

Review

Isolation and Purification of Actinides Using N,O-Hybrid Donor Ligands for Closing the Nuclear Fuel Cycle

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Abstract: Despite the fact that in the mass consciousness nuclear power is associated with increased environmental risks, this type of energy today remains one of the cleanest, most efficient and carbon neutral. Further development of nuclear energy is hampered by the problem of appropriate handling of spent nuclear fuel (SNF). A very attractive concept of the closed nuclear cycle has been developed to solve it. A real-life implementation of this concept requires the development of technological processes for the efficient separation of minor actinides from the rest of the SNF components. Recent progress in this area has been closely associated with N,O-hybrid donor ligands for liquid–liquid extraction. This work systematically reviews the available literature on the topic and provides detailed explanations on the behavior of the most perspective ligands. Notably, another important aspect of the application of N,O-hybrid donor ligands in nuclear cycle analytics through their incorporation in chemical sensors is also discussed.

Keywords: actinide; lanthanide; separation; extraction; N,O-hybrid extractant



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1. Introduction

Society's serious concerns about the negative impact on the environment caused by the steady growth of carbon dioxide emissions into the atmosphere makes the development of novel reliable, efficient and carbon neutral methods of energy production a high-priority strategic task influencing the development of our civilization. The solution to this problem is being actively discussed at various levels.

Energy sources such as solar and wind do not provide stability and require backup power sources. Therefore, interest in nuclear energy has suddenly increased, especially in developing countries [1,2].

One of the important tasks facing the nuclear power industry is to solve the problem of handling the high-level waste (HLW) generated during the reprocessing of irradiated nuclear fuel. To date, the main process used in various countries for the processing of spent nuclear fuel (SNF) has been the PUREX process, which provides for the separation of uranium and plutonium and their purification from fission products. At the same time, long-lived alpha emitters Cm, Am, together with Cs, Sr and rare earth elements (REE), remain in the liquid HLW fraction.

In the open fuel cycle, nuclear fuel after operation in the reactor (spent nuclear fuel) is considered a waste and is sent to storage. In this case, only a part of the uranium-235 isotope is used. A closed fuel cycle, in which spent nuclear fuel is reprocessed and the separated fissile nuclides—uranium, plutonium, and, in the future, americium—are reused to produce energy, dramatically increases the efficiency of using nuclear fuel. The development of a closed fuel cycle, including both thermal reactors and fast neutron reactors, is being actively pursued [3–6]. The inclusion of more energy-efficient fast reactors in the fuel cycle will allow the extraction of up to 70 times more energy from fuel compared to existing thermal reactors.

Various technologies are being developed in many countries to provide viable, sustainable, and long-term storage solutions for SNF [7,8]. The novel environmentally friendly processes for SNF reprocessing should be based on a simple and efficient separation strategy, and the development of an efficient separation ligand for minor actinides is strongly desired. One of the areas of such research is the separation of americium into a separate fraction for the purpose of its subsequent afterburning in the reactor. Isolation of americium will solve two problems—reduction of the waste activity and the obtaining of additional energy.

Americium should be separated from lanthanides (Ln), because the latter have a high neutron capture cross section. Minor actinides such as americium and curium are chemically very similar to the rare earth elements, so separating them is a rather difficult task.

The ideal extractant for separating actinides and lanthanides must satisfy a whole set of requirements, many of which are poorly compatible or even contradictory. For example, such extractants must selectively bind lanthanide (Ln^{3+}) and actinide (An^{3+}) cations in the presence of transition metal ions, whose concentrations in the highly active PUREX process raffinate can exceed the concentrations of target cations by an order of magnitude or more. They should have exceptionally high radiation stability as well as high hydrolytic stability in a wide range of acid concentrations. Optimal values of distribution ratios of target cations Ln^{3+} and An^{3+} between organic and aqueous phases should be combined with high selectivity in $\text{An}^{3+}/\text{Ln}^{3+}$ pairs, and their high Lewis basicity (ability to bind target cations) with low Brønsted basicity (protonation ability). High extraction rates and achievement of extraction equilibria in a wide pH range are required. The presence of phosphorus and sulfur in the extractant molecule is undesirable as it prevents the final utilization of the spent extraction mixture. In addition, the extractants should be nontoxic, accessible in synthesis, and inexpensive.

Similar requirements are imposed on another component of the extraction mixture—the diluent. It should dissolve well the extractant and solvate of the extractant with metals, should have low viscosity, and a density different from that of the aqueous solution, along with low solubility in aqueous solutions, etc. It is also desirable for it to be inexpensive and nonpoisonous.

New extractants for the isolation and separation of actinides from high-level waste are being actively studied all over the world, and extraction processes based on them are being developed [9–13]. Separation of americium and curium from REE is possible using dialkyl phosphoric acids or alkyl phosphonic acids. The TALSPEAK process [14] and its modifications [15–17] are based on the use of chelating agents.

The solution of bis(2-ethylhexyl)diglycolamic acid (GDEGDHA) in *n*-dodecane (*n*-DD) has also been proposed for the extraction of Eu(III) and Am(III) [18]. Extraction reaches its maximum at pH 2. All these processes work at low acid concentrations. However, the separation process is preferably carried out in an acidic media (more than 1 M of nitric acid) to avoid precipitation. The flowsheet for the separation of americium and REE from PUREX raffinate using a solution of *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) in meta-nitrobenzotrifluoride (F-3) has been developed [19] and successfully tested under dynamic conditions [20] using simulated solutions.

The concentrations of rare-earth elements in the raffinates of the PUREX process significantly exceed (by more than an order of magnitude) the concentrations of minor actinides. Therefore, it is desirable to use actinide-selective extractants in order to minimize the extraction of REE into the organic phase. The use of chelating agents for back-extraction complicates the handling of actinide back-extract, so it is desirable to carry out extraction in an acidic medium, and back-extraction in the weakest possible solution of nitric acid (water).

Polynitrogen-containing heterocyclic compounds [21–24] exhibit very high selectivity to actinides. Compounds such as bis-triazinylpyridine (BTP), bis-triazinylbipyridines (BTBP) and bis-triazinylphenanthrolines (BTPhen) [25] extract americium better than europium with separation factors greater than 100. However, there are limitations to their

use due to their slow extraction (or back-extraction) kinetics and the ability to carry out extraction at relatively low concentrations of nitric acid.

An alternative to polynitrogen-containing ligands is N,O-hybrid ligands, which have both nitrogen atoms (“soft” reaction centers) and oxygen atoms (“hard” reaction centers) in their structure. The combination of hard and soft reaction centers opens up wide possibilities for the creation of a ligand that ensures the isolation and separation of actinides in a single extraction cycle. Derivatives of nitrilotriacetic acid and iminodiacetic acid show selectivity both in the separation of actinides—lanthanides, [26–31], and in the separation of americium from curium [32]. However, the extraction ability of these compounds decreases with increasing concentrations of nitric acid.

It has been found that N,O-hybrid ligands having a heterocyclic nitrogen atom in the molecule, are able to selectively extract actinides from solutions with a high concentration of nitric acid. The only review of studies on the extraction of actinides and REE by N,O-hybrid ligands was published in 2014 [33]. However, great progress has recently been made in the study of hybrid extractants.

The purpose of this work is to review the current situation in the field of chemistry of N,O-hybrid extractants having a heterocyclic nitrogen atom in the molecule. These ligands are very promising for the creation of technological processes for the isolation and separation of actinides necessary for the closure of the fuel cycle.

2. Amides of 2-Pyridinecarboxylic (Picolinic) Acid (PA)

Amides of 2-pyridinecarboxylic (picolinic) acid (Figure 1) are bidentate ligands and show selectivity to actinides [34]. The extraction capacity series with respect to metals has the following form: U(VI) < Ln(III) < Th(IV) [35]. Unfortunately, extraction is possible only at very low concentrations of nitric acid.

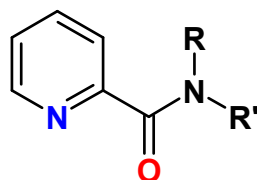


Figure 1. Amides of 2-pyridine-carboxylic acid (PA).

Calixarene-based picolinamide extractants [36–38] and pillar-arene-based picolinamide extractants [39] could extract Am(III) over Eu(III) selectively at around pH 3.0 with moderate separation factors ($SF_{Am/Eu}$ 4–10). However, they extract actinides only from solutions with a nitric acid concentration of less than 0.5 mol/L, and therefore there is little interest in them. The addition of cobalt dicarbollide derivatives makes it possible to shift the working interval of extraction to 1 mol/l of nitric acid.

3. Diamides of 2,6-Pyridinedicarboxylic (Dipicolinic) Acid (DPA)

The combination of “soft” and “hard” donor centers in one molecule provides a high extraction ability with respect to f-elements (due to the oxygens of the amide groups) and a greater affinity for americium and other actinides than for lanthanides (due to the nitrogen of the pyridine ring). The presence of two amide groups in the molecule significantly reduces the basicity of the pyridine nitrogen, which makes it possible to use dipicolinic acid diamides ($pK_a = 0.14$) in solutions with high acidity.

Tetraalkyldiamides of dipicolinic acid (Figure 2) have good solubility in organic solvents and are effective extractants of tetra- and hexavalent actinides (U(VI) and Th(IV)) [40–42]. However, their extraction ability with respect to trivalent actinides and lanthanides is very low [43]. The interest in the study of DPA increased after the selectivity of dialkyl-diaryl diamides of pyridinedicarboxylic acid to americium compared to lanthanides was discovered [44,45]. It was shown that tetraalkyl- and tetraaryl-substituted DPAs, as well

as dialkyl- and diaryl-substituted DPAs, have a low extraction ability with respect to lanthanides and americium. N,N' -dialkyl- N,N' -diaryldiamide DPA have the maximum extraction ability [46]. A separation factor D_{Am}/D_{Eu} of 6 was achieved for solutions of dialkyl diaryl diamides of dipicolinic acid upon extraction from 1–2 M HNO_3 . The extraction ability of N,N' -dialkyl- N,N' -diaryldiamide DPA, depending on the length of the alkyl radical, increases when moving from the methyl radical to the ethyl one, and then begins to decrease.

