



ATALANTE 2012

International Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Effect of the structure of Amido-polynitrogen Molecules on the complexation of Actinides

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Abstract

The complexation and solvent extraction of Eu(III) and actinides in different oxidation states (Am(III), Pu(IV), Np(V)) by bitopic molecules with a dipyrindyl-phenanthroline cycle as nitrogen unit and one or two amido functions are described. The complexation has been studied in methanol-water solution with hydrophilic molecules to enhance knowledge about this new family of ligands and to identify the most interesting structural effect. Some extraction tests have been performed with lipophilic molecules of the family to check the possible utility of the new class of ligands under representative fuel reprocessing conditions. These first studies have demonstrated that the presence of a preorganized N-donors unit like dipyrindyl-phenanthroline improves the ligand's affinity for actinides and its An/Ln selectivity.

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Keywords: Actinides ; polynitrogen ligands ; phenanthroline ; amides ; complexation ; extraction

Introduction

In the framework of nuclear fuel reprocessing, various options to reduce the toxicity and thermal emissions of nuclear waste are studied. Among others, recycling minor actinides is of great interest. The GANEX process (Group ActiNide EXtraction) aims at the recovery of all transuranium elements from the high activity spent fuel dissolution solution.

To achieve the extraction of actinides (from U(VI) to Cm(III)) and their separation from lanthanides(III), new extracting molecules have been synthesized. The extraction of light actinides (U, Np, Pu) with high oxidation states can be realized using oxygen donors like organophosphates or dialkylamides. [1,2] The extraction of minor actinides Am(III) and Cm(III) without lanthanide(III) cations is made all the more difficult given the chemical

similarities between the two groups of elements, for example a strong hydration and similar ionic radii. To accomplish the separation, extractants with soft donors atoms like sulfur or nitrogen have been tested to take advantage of the enhanced covalent bonding contribution that can occur with actinides. Among them, polynitrogen aromatic molecules have been extensively investigated. [3,4] Some examples of efficient molecules are 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (RBTP), 2,4,6-tri(pyridine-2-yl)-1,3,5-triazine (TPTZ), 2-amino-4,6-di(pyridine-2-yl)-1,3,5-triazine (ADPTZ) and 2,2':6'2''-terpyridine (TPY).

An important property when designing new ligands for An(III)/Ln(III) separation is the basicity of the molecules because the actinides are preferably extracted from highly acidic nitric acid solutions. In this context, new molecules combining a nitrogen ring allowing the An(III) / Ln(III) separation and two amide groups to extract actinides with higher oxidation states have been tested by C. Marie [5,6]. The best results were obtained with the polyaromatic unit terpyridine, for example with the N,N,N',N'-tetraoctyl 6,6':2,2':6',2''-terpyridine diamide. The selectivity over lanthanides was obtained but the extraction of actinides was quite low ($D_{Am \text{ and } Cm} < 1$ under classical conditions). [5]

Recently new ligands with phenanthroline as a polynitrogen unit have been described: BTPPhen (2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline) without any amide function by F. Lewis et al. [7] or with one amide function PTA (N-octyl-N-phenyl-1,10-phenanthroline-2-carboxamide) [8]. With BTPPhen ligand the presence of the phenanthroline motif leads to a rapid and efficient separation of actinides from lanthanides. In the case of PTA, the amide function grafted on the phenanthroline cycle leads to the extraction of Pu(IV), Am(III) and Cm(III) with a selectivity over lanthanides > 5 . However the solubility of the ligand was so low in classical diluents that the extraction tests were performed in chloroform.

After analysis of these results, we predicted that amide grafted on pyridine-phenanthroline unit could improve the extraction of actinides and maintain the Am/Eu selectivity. The synthesis of different ligands has been optimized and this paper summarizes extraction and complexation results obtained with selected lipophilic and hydrophilic 2,9-dipyridyl-[1,10]phenanthroline grafted with one or two amide groups (Figure 1).

