Inorg. Chem. Commun.* **2001**, *4*, 12. (b) Iveson, P. B.; Rivière, C.; Guillaneux, D.; Nierlich, M.; Thuéry, P.; Ephritikhine, M.; Madic, C. *Chem. Commun.* **2001**, 1512. (c) Berthet, J.-C.; Miquel, Y.; Iveson, P. B.; Nierlich, M.; Thuéry, P.; Madic, C.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **2002**, 3265.
(78) (a) Colette, S.; Amekraz, B.; Madic, C.; Berthon, L.; Cote, G.; Moulin, C. *Inorg. Chem.* **2002**, *41*, 7031. (b) Colette, S.; Amekraz, B.; Madic, C.; Berthon, L.; Cote, G.; Moulin, C. *Inorg. Chem.* **2003**, *42*, 2215. (c) Colette, S.; Amekraz, B.; Madic, C.; Berthon, L.; Cote, G.; Moulin, C. *Inorg. Chem.* **2004**, *43*, 6745. (d) Steppert, M.; Walther, C.; Geist, A.; Fanghänel, T. *New J. Chem.* **2009**, *33*, 2437.
(79) (a) Denecke, M. A.; Rossberg, A.; Panak, P. J.; Weigl, M.; Schimmelpfennig, B.; Geist, A. *Inorg. Chem.* **2005**, *44*, 8418. (b) Miguirditchian, M.; Guillaneux, D.; Francois, N.; Airvault, S.; Ducros, S.; Thauvin, D.; Madic, C.; Illemassène, M.; Lagarde, G.; Krupa, J.-C. *Nucl. Sci. Eng.* **2006**, *153*, 223. (c) Denecke, M. A.; Panak, P. J.; Burdet, F.; Weigl, M.; Geist, A.; Klenze, R.; Mazzanti, M.; Gompper, K. *C. R. Chim.* **2007**, *10*, 872. (d) Trumm, S.; Panak, P. J.; Geist, A.; Fanghänel, T. *Eur. J. Inorg. Chem.* **2010**, 3022. (e) Banik, N. L.; Schimmelpfennig, B.; Marquardt, C. M.; Brendebach, B.; Geist, A.; Denecke, M. A. *Dalton Trans.* **2010**, *39*, 5117.
(80) Foreman, M. R. S.; Hudson, M. J.; Drew, M. G. B.; Hill, C.; Madic, C. *Dalton Trans.* **2006**, 1645.
(81) (a) Retegan, T.; Berthon, L.; Ekberg, C.; Fermvik, A.; Skarnemark, G.; Zorz, N. *Solvent Extr. Ion Exch.* **2009**, *27*, 663. (b) Trumm, S.; Lieser, G.; Foreman, M. R. St. J.; Panak, P. J.; Geist, A.; Fanghänel, T. *Dalton Trans.* **2010**, *39*, 923. (c) Hubscher-Bruder, V.; Haddaoui, J.; Bouhroum, S.; Arnaud-Neu, F. *Inorg. Chem.* **2010**, *49*, 1363.
(82) Steppert, M.; Císařová, I.; Fanghänel, T.; Geist, A.; Lindqvist-Reis, P.; Panak, P.; Štěpnička, P.; Trumm, S.; Walther, C. *Inorg. Chem.* **2012**, *51*, 591.
(83) For a similar 1:2 structure between a quadridentate phenanthroline-derived ligand and Eu^{III}, see: Zong, R.; Zhang, G.; Eliseeva, S. V.; Bünzli, J.-C. G.; Thummel, R. P. *Inorg. Chem.* **2010**, *49*, 4657.
(84) (a) Benay, G.; Schurhammer, R.; Wipff, G. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11089. (b) Benay, G.; Schurhammer, R.; Wipff, G. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2922.
(85) Mokhodoeva, O. B.; Myasoedova, G. V.; Zakharchenko, E. A. *Radiochemistry* **2011**, *53*, 35.
(86) Alvila, L.; Pakkanen, T. A.; Krause, O. *J. Mol. Catal.* **1993**, *84*, 145.
(87) Schubert, U. S.; Nuyken, O.; Hochwimmer, G. *J. Macromol. Sci. A* **2000**, *37*, 2000.
(88) Okutani, T.; Oishi, Y.; Uchida, K.; Arai, N. *Nippon Kagaku Kaishi* **1986**, *7*, 853.
(89) Zhang, A.; Zhu, Y.; Liu, Y.; Chai, Z. *Ind. Eng. Chem. Res.* **2011**, *50*, 6898.
(90) Hoshi, H.; Wei, Y.-Z.; Kumagai, M.; Asakura, T.; Morita, Y. *J. Alloys Compd.* **2006**, *408–412*, 1274.
(91) Zhang, A.; Wang, W.; Chai, Z.; Kuraoka, E. *Eur. Polym. J.* **2008**, *44*, 3899.
(92) Zhang, A.; Kuraoka, E.; Kumagai, M. *J. Radioanal. Nucl. Chem.* **2007**, *274*, 455.
(93) Usuda, S.; Liu, R.; Wei, Y.; Xu, Y.; Yamazaki, H.; Wakui, Y. *J. Ion Exchange* **2009**, *21*, 35.
(94) Wei, Y.-Z.; Hoshi, H.; Kumagai, M.; Asakura, T.; Morita, Y. *J. Alloys Compd.* **2004**, *374*, 447.
(95) Wei, Y.; Sabharwal, K. N.; Kumagai, M.; Asakura, T.; Uchiyama, G.; Fujine, S. *J. Nucl. Sci. Technol.* **2000**, *37*, 1108.
(96) (a) Hoshi, H.; Wei, Y.; Kumagai, M.; Asakura, H.; Uchiyama, G. *J. Nucl. Sci. Technol.* **2002**, No. Suppl. 3, 874. (b) Matsumura, T.; Matsumura, K.; Morita, Y.; Koma, Y.; Sano, Y.; Nomura, K. *J. Nucl. Sci. Technol.* **2011**, *48*, 855.