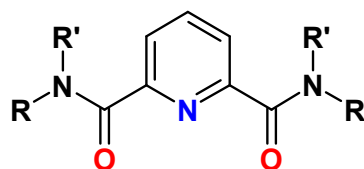


Figure 2. Diamides of 2,6-pyridine-dicarboxylic acid (DPA).

Solutions of N,N' -dialkyl- N,N' -diaryldiamides of dipicolinic acid in polar solvents effectively extract actinides (III, IV, VI) [47,48] and lanthanides (III) from solutions with a nitric acid concentration of 1–6 M. With increasing acidity of the aqueous phase, the values of the distribution ratios of lanthanides increase to 6 M nitric acid [49,50].

It should be noted that the distribution ratios of heavier lanthanides increase much faster than those of light lanthanides with increasing concentrations of nitric acid (for 2 M nitric acid the ratio $D_{Lu}/D_{La} = 0.61$, but for 6 M nitric acid $D_{Lu}/D_{La} = 10$) [51].

The extraction of actinides from nitric acid solutions with solvent on the base of Et(pFPh)DPA in F-3 was studied [52]. The sequence of distribution ratios for the extraction of actinide ions from 3 M HNO_3 is: Pu(IV) > Np(V) \geq U(VI) > Am(III) > Cm(III). It may vary depending on the concentration of nitric acid. Distribution ratios of U(VI) and Pu(IV) from 5 mol/l HNO_3 are similar. Despite the fact that diaryl-substituted DPAs do not extract americium and lanthanides, N,N' -di-p-tolylDPA extracts uranium(VI), but there is very little that extracts thorium (IV) [53].

A general approach to solving the actual practical problem of separating 4f- and 5f-elements with very similar properties based on quantum-chemical supercomputer DFT (non-empirical PBE-functional, extended relativistic full-electron basis) simulation of a large number of pyridine-2,6-dicarboxylic diamide (dipicoline) complexes of Ln^{3+} and An^{3+} with polydentate N,O-ligands is presented in [54].

The method makes it possible to accurately calculate the geometric parameters of ligands and complexes and the binding energies of the metal with the ligand, which allows for a direct comparison of the calculation results with experimental data. Based on the calculations performed, a high extraction ability of DPA analogues with a rigid structure was predicted [55]. Subsequently, this forecast was fully confirmed (see section Py-lactams)

DPA solutions have a rather high radiolytic stability [42,55]. The main products of radiolysis are amines and carboxylic acids [42].

The extraction ability of DPA varies depending on the diluent in the series F-3~phenyl trifluoromethylsulfone (FS-13)~diethylene glycol bis-tetrafluoropropyl ether > dichloroethane > chloroform [47].

These data are in good agreement with the obtained dependences of the effect of the diluent on extraction with Et(m)TDPA from 3 M HNO_3 . The highest distribution ratios are observed for nitrobenzene and FS-13, the lowest for toluene and isopropylbenzene [56].

The use of polar solvents provides high extractability and high metal capacity of the organic phase.

The influence of an ionic liquid (1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C4mim][Tf2N]) on the extraction properties of N,N' -diethyl- N,N' -di(p)-fluorophenyl DPA was studied in [57]. With increasing concentrations of nitric acid, the extraction ability of DPA in the ionic liquid decreases, in contrast to F-3 and FS-13, where it increases. The equilibration time for the extraction of americium is about 20 min.

The extractability of DPA with respect to some other metals, including fission products, has been studied in several works. It is shown that molybdenum is practically not extracted by DPA solutions, while technetium is extracted from weakly acidic solutions [58]. Palladium and zirconium are well extracted by DPA [46]. Note also the noticeable extraction of lead, cadmium and copper.

A flowsheet for HLW processing on the base of (Et(pFPh)DPA) in F-3 was proposed in [58]. The advantage of this flowsheet is the possibility of simultaneous extraction of all actinide elements present in nuclear waste and their separation into fractions. Extraction of palladium and zirconium can be eliminated by adding complexons.

The addition of cobalt dicarbollide or chlorinated cobalt dicarbollide to DPA dramatically increases the extraction ability of both tetraalkyldiamides [44,59–61], and dialkyldiaryl diamides [62–65] with respect to americium and europium. The modified UNEX extractant CDA-PEG-DPA was tested in a dynamic test [66,67].

Dipicolinic acid diamides are tridentate ligands. Two oxygens of the amide groups and nitrogen of the pyridine ring participate in the formation of the complex with metals.

Complexes of diamides of various structures with actinides [68–70] and lanthanides [71–74] were obtained and studied.

The complexes of uranyl nitrate with dialkyldiaryl DPA and tetraalkyl DPA have the same metal:ligand ratio of 1:1. However, the structure of the complexes is very different—if for dialkyldiarylDPA a tridentate coordination of the uranyl ion is observed, then for tetraalkyl DPA a linear structure of the complex is found, which is characteristic of complexes with dipicolinic acid [69].

The complexation of N,N,N',N'-tetraethyl-2,6-carboxamidopyridine (tetraethylDPA) with trivalent lanthanides, Y(III), Am(III) and Cm(III) was studied with a combined NMR spectroscopic and time-resolved laser fluorescence spectroscopic (TRLFS) methods. NMR and TRLFS methods showed a higher stability of the Cm(III) complex compared to the corresponding Eu(III) complex [75].

The structure of the complex with lanthanides varies depending on the structure of DPA, so for unsubstituted DPA [73] and for tetraethylDPA, metal:ligand = 1:3 complexes are formed [71], and for N,N'-dimethyl-N,N'-diphenylpyridineDPA metal:ligand = 1:2 complex is formed [73].

The relative stability of metal:tetramethyl DPA 1:2 and 1:3 complexes in methanol solution was discussed on the basis of spectra and quantum calculations [74].

The complex formation of actinides and lanthanides with dipicolinic acid diamides and their dithio analogs was studied using DFT calculations. A higher selectivity of An(III)/Ln(III) complexation was shown for dithioligands [76].

Unfortunately, thio-derivatives have very low extraction ability with respect to actinides [77].

Differences in the mechanism of extraction of metals by solutions of N,N'-aryl DPA containing intramolecular hydrogen bonds and N,N'-aryl- N,N'-diethyl DPA are shown in [78]. The authors convincingly demonstrated the effect of intramolecular hydrogen bonds on extractions by the example of extraction of d-elements. Extraction of transition metal picrates including Ag^+ , Hg^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} salts with solutions of N,N'-aryl- N,N'-diethyl DPA was demonstrated. Extraction percentage decreased in the order $\text{Hg}^{2+} > \text{Ag}^+ > \text{Cu}^{2+} > (\text{or } \geq) \text{Ni}^{2+} \sim \text{Co}^{2+} \sim \text{Zn}^{2+} \sim \text{Pb}^{2+} \sim \text{Cd}^{2+}$. The authors explained the low extractability of N,N'-diaryl DPA compared to diethyldiaryl DPA by the effect of intramolecular hydrogen bonding.

However, in the extraction of metals with solutions of dialkyldiaryl DPA F-3 from nitric acid, for all DPAs, the extraction of soft cations is much higher than that of hard ones. The sequence of extraction of nitrates by N,N'-diethyl N,N'-di(2-methoxyphenyl) DPA Et(oMeOPh)DPA is $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} \gg \text{Zn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$. The structure of the diamide affects the selectivity of the extraction. Although the general trend continues—soft cations are extracted better, and the order in the extractability sequence for soft

ions for N,N'-diethyl N,N'-di(2,6-dimethylphenyl) DPA Et(2,6-diMePh)DPA changes: $Pb^{2+} > Cu^{2+} > Cd^{2+} \gg Zn^{2+}, Co^{2+}, Ni^{2+}$ [51].

DPA have been proposed as a ligands for the solid-phase extraction for An/Ln(III) separation [79–82].

4. Amides of 1,10-Phenanthroline-2-carboxylic Acid (PTA)

Amides of 1,10-phenanthroline-2-carboxylic acid (Figure 3) contain three reaction centers—two nitrogen atoms and one oxygen atom. The presence of two soft reaction centers leads to an increase in the selectivity of americium–europium. It has been shown that the amide oxygen deviates from the plane of the phenanthroline moiety [83].

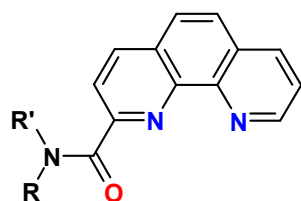


Figure 3. Amides of 1,10-phenanthroline-2-carboxylic acid (PTA).

A process for the selective isolation of transplutonium elements from acidic solutions has been proposed and patented [84,85]. The process provides for the use of 0.5 M N-octyl-N-tolyl-1,10-phenanthroline-2-carboxamide (**OcToIPTA**) solution in chloroform as an extractant. During extraction from 1 M of nitric acid, Am is selectively extracted with a separation factor $SF(Am/Eu) = 20$. Distribution ratios are $D_{Am} = 6$, $D_{Eu} = 0.3$.

Am and Eu extraction with N, N-dialkyl-1,10-phenanthroline-2-amides (alkyl = ethyl, butyl, hexyl) in chloroform was studied in [86]. The highest $SF_{Am/Eu}$ was determined to be (7.6 ± 0.3) at an acidity of around 10^{-4} mol/L. Extraction is negligible when nitric acid concentration is higher than 0.01 mol/L.

Extraction of Am, Cm and Eu with solutions of N-ethyl-N-tolyl-2-amide-1,10-phenanthroline in nitrobenzotrifluoride have been studied [87]. Complexes of the type $M(NO_3)_3L$ and $M(NO_3)_3L_2$ are formed in the extraction system, and their extraction equilibrium constants follow the order $Am(III) > Cm(III) > Eu(III)$. The D_M ($M = Am, Cm, \text{ and } Eu$) values sharply decrease as the acidity in the aqueous phase increases, so extraction is possible only from solutions with nitric acid concentrations lower 0.01 mol/L.

The selectivity of the extraction of lanthanides by **OcToIPTA** in chloroform varies significantly depending on the type of counter ion. The distribution ratios in the series of lanthanides generally increase from lanthanum to lutetium for chloride and perchlorate. In the case of nitrate, the maximum distribution ratios are observed for neodymium–praseodymium [88].