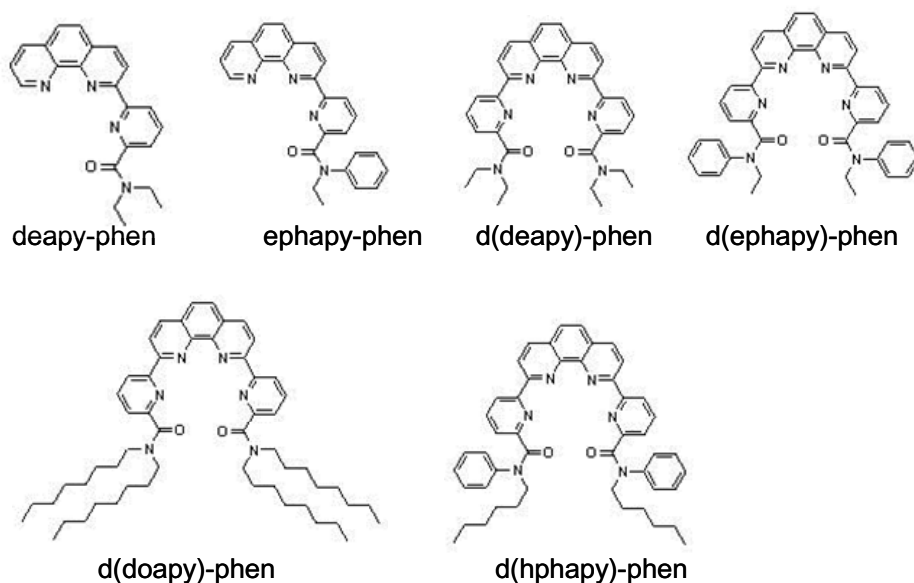


Fig.1. Molecules tested in the family of mono or di (amido-pyridine) phenanthroline with their acronyms

Preliminary solvent extraction experiments were carried out to evaluate the ability of lipophilic ligands to selectively extract the actinides (Am(III), Cm(III), Pu(IV) and Np(V and VI)) from other fission products (especially Eu(III) considered as representative of lanthanides). In order to understand the affinity and selectivity of this new class of ligands, protonation and complexation properties were investigated with the hydrophilic members diluted in homogeneous media (methanol-water mixture). The stability constants were obtained using classical UV-visible absorption spectra and additional measurements as NMR and ESI-MS were performed to study the coordination modes.

2. Experimental methods

2.1. Ligands' synthesis

The synthesis scheme was as follows: 1) addition of 2-bromo-6-methylpyridine through the lithiated species on [1,10]-phenanthroline to obtain the corresponding 2-(6-methylpyridin-yl) ligand, 2) oxidation of the methyl group with SeO_2 to obtain the 6-[1,10]phenanthroline-2-yl-pyridine-2-carboxylic acid 2, 3) amide introduction by a peptide coupling route in presence of the suitable amine after synthesis of the acid chloride with SOCl_2 . For molecules with 2 amide functions (d(deapy)-phen, d(ephapy)-phen, d(doapy)-phen and d(hphapy)-phen), the synthesis route begins with the synthesis of 2,9-dichloro-[1,10]phenanthroline, followed by a Stille coupling with 2-methyl-(6-tributylstannyl)pyridine to produce the 2,9-(6-methylpyridin-2-yl)-[1,10]phenanthroline. Oxidation with SeO_2 and peptide coupling steps under similar conditions as previously described allow then to produce the desired ligands.

Solvents were purified and dried prior to use. All reactions were monitored by TLC on commercially available pre-coated plates (Kieselgel 60 F254) and the products were visualized with a Mohr solution (10 g of FeSO_4 in 100 mL of H_2O). The products were checked at each step by ^1H and ^{13}C NMR spectroscopy, FTIR and mass spectrometry.

2.2. Extraction and complexation studies

Extraction experiments were performed in glove boxes with the ligand 0.01 M in *n*-octanol and an aqueous 3 M HNO_3 stock solution spiked with trace amounts of ^{152}Eu , ^{244}Cm , ^{241}Am and ^{239}Pu . Np extraction was carried out with a laboratory stock solution $^{237}\text{Np(V)}$ in HCl 1 M diluted in HNO_3 3 M. Equal volumes of each phase were contacted 60 min by means of an automatic vortex shaker at 25.0°C. Distribution coefficients were determined from alpha and gamma-counting spectrometry.

The protonation and complexation constants were measured in methanol-water (75-25%-vol) because the molecules' solubility in aqueous medium was not sufficient (as usual with polynitrogen ligands). The acid and metallic cation were introduced as HCl or chloride salt from stock solutions. The stability of the neptunium(V) solution has been checked with absorption spectroscopy (absence of Np(VI) at 1200nm) before and after addition of ligand. The temperature of the cell was maintained at 21.0°C by an external thermostated bath. Densities of methanol-water solutions were controlled to improve the accuracy of concentration measurements. Conditional stability constants were determined by following the ligand absorption bands (between 200 and 350 nm) and their values were fitted to experimental spectra with Hyperquad or Hypspec softwares.