The mechanisms of complexation and structural properties of complexes formed by an asymmetric Et-Tol-PTA ligand with typical lanthanides, depending on the type of anion, have been systematically studied [89].

A synergistic mixture of N-methyl-N-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA) with pivaloyl trifluoroacetone (HA) extracts samarium better than other lanthanides [90].

Hybrid adsorbents have been prepared through functional immobilization of **OcToIPTA** [91] or N-methyl-N-phenyl-1,10-phenanthroline-2-carboxamide (**MePhPTA**) [92,93] into large and cage-pored mesoporous silica monolith. These adsorbents indicated the high sorption capacities for lanthanides at pH 4. It was shown that O and N donor atoms of the HA were strongly coordinated to lanthanide ions to form stable complexes. However, the bond distance of O donor atoms was shorter than that of N donor atoms. **MePhPTA** also forms complexes of the composition $Me:L = 1:2$ with europium and neodymium [94], as well as with other lanthanides [95].

5. Diamides of 2,2'-Dipyridyl-6,6'-dicarboxylic Acid (BPyDA)

BPyDA (Figure 4) are tetradentate ligands; two nitrogen atoms of pyridine rings and two oxygens of amide groups participate in the formation of a complex with metals [96]. The first extraction mixture studied, containing BPyDA and having a high selectivity for separation of americium–europium, was a mixture with chlorinated cobalt dicarbollide [97–99]. BPyDA–CCD mixtures in polar fluorinated diluents selectively extract americium from solutions of nitric acid (0.5–1 M HNO₃). Separation factor SF(Am/Eu) is greater than 20. BPyDA has been tested as a component of modified UNEX extractant [100].

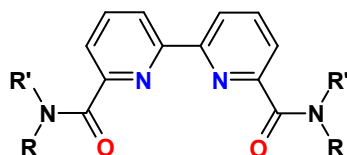


Figure 4. Diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid (BPyDA).

Subsequently, it was shown that BPyDA solutions also extract actinides, while the selectivity of separation from lanthanides is preserved [101]. The structure of BPyDA strongly influences their solubility and extractability [102,103]. Tetraalkyl-BPyDA is significantly inferior to dialkyl-diaryl-BPyDA in terms of extraction ability. BPyDA containing bromine atoms in pyridine rings also have a low extraction ability [102]. With an increase in the acidity of the aqueous phase to 5 M HNO₃, an increase in the distribution ratios of metals occurs. Separation factor D(Am)/D(Eu) for all compounds studied was in the range from 8 to 18 [102,103].

BPyDA selectively extracts actinides (Am(III), Pu(IV), Np(V), U(VI)) from 2–6 M nitric acid solutions. The distribution ratio values decrease in the order U(VI) > Pu(IV) ≥ Np(V) > Am(III) > Cm(III) > Ln [51,104]. Technological flowsheets for separating actinides from rare earth elements with a BPyDA solution in a polar diluent have been proposed [58] and tested [105].

BPyDA complexes with various ions have been obtained and characterized. In all cases, BPyDAs are tetradentate ligands. Decacoordinated lanthanide ions in BPyDA complexes are bonded by the tetradentate ligand and three bidentate nitrate groups [106].

The effect of the size of lipophilic aliphatic substituents in the BPyDA ligands on the photophysical characteristics of europium and gadolinium complexes was studied [107–109]. Quantum-chemical modeling of the structure of BPyDA and BPyDA-REE complexes has been carried out [103,110].

The thermal stability [111–113] and irradiation effects [114,115] on BPyDA and DPA solutions have been studied. These compounds were shown to be moderately resistant to radiolysis, and DPA is somewhat more stable than BPyDA.

The thermodynamics of Th(IV) complexes with N,N,N',N'-tetramethyl-2,2'-bipyridine-6,6'-dicarboxamide (TMBPyDA) and N,N,N',N'-tetramethyl-1,10-phenanthroline-2,9-dicarboxamide (TMPhenDA) were determined by spectrophotometry and calorimetry [116].

The formation of dimeric complexes of uranyl with TMBPyDA was found [117].

BPyDA extracts cadmium much more strongly than DPA [95], and also exhibits very high selectivity in the extraction separation of scandium from other rare earth elements [118]. Separation factors SF (Sc/Ln) reach several thousand.

6. Diamides of 6,6''(2,2':6',2''-Tripyridine)-dicarboxylic Acid (TPyDA)

TPyDA (Figure 5) are pentadentate ligands. It has been shown that all five reaction centers are indeed involved in the formation of the complex with uranium [119,120].

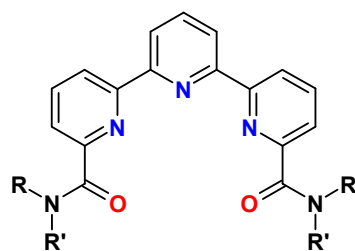


Figure 5. 6,6''(2,2':6',2'')-tripyridine)-dicarboxylic acid diamides (TPyDA).

The solutions of TPyDA in nitrobenzene has high extraction ability to Pu(IV), Np(V, VI), U(VI) [121,122]. However, they extract both lanthanides and americium very weakly. The $SF_{Am/Eu}$ is only 5, despite the presence of three “soft” reaction centers. Metal distribution ratios decrease with increasing nitric acid concentrations in the aqueous phase due to the high basicity of the ligand ($pK_a = 1.0$), resulting in easy protonation [123].

7. Diamides of 1,10-Phenanthroline-2,9-dicarboxylic Acid (PHENDA)

PhenDA (Figure 6) were proposed in 2011 [124] as a basis for the development of the selective solvent extraction of Am(III). The protonation and complex (ML^{n+}) formation constants determined for unsubstituted PhenDA showed that it has a very low proton affinity ($pK = 0.6$) and should have a reasonably high affinity for f-elements (Ln^{3+} , Th^{4+} and UO_2^{2+}) [1] and unusually low affinity for Cu(II), Ni(II), Co(II), Zn(II), and Mg(II) [125].

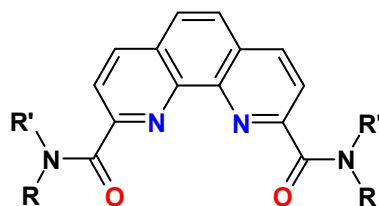


Figure 6. 1,10-phenanthroline-2,9-dicarboxylic acid diamides (PhenDA).

The results of DFT calculations [126] showed that ligand PhenDA had the smallest reorganization energy among the three ligands, with similar structures but different bridging frameworks, Et-Tol-PhenDA, Et-Tol-BPyDA and Et-Tol-PyDA, suggesting a less geometrical rearrangement in the complexing state due to the rigidity of phenanthroline ring.

The effect of structure on the extraction properties of PhenDA was investigated [127–130]. As for other dicarboxamides, an anomalous aryl strengthening effect was observed for PhenDA [123]. The highest extraction ability to f-elements was found for ligands with both alkyl and aryl substituents at amidic nitrogen.

PhenDA has a very high extraction ability for actinides. The extraction ability of PhenDA decreases in the following order: Th(IV) > U(VI) > Pu(IV) > Np(V) > Am(III) > Cm(III) [52,131,132]. The extraction of actinides Th(IV), U(VI), Am(III) and Eu(III) from nitric acids solutions with 0.01 M Et-Tol-PhenDA in cyclohexanone has been studied [126]. The separation factors of Th(IV), U(VI), and Am(III) toward Eu(III) are 2277, 277, and 67 in 1.0 M HNO_3 , respectively.

Overall SF (Am/Cm) is close to 2, and depends weakly on the acidity of the aqueous phase and the type of organic diluent [52,133]. The influence of the diluent on the extraction of americium, curium and lanthanides with tetradodecylPhenDA was studied in [131]. Diluents affect the extraction ability in the following order: nitrobenzene > nitrophenyloctyl ether ~ F-3 > toluene ~ dodecane + 10% 2-ethylhexanol.

The effect of the structure of Phen-diamides on Am(III) and Cm(III) separation was investigated in [51]. It was found that ligands with electron-withdrawing chlorine atoms at positions 4 and 7 of the phenanthroline moiety possessed the highest selectivity to Am over Cm ($SF_{Am/Cm} = 6.0 \pm 0.5$) among all studied diamides.

The structure of PhenDA complexes with actinide nitrates was investigated in solid crystals by XRD [130,131,134], in solutions by ESI-MS, UV-vis spectroscopy and EX-AFS [128], and also on the basis of DFT calculations [135–140]. The solvation numbers determined using the results of metal extraction with TBuPhenDA in F-3 from 3 M HNO₃ [52] were 1 for all actinides—U(VI), Pu(IV), Am(III), Cm(III). Therefore, the following complexes of 1:1 stoichiometry were formed in the organic phase: L·UO₂(NO₃)₂, L·Pu(NO₃)₄, L·Am(NO₃)₃ and L·Cm(NO₃)₃. The same stoichiometry for PhenDA complex with uranyl nitrate was determined in [130,134,141]. At the same time, solvation numbers reported for Pu(IV) and Am(III) extraction from 1 M HNO₃ with Et-Tol-PhenDA in F-3 were higher, and were equal 1.6 for Am(III) and 1.8 for Pu(IV) [129]. A Pu solvation number of 1.43 was determined for extraction with Et-Ph-PhenDA in 1-octanol from 4 M HNO₃ [134].

The crystal complexes of various PhenDA (Et(pTol)PhenDA, MePhPhenDA, TEt-PhenDA) with uranyl nitrate were synthesized and characterized in [130,131,135]. X-ray diffraction measurements showed the formation of the [UO₂(PhenDA)NO₃]₂·NO₃ complex. PhenDA acts as a tetradentate ligand. Two N atoms of phenanthroline ring and two O of carboxylic groups formed bounds with UO₂²⁺ ion. A dimeric structure [(UO₂)₂(O₂)(TMePhenDA)₂](ClO₄)₂, which is the dimer of complex [UO₂(TMePhenDA)]²⁺ bridged by a peroxide group, was determined using XRD for the complex of TMe-PhenDA with uranyl perchlorate [117].

A 1:1 coordination mode was determined by X-ray crystallography for the crystal structure of Et-Tol-PhenDA with thorium nitrate [Th(PhenDA)(NO₃)₄] [131]. The complex of TMePhenDA with thorium perchlorate [Th(TMePhenDA)₂(CH₃OH)₂](ClO₄)₄ includes two molecules of diamide coordinated to the metal ion in a tetradentate fashion through two aromatic N-donors and two carbonyl O-donors [116].

High-efficiency sorbents prepared by the functionalization of graphene oxide with phenanthroline diamide have been proposed [142] for the separation of U(VI) and Th(IV) from lanthanides from acidic waste solutions. At pH 0, the separation factors of U(VI) and Th(IV) over Eu(III), Nd(III) and Sm(III) were all higher than 23.

Using DFT simulations [143], it was predicted that N,N'-dialkyl-N,N'-diaryl-1,10-phenanthroline-2,9-dicarboxamides should possess higher affinity for light lanthanides having larger ionic radii, and should exhibit higher selectivity than diamides BPyDA due to their more rigid geometry. The results of calculations clearly showed this general trend, i.e., the significant decrease in metal-to-ligand binding energies in the complexes [(L)Ln(NO₃)₃] (L = EtPh(Cl)PhenDA) with increasing atomic number of the lanthanide. This prediction was confirmed in solvent extraction experiments [127,144]. In accordance with the results of theoretical simulation, N,N'-dialkyl-N,N'-diaryl-PhenDA (Et(pHexPh)(Cl)PhenDA, Et(pEtPh)PhenDA) exhibited high affinity for light lanthanides. The distribution ratios D from La to Lu decreased sharply with increasing atomic number of Ln³⁺. The high affinity of the N,N'-dialkyl-N,N'-diaryl-PhenDA to light lanthanides limits the possibility of their usage for Am separation from HLW, because its separation from light lanthanides will be unsatisfactory. The selectivity of Am extraction over lanthanides increases from La(III) to Lu(III). The separation factors of Am(III) toward La(III) and Ce(III) determined for 0.05 M Et(pEtPh)PhenDA in F-3 were SF (Am/La) = 1.0 and SF (Am/Ce) = 2.0 in 3 M HNO₃ [127]. The Am/Eu separation factor under these conditions is SF (Am/Eu) = 38. The same dependence of Ln distribution ratio on atomic number was noted in [145,146]: with increasing atomic number of Ln, both the extraction efficiency and the concentration of metal ions in organic export decrease rapidly. Unfortunately, the selectivity of Am extraction over Ln was not evaluated. Surprisingly, the results published in [132] for Ln extraction with 0.01 M Et(pTol)PhenDA in F-3 from nitric acid solutions did not show any dependence of Ln distribution ratios on metal atomic number, but showed high selectivity of Am extraction over Ln. Depending on the acidity of the aqueous phase (1–4 M HNO₃), the SF (Am/La) were within 7.8–11.7.

From the point of view of Am(III) and Ln(III) separation, PhenDA with 4 alkyl substituents on amidic N atom are the most promising. The character of Ln extraction with

tetraalkyl-PhenDA is completely different from that of dialkyl-diaryl-PhenDA [127,133]. The distribution ratios of Ln(III) are close to one another. The change in the pattern of lanthanide extraction across the row depends slightly on the diluent type and the acidity of the aqueous phase, but overall, there are two shoulders in the extraction pattern with break point on Gd. The separation factors determined in 3–4 M HNO₃ for the solvents on the base of TBuPhenDA and TDdPhenDA in F-3 are moderate ($SF_{Am/Ln} > 4-5$), but sufficient for the development of workable Am/Ln separation flowsheet.

The composition of the complexes of PhenDA with Ln(III) nitrates in crystals and in organic solutions was investigated. The slope analysis, ESI-MS study, UV–vis titration and DFT simulations indicated [127,133,135,139,144,145,147] that both Ln(L)(NO₃)₃ and Ln(L)₂(NO₃)₃ complexes were able to form in loaded organic phase.

The crystal complexes of various PhenDA with Ln(III) nitrates were synthesized and characterized by XRD. The structures with Me:L = 1:1 ratio [Ln(L)(NO₃)₃] were determined for complexes of PhenDA with Nd [127], Gd [127], and Eu [148]. At the same time, two types of structures were found for complexes of PhenDA with lanthanum nitrate: [La(L)₂(NO₃)₂][NO₃] [127,148] and [La(L)(NO₃)₃] [145,148,149].

The complexation of TMe-PhenDA and T(iBu)-PhenDA with Ln(III) perchlorates was studied in [150] using various analytical techniques, such as absorption spectroscopy, TRLFS, and NMR. It was shown that, in solution, ligand TMePhenDA as well as T(iBu)-PhenDA formed ML and ML₂ complexes with Nd(III) and Eu(III) through the same (ON–N–O) coordination mode. The study of crystal complexes of TMe-PhenDA with Nd(III) and Eu(III) perchlorates showed the formation of the structure with a ratio of Me:L = 1:2 only.

The extraction and complexation of Am(III) and Ln by different ligands with different substituent groups on the diamide moiety in an ionic liquid (IL), C₄mimNTf₂, have been studied [151–153]. The extraction ability of the PhenDA decreased with increasing concentration of nitric acid in the initial solution, as well as for DPA [56]. PhenDA with lipophilic substituents can be used as a solution in octanol [134,154].

Et-Tol-PhenDA was used in a novel cloud point extraction (CPE) procedure to pre-enrich Th(IV) and U(VI) [155].

8. Py-Lactams

Brayntsev and Hay [156] calculated the selectivity in the extraction separation of Am and Eu with various lactams with saturated lactam rings (Figure 7) using different DFT methods.

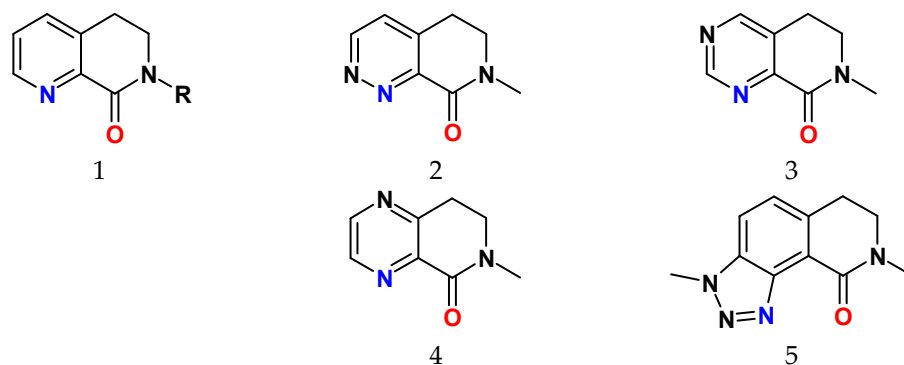


Figure 7. Structures of studied lactams.

The gas phase thermodynamic parameters calculated for extraction equilibrium described by Equation (1) are presented in Table 1.

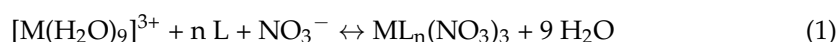


Table 1. Calculated extraction energies (ΔG_{ext}) and predicted selectivities of ligands in the separation of Am(III) and Eu(III) ($\Delta\Delta G_{\text{ext}}(\text{Am-Eu})$) by solvent extraction into kerosene. Reprinted with permission from ref. [157]. Copyright 2015 Royal Society of Chemistry.

Complex $M(L)_2(NO_3)_3$	$\Delta G_{\text{ext}}, \text{kcal}\cdot\text{mol}^{-1}$		$\Delta\Delta G_{\text{ext}}(\text{Am/Eu})$
	Am	Eu	
1 (R = Me)	−23.66	−21.77	−1.89
2	−16.60	−14.47	−2.14
3	−18.39	−16.84	−1.55
4	−19.62	−18.10	−1.53
5	−21.36	−18.92	−2.44

According to the calculation results, all studied lactams should selectively extract Am over Eu. The authors showed that ligand 1, which has a preorganized structure, extracts both europium and americium better by approximately eight orders of magnitude than the corresponding picolin amide. The selectivity of the Am(III)/Eu(III) extraction appears to be insignificant. The separation factor SF (Am/Eu) = 13.2 was noted for a solution of ligand 1 in 1,2-dichloroethane. Unfortunately, no other published experimental data on the extraction ability of the discussed ligands were found.

9. Py-Dilactams (PyDilac)

In 2014 Ustyunyk et al. [54], during detailed DFT simulation of pyridine-2,6-dicarboxamides and their complexes $LM(NO_3)_3$ ($M = \text{Am}, \text{Eu}$), assumed that dilactams of pyridine-2,6-dicarboxylic acid (Figure 8) should exhibit much better extraction properties. The inclusion of both amide groups into the six-membered rings makes it possible to build a rigid structure with the almost zero pre-organization energy. It was predicted that the extraction ratio and the separation factor $SF_{\text{Am/Eu}}$ should increase by about two orders and one order of magnitude, respectively, upon moving to this more conformationally rigid structure PyDilac A from the diamide with open structure (DPA). The results of DFT study for PyDilac B were reported in [158]. The gas-phase thermodynamic parameters and predicted $SF_{\text{Am/Eu}}$ presented in Table 2 were calculated using Equation (2).