The ESI-MS (Electrospray Ionisation Mass Spectrometry) measurements were recorded in positive ionization mode using a Bruker Esquire-LC quadrupole ion trap equipped with an electrospray interface.

Two-dimensional ^{15}N NMR (gHMBC pulse sequence) experiments were performed on a 400 MHz Varian Inova spectrometer with a 5 mm Z-gradient HCX reverse probe. Ligands were diluted in $\text{CD}_3\text{OD-D}_2\text{O}$ solutions to readily observe protons of the ligands at a 0.01 mol/L concentration. All NMR measurements were acquired at 25 °C.

3. Results and discussion

3.1. Liquid-Liquid Extraction

The extraction of actinides in different oxidation states (Am(III), Cm(III), Pu(IV) and Np(V and VI)) from 3 M HNO₃ was measured with two lipophilic ligands (d(doapy)-phen and d(hphapy)-phen). Extraction data are summarized in Table 1 and compared with those of te-tpyda (N,N,N',N'-tetraoctyl 6,6'-2,2':6',2''-terpyridine diamide) whose molecular structures are similar to d(doapy)-phen but with terpyridine unit instead of the dipyrindinyl phenanthroline motif [5].

The replacement of the central pyridine by a phenanthroline unit leads to better extraction of all actinides (for example, $D_{Pu} = 2.2$ as opposed to 0.35), though the extraction of actinides(III) remains low. This feature could be explained by the increase of the number of N donor atoms (4 with dipyridine phenanthroline instead of 3 with terpyridines) and by the preorganization of the 2,9-dipyridyl-1,10-phenanthroline ring. The cis-locked 1,10-phenanthroline motif is favorable for cations complexation, as already described [9].

The presence of the phenanthroline moiety enhances also the Am(III)/Eu(III) selectivity ($FS_{Am/Eu} > 18$). This separation factor is comparable to the value presented by Yaita with the PTA[8], which confirms the interest of the phenanthroline core.

Table 1: Distribution coefficients of actinides and Eu(III) by diamidopolynitrogen ligands (extractant 0.01 mol/L in *n*-octanol – cations as traces – [HNO₃]_{aq}^{init}=3 mol/L –25.0°C)

Extractant	te-tpyda [5]	d(doapy)-phen	d(hphapy)-phen
[HNO ₃] _(mol/L)	2.5	2.6	2.6
$D_{Eu(III)}$	1.1×10^{-3}	6.3×10^{-3}	0.091
$D_{Am(III)}$	4.6×10^{-3}	0.17	1.8
$D_{Cm(III)}$	2.6×10^{-3}	7.0×10^{-2}	0.74
$D_{Pu(IV)}$	0.35	2.2	14.8
$D_{Np(V-VI)}$	nd	11.0	16.6
$FS_{Am/Eu} - FS_{Pu/Eu}$	5 - 320	26 - 335	19 - 166

The substitution of an ethyl group by a phenyl group on each nitrogen of the amide function leads to higher extraction, as already observed with amido-terpyridines [5] and other oxygen donors ligands. The effect is often explained by the delocalization of the lone pair of the nitrogen to the oxygen of the amide function leading to a stronger cation-ligand bond.

3.2. Complexation in homogeneous medium

To complete a more comprehensive study of this family, protonation and complexation studies have been performed with hydrophilic molecules: two ligands with only one amido pyridine and therefore 3 N-donor atoms (deapyr-phen and d(ephapy)-phen) and two ligands with two amidopyridine motifs and therefore 4 N-donor atoms (d(deapyr)-phen and d(ephapyr)-phen), see Figure 1.

3.2.1 Basicity of the molecules

Protonation constants of the new ligands were measured by UV-visible absorption spectroscopy in the range of $\pi-\pi^*$ transitions of the aromatic cycle electrons, see an example in Figure 2. Only one protonation constant was obtained.

^1H - ^{15}N correlation spectra (gHMBC pulse sequence) of the ligand d(deapy)-phen 10^{-2} M in $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ were recorded in neutral and acidic conditions in order to identify the protonation sites. Without DCI , ^{15}N chemical shifts are -83.6 ppm for N8 and N11 and -80.76 ppm for N1 and N24, see figure 2 right. In the presence of DCI (0.32 M), the most important variation was observed for phenanthroline nitrogen: one atom stays at -83.6 ppm whereas the other one appears at -152.1 ppm. The chemical shifts of the pyridine nitrogen atoms (N1 and N24) change less than 2 ppm. These results indicate that the protonation occurs on one nitrogen of the phenanthroline heterocycle (N8 or N11).