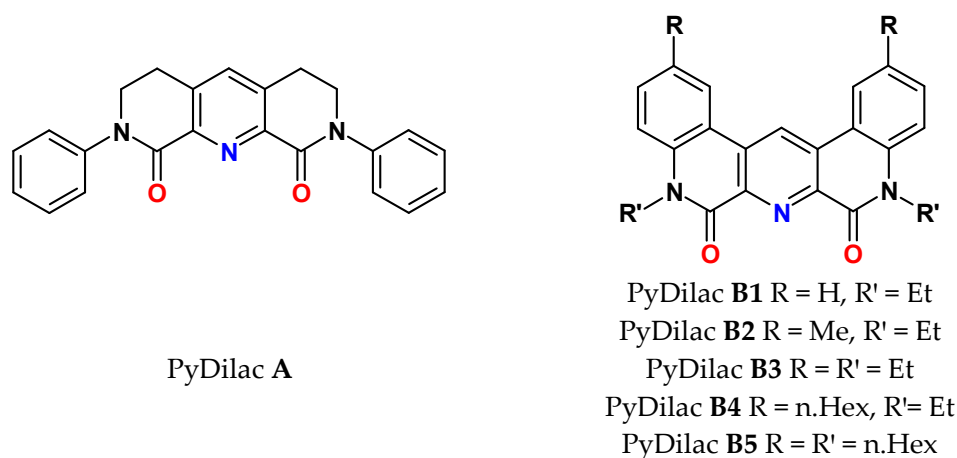


Figure 8. The structures of studied dilactams.

Table 2. The Gibbs energies of formation of complexes and Am-Eu separation factors, based on [53,158]. Me stands for Am or Eu.

Complex	$\Delta\Delta G_{\text{ext}}(\text{Am/Eu})$	$SF_{\text{Am/Eu}}$	Reference
Me(PyDilac A)(NO ₃) ₃	−1.9	24.8	[54]
Me(PyDilac B1)(NO ₃) ₃	−2.2	40.1	[158]
Me(PyDilac B1) ₂ (NO ₃) ₃	−2.0	29.1	[158]

The theoretical prediction made was verified experimentally in [159]. Three new dilactams PyDilac **B3**, PyDilac **B4** and PyDilac **B5** were synthesized, and their extraction ability and selectivity toward Am(III) and Eu(III) were investigated. In strict accordance with the prediction made, the dilactams selectively extracted Am (III) from nitric acid solutions. Values of $SF_{\text{Am/Eu}} \sim 20\text{--}30$ were achieved for 1 mM solution of PyDilac **B5** in F-3. The distribution ratios of Am(III) for PyDilac **B5** were more than three orders of magnitude higher than that found for Et(pT)DPA, which is a conformationally labile analog of PyDilac **B** with an open structure.

P.I. Matveev [160] studied the extraction of lanthanides and Cm(III) from nitric acid solution with PyDilac **B5** in F-3. The extraction ability of PyDilac **B5** for Cm(III) was almost the same as that for Am(III). The separation factors of Am over Cm ($SF_{\text{Am/Cm}}$) depend slightly on the acidity of the aqueous phase and are within 1.0–1.4. The character of metal extraction across the series was similar to that previously published by Paulenova et al. in [50] for Ln extraction from 0.5–1.0 M HNO₃ with Et(o)TDPA in FS-13. The distribution ratios increased from lanthanum to cerium, with the maximum being found for Nd and Sm, followed by a decrease from Sm to Gd, and were almost constant for heavy lanthanides (Gd–Lu). This lanthanide extraction pattern was confirmed later for PyDilac **B4** in [161].

The radiolysis of PyDilac **B5** was investigated in [162]. The rather unique dependence of dilactam extraction properties on irradiation was demonstrated. The samples of solvent (0.05 M PyDilac **B5** in dodecanol/“Isopar-M”) in contact with nitric acid solutions fully retained their extraction properties following irradiation at up to 500 kGy.

The crystal complex of PyDilac **B3** with water was synthesized and characterized in [163]. The XRD analysis showed that there were two solvate water molecules in the complex: one of them was linked via hydrogen bonds of approximately the same length with the oxygen atoms of both amide groups, the second water molecule was located at the lipophilic moiety of molecule and held by shortened C—H . . . O contacts. The dimers were combined via a hydrogen bond network including solvate water molecules into a one-dimensional polymer structure. Additionally, DFT calculations for the dilactam structures and their complexes with water, hydroxonium ion and trifluoroacetic acid were performed. The calculations showed that dilactams easily form adducts with one and two molecules of trifluoroacetic acid. The acid molecules form hydrogen bonds in both structures with the carbonyl oxygen atoms of the dilactam. These conclusions were confirmed by experimental data of NMR, UV-vis and IR spectroscopy. Complexes of lactams with lanthanum thiflate [(PyDilac **B3**)₂·La(NO₃)₃] and europium nitrate [(PyDilac **B5**)₃·Eu(NO₃)₃] were characterized by elemental analysis, mass spectrometry and NMR.

10. Phen-Dilactams (PhenDilac)

The selectivity in the extraction separation of Am and Eu was evaluated using DFT simulations for model Phen-dilactam PhenDilac **A1** (Figure 9) in [156]. Gas-phase thermodynamic parameters were calculated for extraction equilibrium as described by Equation (1). The calculations modeled the extraction of Am(III) and Eu(III) from nitric acid solution with PhenDilac **A1** solution in kerosene. The results showed that PhenDilac **A1** should selectively extract Am(III) over Eu(III). The calculated extraction energies of extraction equilibrium (ΔG_{ext}) with M(PhenDilac **A1**)(NO₃)₃ complex formation in the organic phase were $-22.23 \text{ kcal}\cdot\text{mol}^{-1}$ for Am(III) and $-20.53 \text{ kcal}\cdot\text{mol}^{-1}$ for Eu(III), and the predicted selectivity of PhenDilac **A1** $\Delta\Delta G_{\text{ext}}(\text{Am/Eu})$ was $-1.70 \text{ kcal}\cdot\text{mol}^{-1}$.

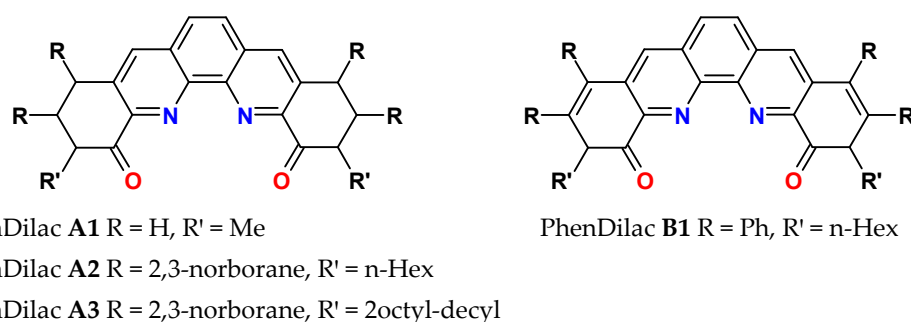


Figure 9. Structures of studied Phen-dilactams.

The extraction properties of two dilactams of 1,10-phenanthroline-2,9-dicarboxylic acid with saturated (PhenDilac **A2**) and unsaturated (PhenDilac **B1**) δ -lactam rings were studied in [164]. The rigid structure of dilactams provides them with very high affinity to f-elements and high selectivity to Am(III) over Ln(III) (Table 3). The extraction of Am and Eu from 0.03–3 M HNO₃ solution into 1,2-dichloroethane was studied. The distribution ratios increased with increasing aqueous phase acidity. The separation factors reported for PhenDilac **B1** varied in the range 100–500, with a maximum at 0.3 M HNO₃. D values for Am(III) extraction by PhenDilac **A2** and PhenDilac **B1** are more than six orders of magnitude higher in comparison to the less preorganized **TOctPhenDA**. The higher extraction ability of Phen-dilactams in comparison to the Phen-DA with open structure is explained by the higher pre-organization energy of the latter. The DFT calculations using the B3LYP functional performed for model ligands showed that preorganization energy of Phen-dilactams ($\Delta E_{\text{reorg}} = 4.3\text{--}4.4$ kcal/mol) was much smaller than that of model PhenDA ($\Delta E_{\text{reorg}} = 21.1$ kcal/mol).

Table 3. Separation of Am(III) and Eu(III) from 3 M HNO₃ by 1.0 mM ligands PhenDilac **A2**, PhenDilac **B1** and **TOctPhenDA** in 1,2-dichloroethane. Adapted with permission from ref. [165]. Copyright 2017 American Chemical Society.

Ligand	D_{Am}	D_{Eu}	$SF_{\text{Am/Eu}}$
PhenDilac A2	>1000	>1000	n.a.
PhenDilac B1	3525 ± 292	17 ± 5	211 ± 47
TOctPhenDA	0.0031 ± 0.0002	0.0005 ± 0.0001	6.5 ± 1.5

In contrast to the data published in [156], where selective Am(III) extraction was predicted for PhenDilac **A1** with saturated lactam rings, the DFT calculations performed in [164] showed that ligand PhenDilac **A** with saturated lactam rings should not possess selectivity for Am(III). This effect can be explained by the different manner of the delocalization of lone-pair electrons on the N_{amide} . In the case of PhenDilac **A**, the lone-pair electrons on the N_{amide} are delocalized over the $N\text{--}C=O$ fragment only, leading to the enhancement of Lewis base donor strength of the amide oxygen atoms. In the case of PhenDilac **B** with unsaturated lactam rings, the lone-pair electrons on the N_{amide} are delocalized over the $N\text{--}C=O$ and $N\text{--}C=C$ moieties, thereby decreasing the Lewis basicity of the ligand, weakening metal–ligand coordination, and making the ligand more selective to Am(III). These calculations were confirmed in [161], where extraction of Am(III) and Ln(III) from 3 M HNO₃ solution with 4 mM solution of PhenDilac **A3** in Isopar L–Exxal 13 (10 vol.%) mixture was investigated. The results revealed that both metals were equally well extracted into the organic phase by ligand PhenDilac **A3** ($D_{\text{Am}} = 268 \pm 13$, $D_{\text{Eu}} = 279 \pm 14$), with no apparent selectivity for one or the other.

The intra-group separation of Ln with PhenDilac **A2** and PhenDilac **B1** from HCl and HNO₃ solutions was investigated in [166]. The character of Ln extraction found for PhenDilac **A2** and PhenDilac **B1** coincided with that previously found for dialkyl-

diaryl-substituted PhenDA [127,143]: the distribution ratio values decreased steeply with decreasing metal ionic radii from La to Lu. This fact confirms once more that the character of the Ln extraction across the series is determined by the size of the cavity formed by donor atoms of the ligand, in particular by the distance between the oxygen donor atoms. The authors noticed the extremely high separation factor for La(III) over Lu(III) of 1.7×10^4 found for PhenDilac A2. The DFT calculations showed that ligand PhenDilac A with saturated lactam rings was more rigid than ligand PhenDilac B and exhibited a larger reorganization energy upon complexation with Lu(III) compared with complexation with La(III). Additionally, it was predicted that the ligand with the five-membered lactam rings (instead of the six-membered rings in PhenDilac A and PhenDilac B), with a larger distance between the oxygen donor atoms, should exhibit enhanced selectivity towards Ln(III) with larger ionic radii.

The extraction data [161,164] and DFT calculations [167] showed that both 1:1 and 2:1 ligand–metal complexes were present in the organic phase. At the same time, only 1:1 ligand–metals complexes were observed during the investigation of the five crystal complexes of PhenDilac A2 with Pr^{3+} , Nd^{3+} , Eu^{3+} , Gd^{3+} , and Tb^{3+} by the single-crystal X-ray diffraction [164].

The evaluation of d-element extraction with 3a and 4a revealed that studied dilactams has high affinity to Pd(II) and Ag(I) but in contrast to PhenDA possess very low extraction ability to Cu(II) [161].

11. 1,10-Phenanthroline-2,9-(2-dipyridyl)-6,6'-dicarboxylic Acid Diamides (Py-Phen)

Py-Phen—ligands (Figure 10) with six reaction centers (four nitrogen atoms and two oxygens of amide groups) exhibit high extraction ability for plutonium and neptunium and a moderate one for americium [165,168].

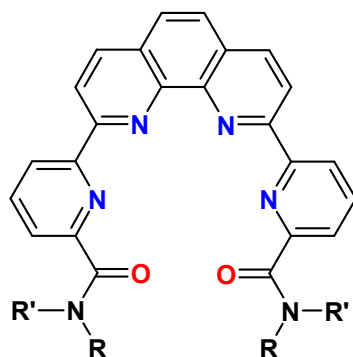


Figure 10. Diamides of 1,10-phenanthroline-2,9-(2-dipyridyl)-6,6'-dicarboxylic acid (**Py-Phen**).

The selectivity of americium–europium is close to that of PhenDA, about 19–26, depending on the substituents at the amide nitrogen atom. The complexation of Am(III) and Eu(III) was investigated in [169] on the basis of DFT calculations.

12. Other N,O Hybrid Amide Extractants

Unusual selectivity towards Pu(IV) over Am(III) was observed for N,N,N',N' tetra-isobutyl pyridine diglycolamide (**PDGA**) (Figure 11) solutions in nitrobenzene. The extraction mechanism in molecular diluent and 3-methyl-1-octyl imidazolium bis[(trifluoromethyl)sulfonyl] imide solutions was discussed in [170].

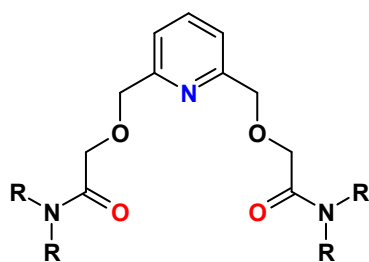


Figure 11. *N,N,N',N'* tetra-isobutyl pyridine diglycolamide (**PDGA**) (R = *i*Bu).

TAP (R = Oct)

Three tri-aryl-pyridine (**TAP**) diamides (Figure 12) containing a pyridine spacer showed selective Pu(IV) extraction [171]. The extraction of Am(III), Eu(III), Sr(II) and Cs(I) was <0.1%.

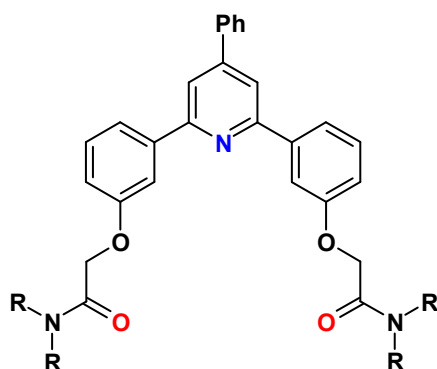


Figure 12. Tri-aryl-pyridine diamides.

New extractants with pyrrolidone groups has been proposed for selective uranium extraction from the phenanthroline skeleton [172]. These extractants had high radiation stability.

13. *N*-Heterocyclic Diphosphine Oxides (**PyPO**, **BPyPO**, **PhenPO**)

Extraction properties of **PyPO** (Figure 13) and two pyridine-2,6-diphosphine dioxides: **Ph₂PyDPO** (*P,P',P'*-tetraphenylpyridine-2,6-diphosphine oxide) and **tBuPhPyDPO** (*P,P'*-ditretbutyl-*P,P'*-diphenylpyridine-2,6-diphosphine oxide) (Figure 14) were studied in [173]. The extraction ability of *P,P*-diphenyl pyridine-2-phosphine oxide was extremely low due to its high basicity. In the extraction of Am(III) from 1–3 M HNO₃, the distribution ratios did not exceed 0.005.

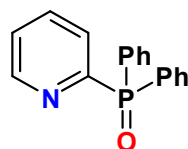


Figure 13. *P,P*-diphenyl pyridine-2-phosphine oxide **PyPO**.

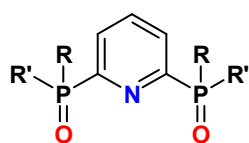


Figure 14. *P,P,P',P'*-tetraphenylpyridine-2,6-diphosphine oxide **PyDPO**.

The distribution ratios of americium upon extraction from 1–2 M HNO₃ with a solution of 0.001 M **Ph₂PyDPO** in nitrobenzene reached values of 30–40 while exhibiting moderate selectivity with respect to americium ($SF(\text{Am}/\text{Eu}) = 7.3\text{--}8.5$) and relatively high selectivity for N,O-donor ligand selectivity with respect to curium ($SF(\text{Am}/\text{Cm}) = 3.0\text{--}3.5$). The values of the solvate numbers Am(III), Cm(III), and Eu(III) calculated by the slope analysis method were close to 2, i.e., a solvate with the ratio M:L = 1:2 was formed in the organic phase. The extraction ability of tBuPhPyDPO was much lower: the distribution ratios of Am during extraction from 1–2 M HNO₃ with a solution of 0.001 M tBuPhPyDPO in nitrobenzene did not exceed 0.1. The authors explained this difference in the extraction ability of the two ligands on the basis of the presence in the case of tBuPhPyDPO of large steric hindrances created by the bulky tBu substituent.

NMR titration in acetonitrile-d₃ showed that all possible centers of ligand complexation, namely, the N atoms of the pyridine ring and the O atoms of the phosphine oxide groups, participated in the formation of a complex with a metal ion.

Pyridine-di-phosphonates were discussed as chelators for trivalent f-elements. The separation factor $SF_{\text{Am}/\text{Eu}}$ for the best extractant reached values of up to 10 [174].

Three representatives of ligands were synthesized, having phenyl substituents at the phosphorus atom and various N-heterocyclic cores—pyridine-2,6-diphosphine oxide, 2,2'-bipyridyl-6,6'-diphosphine oxides (**BDPO**) (Figure 15) and 1,10-phenanthroline-2,9-diphosphine oxides (**PhenDPO**) (Figure 16) [175].

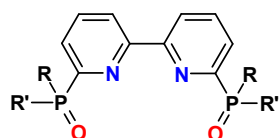


Figure 15. 2,2'-bipyridyl-6,6'-diphosphine oxides (**BDPO**).

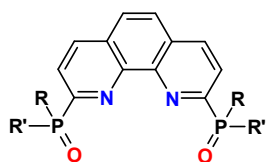


Figure 16. 1,10-phenanthroline-2,9-diphosphine oxides (**PhenDPO**).

It was shown by XRD analysis that, in the free state, the compounds adopted a conformation in which the oxygen atoms of the phosphine oxide groups were maximally removed from the nitrogen atoms of the pyridine ring (anti-conformation). Two complexes of these ligands with lanthanides were synthesized and studied: Gd(**BDPO**)(NO₃)₃ and Eu(**PhenDPO**)(TFA)₃·H₂O. Both complexes were mononuclear, and in both complexes the ligand was a tetradentate coordinated to the metal. The Gd coordination number in the Gd(**BDPO**)(NO₃)₃ complex was 10.

On the other hand, 2,3-bis(diphenylphosphoryl)pyridine in dichloroethane effectively extracts both U(VI), Th(IV) and REE from 3 M nitric acid [176]. It has been shown that in the U(VI) complex with the ligand, uranium is coordinated to two oxygens of the PO groups. The nitrogen atom of the pyridine ring is not involved in coordination.

The extraction properties of tetraethyl (1,10-phenanthroline-2,9-diyl)phosphonate (**C2-POPPhen**) (Figure 17) were investigated [177]. A 0.01 M solution of **C2-POPPhen** in meta-nitrobenzotrifluoride efficiently extracts Am(III) and Eu(III) from nitric acid solutions. Americium is extracted better than europium, and the Am(III)/Eu(III) separation factor is ~7. The values of the distribution ratios increase quite rapidly with increasing acidity, reaching ~30 in 3 M HNO₃. The solvation numbers determined by the equilibrium shift method are 1.44 ± 0.07 for Am(III) and 1.43 ± 0.02 for Eu(III). The authors explain the non-integrity of the solvation numbers by the simultaneous presence in the organic phase of complexes of the composition with Me:ligand ratios equal to 1:1 and 1:2.

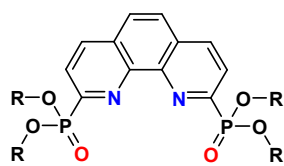


Figure 17. (1,10-phenanthroline-2,9-diyl)phosphonate **POPhen**, R = Et – **C2-POPhen**, R = Bu – **C4-POPhen**.

The extraction properties of tetrabutyl (1,10-phenanthroline-2,9-diyl)phosphonate **C4-POPhen** in meta-nitrobenzotrifluoride were studied in [178]. The extraction capacity of **C4-POPhen** was significantly higher than that of **C2-POPhen**. The Am(III) distribution ratios when extracted from 3 M nitric acid with 0.01 M **C4-POPhen** solution reached ~200. At the same time, the Am(III)/Eu(III) separation ratios for 1–3 M HNO₃, as for **C2-POPhen**, were on average ~7. The solvate numbers determined for **C4-POPhen** by the equilibrium shift method are 1.82 ± 0.04 for Am(III) and 1.82 ± 0.02 for Eu(III). According to the authors, such values of solvate numbers indicate the presence of mainly MeL₂ complexes in the organic phase. The authors noted the rapid kinetics of extraction.

Extraction of individual lanthanides (La, Eu, Lu) from various acids (HCl, HNO₃, HClO₄) with 0.01 M solution in octanol was studied in [179]. The values of the lanthanide distribution ratios increased in the order La < Eu < Lu. The extraction ability of **C4-POPhen** increased in the order HClO₄ > HNO₃ > HCl, which is typical for polydentate neutral ligands.

The introduction of branched alkyl substituents increased the selectivity of the Am(III)/Eu(III) separation from 7 to 14 [180].

Quantum-chemical modeling of the structures of four N,O-donor ligands based on phenanthroline core (**EtTolPhenDA** and its organophosphorus analogs) and their complexes with Am(III) and Eu(III) was carried out [140]. According to the calculations, Et-Tol-PhenDA is the “softest” ligand, and has a higher complexing ability and higher Am(III)/Eu(III) selectivity.

Am-Ln extraction with 2,9-bis(diphenylphosphine oxide)-1,10-phenanthroline (**Ph₂PhenDPO**) ligand was studied [181]. The extraction ability of **Ph₂PhenDPO** is noticeably higher than that of phosphonate analogues such as **C4-POPhen**. However, separation factors SF(Am/Eu) are very low (0.5–2.1 for extraction from 0.1–4 M HNO₃). The values of the lanthanide distribution ratios decrease in the following order Eu > Lu > La.

Tetradentate ligands 2,9-di(phenyl-ethylphosphine oxide)-1,10-phenanthroline **EtPh-PhenDPO** and 2,9-di(phenyl-ethoxy phosphinyl)-1,10-phenanthroline **Et-Ph-PIPhen** show high extraction ability and moderate selectivity for Am/Eu [182].

Two phosphine oxide-functionalized 1,10-phenanthroline ligands, tridentate and tetradentate, were compared [183]. Tetradentate 2,9-bis(butylphenylphosphine oxide)-1,10-phenanthroline (**BuPhPhenDPO**) (Figure 18) effectively extracts both Am(III) and Eu(III) from acidic solution. At the same time, tridentate ligand 2-(butylphenylphosphine oxide)-1,10-phenanthroline (**BuPhPhenPO**) practically does not extract these ions. It is very similar to the difference between mono- and diamides of phenanthroline dicarboxylic acid.

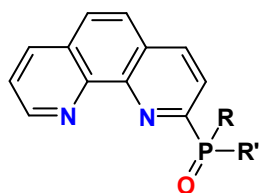


Figure 18. 2-(butylphenylphosphine oxide)-1,10-phenanthroline **PhenPO**. R = Bu; R' = Ph (**BuPhPhenPO**).

The dependences of extraction ability and selectivity in relation to organophosphorus derivatives of heterocyclic compounds have been actively studied using quantum chemistry methods [184–187].

14. N,O-Hybrid Donor Ligands for Sensors in SNF Reprocessing

Another important aspect associated with N,O-hybrid donor ligands and their application in the nuclear energy cycle is related to SNF reprocessing monitoring. The chemical analysis of SNF reprocessing media is necessary in order to ensure stable and economically effective process operation. In an ideal-case scenario, such an analysis should be performed continuously in on-line automatic mode without the immediate involvement of personnel in order to minimize radiation exposure. In spite of the fact that the PUREX process had already been industrially implemented in the late 1940s, the task of reliable on-line analytical control of process streams is not yet solved. The reasons for this are directly associated with the complexity of this task. Firstly, the technological streams of the process initially formed by dissolution of SNF in strong nitric acid have very complex chemical composition, and roughly half of the elements from the periodic table can be found therein. Obviously, there is no single analytical instrument that can embrace such a variety of analytes. Secondly, the media to be analyzed have rather high radioactivity, and this also implies a series of limitations regarding the direct applicability of conventional analytical instruments. The high acidity of the process streams and the strict safety requirements also limit the list of available instruments. All these circumstances have led to the fact that, nowadays, periodical chemical analysis of PUREX solutions is only being performed in sampling mode with the help of “heavy” analytical methods like inductively coupled plasma–mass spectrometry and atomic emission spectrometry (ICP-MS, ICP-AES). Due to the sampling, transportation and preparation steps, the results of such analyses are typically available several hours after sampling and can in no way be considered to be timely control of the ongoing separation process. There is a growing interest in the development of analytical methods that would be able to cope with all the specifics of PUREX samples and would provide chemical information in real time. Recently, a variety of optical spectroscopic techniques was proposed for such purposes and the relevant literature is reviewed in [188,189]. While such an approach is indeed useful and provides important information on the chemical composition of the media, the optical nature of these methods implies certain limitations, and the most important one is the inability to effectively handle inhomogeneous and light scattering solutions—a common feature in PUREX streams. In view of this, alternative methods are now under development, and the most promising technique reported so far is multisensor potentiometry. This method is based on the use of potentiometric sensors—electrochemical devices capable of quantification of various ions in aqueous solutions [190]. Since a single sensor cannot provide the quantification of numerous analytes, the use of multiple sensors (sensor arrays) is assumed [191]. Each of the sensors in such an array typically has sensitivity towards a broad variety of ions and this sensitivity pattern is individual for each of the sensors. When subjected to a multicomponent sample, these arrays yield complex unresolved analytical signals containing information on multiple chemical components in the analyzed medium. These responses can be effectively converted into qualitative and quantitative information on sample composition using modern machine learning methods (chemometrics in the context of chemical analysis). Obviously, in order to provide for array sensitivity to lanthanides and actinides—the key target analytes in SNF reprocessing—one has to develop potentiometric sensors with varying sensitivity patterns for these elements. In addition, this is where the ligands come into play. Modern potentiometric sensors are usually based on plasticized polymeric sensor membranes, and the key component of these membranes is lipophilic ligands capable of binding target ions at the interface between sensor membrane and sample solution. It can be seen that the elementary actions responsible for both the extraction and the potentiometric response are the same, and thus there are a lot of examples when successful extracting agents are also successful in sensor preparation [190]. The N,O-hybrid donor ligands discussed above exhibit an impressive

performance in potentiometric sensing. The key developments in this field are briefly described below.

The first demonstration of the idea to apply potentiometric sensors in the SNF reprocessing media analysis was proposed in [192], where different ligands of different classes were explored.

A variety of diamides of 2,6-pyridinedicarboxylic (dipicolinic) acid (DPA) have been studied as components of potentiometric sensors, and their sensitivity towards heavy metals and lanthanides has been explored [193,194], with the membranes being prepared from poly(vinyl chloride) as a polymer, *o*-nitrophenyl octyl ether as a solvent plasticizer, and containing either tetraphenyl borate derivatives or chlorinated cobalt dicarbollide as a cation-exchanger. DPAs were added to the membranes at concentrations of 50 mmol/kg. It was found that dialkyl-diaryl-substituted DPA showed higher response towards lanthanides compared to that of tetraalkyl-substituted ligands. The sensitivity of these sensors grew with increasing atomic number of lanthanide, and the highest responses were typically observed for ytterbium and lutetium, where super-Nernstian responses of about 24 mV/pMe³⁺ were observed. The response curves of the potentiometric sensors were linear in the concentration range 10⁻⁵–10⁻² M, with detection limits of around 5.5 pMe³⁺. Later, these DPA ligands were explored in terms of their sensitivity with respect to scandium and yttrium, and these ions were found to be preferable compared to lanthanides.

Diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid (BPYDA) have also been explored in potentiometric sensing [101]. Unlike DPA sensors showing a preference towards heavy lanthanides, the sensitivities of BPYDA-based membrane sensors was higher by about 5–10 mV/pMe³⁺ for light lanthanides. This diversity in response patterns is an important prerequisite for sensor application in multisensor systems, as it allows for simultaneous quantification of both light and heavy lanthanides in their mixtures. The general trends observed in the sensor behavior corresponded well with those obtained in the extraction studies using BPYDA. In this way, the distribution ratios observed in the extraction of heavy lanthanides were about 50, while they were about 300 for the elements in the beginning of the lanthanide series.

It must be noted that the direct translation of the patterns observed in liquid extraction to the potentiometric sensing is not always possible. In this way, diamides of 1,10-phenanthroline-2,9-dicarboxylic acid (PHENDA), demonstrating significant extraction of lanthanides, failed to ensure any reasonable potentiometric sensitivity when employed in plasticized polymeric sensor membranes [127]. At the same time, the response towards transition metal ions (cadmium, lead and copper) was significant, and was in agreement with the extraction behavior of these ligands. The reasons for these discrepancies can be associated with an obvious difference in the composition and properties of the medium where the ligand is acting (solution in organic diluent in case of extraction vs. plasticized polymeric membrane in sensing).

Sensor arrays based on the combinations of the potentiometric sensors containing N,O-hybrid donor ligands were tested in model and real technological solutions related to SNF reprocessing. Ref. [195] reports on the quantification of tetra- and hexavalent actinides (UO₂²⁺ and Th⁴⁺) in mixtures with lanthanides in the concentration ranges and ratios typical for certain technological steps. The sensor array composed of 12 potentiometric sensors based on various extracting agents was employed. The multivariate data from the sensor array were processed with partial least squares regression (PLS). The mean relative errors of actinide quantification in these complex mixtures did not exceed 17%. Although these values may seem high, and the precision of these multisensor systems obviously cannot compete with those of ICP-based methods, the overall simplicity of the approach, the absence of sample preparation steps, and its compatibility with direct on-line measurements in process streams makes multisensor arrays very attractive instruments for implementation in technological monitoring.

Ref. [196] reported on the application of the potentiometric sensors and sensor arrays containing N,O-hybrid ligands for quantification of plutonium in model PUREX raffinate

containing uranium, plutonium, and 1.5 M nitric acid. The content of Pu in model mixtures varied in the range 10–50 mg/L, and the content of U in the range 10–1000 mg/L. The root mean squared error for Pu quantification attained with the multisensor system was 30% lower than that obtained with optical spectroscopy. This can be attributed to the fact that the typical detection limits in potentiometry are two to three orders of magnitude lower than for direct optical spectroscopic measurements.

Further, the potentiometric sensor array based on 10 sensors was applied for direct quantification of thorium and uranium in real process streams of Mayak radiochemical plant [197]. The samples for analysis were derived from the experimental runs with ThorEx and Interim-23 processes intended for reprocessing of SNF containing thorium-232 and uranium. The results obtained with the multisensor system were compared with those from ICP-MS. It was found that PLS data processing yielded mean relative errors in thorium and uranium quantification below 10%.

These data show the very high potential of the N,O-hybrid donor ligands in the future development of the closed nuclear cycle not only as being effective extracting agents for lanthanides and actinides separation, but also as an important part in analytical control of SNF reprocessing, which is required in order to ensure smooth and economically robust technological processes. Obviously, further dedicated studies are required in this direction to transform this appealing concept into a technological solution applied in industry.

15. Conclusions

Closing the fuel cycle provides a more complete use of the energy contained in fissile materials. This implies the need for reprocessing SNF and isolating actinides, including americium. The great efforts of scientists from different countries aimed at solving this problem led to the testing of numerous extraction systems that make it possible to isolate americium and separate it from lanthanides and curium. However, the isolation of americium on an industrial scale has not yet been carried out. Extraction systems based on N,O-hybrid ligands, in our opinion, are promising for creating a technology for isolating and purifying americium.

Two classes of N,O-donor ligands are considered in this review: amides of N-heterocyclic carboxylic acids, and their organophosphorus analogues (phosphine oxides and phosphonates). N,O-donor ligands are a promising class of extractants for the isolation and separation of actinides from high-level radioactive waste. They combine two types of donor atoms in their structure: “hard” donor atoms-oxygen atoms of amide (or phosphine oxide, phosphonate) groups, and “soft” donor atoms-heterocyclic nitrogen atoms. This combination provides N,O-donor ligands with the high extraction ability towards *f*-elements and makes them selective with respect to actinides.

The comparative data on selectivity of americium extraction over europium and lanthanides are presented in Table 4.

Table 4. The comparative data on selectivity of americium extraction over europium and lanthanides.

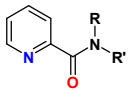
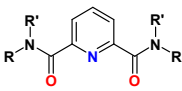
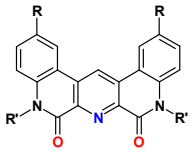
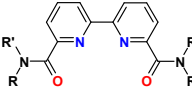
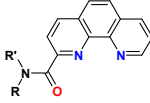
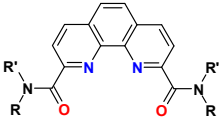
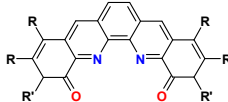
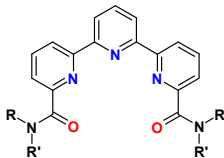
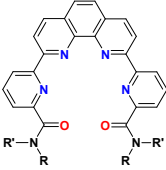
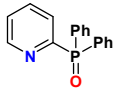
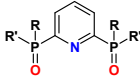

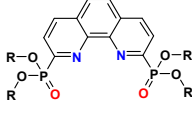
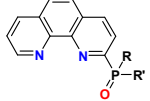
Ligand	Abbreviation	Substituents	Working Area	SF(Am/Eu)	SF(Am/Ln)
	PA	R = R' = alkyl	0.1–0.5 M HNO ₃ + 5 M LiNO ₃	4–13	no data
	DPA	R = alkyl R' = aryl	1–6 M HNO ₃	4–6	>3–4

Table 4. Cont.

Ligand	Abbreviation	Substituents	Working Area	SF(Am/Eu)	SF(Am/Ln)
	PyDilac	R = R' = alkyl	1–6 M HNO ₃	15–30	>10
	BPyDA	R = alkyl R' = aryl	1–6 M HNO ₃	6–18	>10
	PTA	R = alkyl R' = aryl	<1 M HNO ₃	20–50	no data
	PhenDA	R = alkyl R' = aryl	1–6 M HNO ₃	30–70	>0.1–1
		R = R' = alkyl		9–10	>3–5
	PhenDilac	R = aryl R' = alkyl	1–6 M HNO ₃	>200	no data
	TPyDA	R = alkyl R' = aryl	<1 M HNO ₃	5 (almost no Am extraction)	no data
		R = R' = alkyl			
	Py-Phen	R = alkyl R' = aryl	3 M HNO ₃	19–26	no data
	PyPO	R = R' = aryl	1–3 M HNO ₃	no Am extraction	no data
	PyDPO	R = R' = aryl	1–2 M HNO ₃	7–10	no data
	PhenDPO	R = R' = aryl	0.1–4 M HNO ₃	0.5–2.1	no data
		R = alkyl R' = aryl			
	POPhen	R = R' = alkyl	1–3 M HNO ₃	7–14	no data
	PhenPO	R = alkyl R' = aryl	0.1–4 M HNO ₃	no Am extraction	no data

Most articles are devoted to works on amides and diamides of N-heterocyclic dicarboxylic acids, which have been studied for almost 20 years. These studies have shown that

the extraction ability of the amides of N-heterocyclic dicarboxylic acids depends completely on their structure:

- All amides of N-heterocyclic dicarboxylic acids are characterized by an “anomalous aryl hardening” effect. The extraction capacity of diamides substituted with both alkyl and aryl substituents is higher than that of diamides having only alkyl substituents. The type of substituent at the amide nitrogen atoms has a significant influence on the properties of diamides of N-heterocyclic dicarboxylic acids. The maximum extraction capacity is achieved for diethyl diaryl derivatives with donor substituents in the phenyl rings. The introduction of additional acceptor substituents in the aryl and pyridine rings, as one would expect, leads to a decrease in the extraction ability of the diamides.
- In the case of diamides of N-heterocyclic dicarboxylic acids, an increase in structural rigidity leads to an increase in the extraction capacity and selectivity of actinide extraction. When comparing two pairs of ligands, DPA–DilacDPA and PhenDA–DilacPhen, it is clearly seen that the ligands with greater structural rigidity—dilactams and diamides of 1,10-phenanthroline-2,9-dicarboxylic acid, whose “pre-organization” energy is minimal—have the greatest extraction ability.
- An increase in the number of “soft” donors in the ligand structure leads to an increase in the extraction selectivity of actinides, including Am(III). However, the introduction of a large number of “soft donors” into the diamide structure leads to a strong increase in the Brandsted basicity of the ligand, a decrease in its extraction ability in acidic solutions, and even a decrease in selectivity. Ligands in which each heterocycle (pyridine, phenanthroline) has two carboxamide substituents in position 2 to the heterocyclic nitrogen atom have the lowest basicity. All other compounds (monoamides of pyridine-2-carboxylic acid, amides of 1,10-phenanthroline-2-carboxylic acid and tripyridine diamides) have appreciable basicity and cannot be used to extract metals from solutions with high acid concentration.

Diamides of pyridine-2,6-dicarboxylic, 2,2'-dipyridyl-6,6'-dicarboxylic, and 1,10-phenanthroline-2,9-dicarboxylic acids, as well as their structurally rigid analogues—lactams—are characterized by the lowest basicity. In the case of pyridine-2,6-dicarboxylic acid diamides and 2,2'-dipyridyl-6,6'-dicarboxylic acids, the metal distribution ratios increase with increasing acidity of the aqueous phase up to 6 M HNO₃. For the diamides of 1,10-phenanthroline-2,6-dicarboxylic acid, the maximum extraction capacity is reached in the region of 3–4 M nitric acid.

The selectivity of Am(III) separation from lanthanides is traditionally estimated by the Am(III)/Eu(III) pair. However, when creating technological schemes for actinide separation, it is necessary to consider the separation factors of Am(III) from all other lanthanides present (from La to Tb). Dialkyl diaryl diamides of 1,10-phenanthroline-2,6-dicarboxylic acid have high $SF_{Am/Eu}$ (>30) separation factor, but do not allow separation of Am(III) from light lanthanides ($SF_{Am/La} = 1.0$ and $SF_{Am/Ce} = 2.0$). The dialkyl diaryl diamides of pyridine-2,6-dicarboxylic acid and the tetraalkyl diamides of 1,10-phenanthroline-2,6-dicarboxylic acid are of the greatest interest. These ligands have moderate separation factors of Am(III) from lanthanides, but sufficient to create practicable process schemes.

They perfectly correspond to the GANEX-concept (Grouped ActiNide Extraction), which provides for the joint extraction of actinides from high level wastes. In the traditional flowsheet of the GANEX process, actinides are extracted together with lanthanides and then separated using complexing solutions [198,199]. The high extraction ability of N,O-donor ligands with respect to actinides allows selective extraction of actinides regardless of their oxidation degrees, namely U(VI), Pu(IV), Np(V), Am(III) and Cm(III) from acidic wastes and their separation from chemically similar lanthanides at the extraction stage. Stripping of actinides from the saturated organic phase does not require the use of salt-forming complexing agents. Plain dilute nitric acid solutions are successfully used for this purpose.

The highest metal distribution ratios for diamides of N-heterocyclic dicarboxylic acids are achieved using highly polar diluents. Diamides of N-heterocyclic dicarboxylic acids

are polar compounds. They are best soluble in highly polar diluents such as F-3, FS-13 and nitrobenzene. To use hydrocarbon diluents, long alkyl substituents must be present in the ligand structure.

N-heterocyclic phosphorus-containing ligands are much less studied, but the following conclusions can already be made:

- Replacement of amide groups with phosphine oxide or phosphonate groups does not lead to an increase in actinide extraction selectivity;
- As one would expect, heterocyclic phosphine oxides are more radiation resistant than phosphonate derivatives or amides;
- At this point, the extraction of other fission products must be studied to decide whether N-heterocyclic phosphorus-containing ligands are suitable for the creation of process schemes.

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