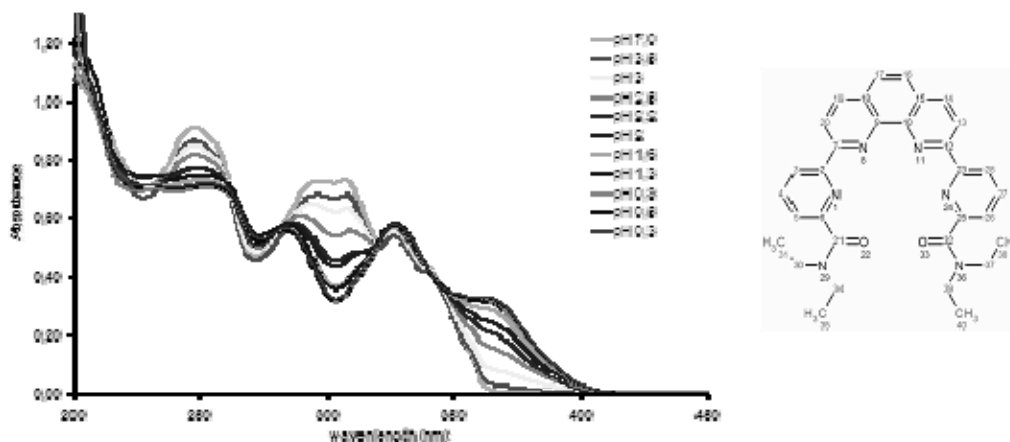


Figure 2: Study of protonation of the ligand d(deapy)-phen: influence of the pH on absorption spectra in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (75 :25%vol), 21°C , path length 1cm (left) and numbering of atoms in the molecule for NMR study (right)

The protonation constants obtained with selected molecules are presented in the first column of Table 3. The basicity is lowered with the addition of a second amide group, as mentioned by C. Marie with amidoterpyridines [6]. This property is interesting in the context of the design of new extractants; we can suppose that the efficiency of molecules will be maintained under high acidity conditions. However the basicity of new molecules is higher than the basicity of related amidoterpyridines. The introduction of a phenyl group on the nitrogen of the amide function has no significant effect, which is consistent with the protonation site on the phenanthroline cycle observed by NMR.

3.2.2. Complexation constants

Stability constants of hydrophilic molecules with f-elements were determined in methanol-water media; see selected values in Table 3. The presence of only one complex (1:1) was checked by different techniques like electrospray ionization mass spectrometry and NMR. ESI-MS is a fast and sensitive technique that allows detection of complexes after their ionization and transfer to the gas phase without disrupting metal-ligand bonds. The major complexes observed with d(deapy)-phen at a cone voltage of 30 V are related to 1-1 compounds (the ions LMCl_2^+ and LMCl_2^+ with Eu(III) and Am(III) and LNpO_2^+ with Np(V)).

The introduction of a second amide function increases the affinity of ligands for cations, though the opposite effect was seen for the proton H^+ . This trend, described previously for amidoterpyridines [6], is an interesting property as discussed above. However the complexation with Np(V) is not affected by the presence of a second amido group. Steric hindrance due to the oxygen $-\text{yl}$ linked to the neptunium could explain this effect. Additional structural studies are in progress to give more information.

Table 3: Conditional stability constants for 1:1 complexes ($\log \beta_1$) in methanol-water solution (75-25%vol)- 21°C-chloride as counterions (*following the absorption bands of the cation instead those of the ligand).

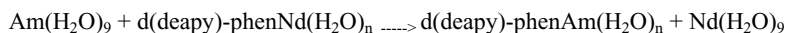
	H ⁺	Eu(III)	Am(III)	Np(V)
te-tpyda [6]	1.02	4.5	3.8*	
deapy-phen	3.46 ±0.05	4.72 ±0.05	6.0 ₅ ±0.1	6.2 ±0.1
ephapy-phen	nd	4.80 ±0.05	6.5 ₅ ±0.1	6.7 ±0.1
d(deapy)-phen	2.45 ±0.05	5.32 ±0.05	6.8 ±0.2	6.4 ±0.1
d(ephapy)-phen	2.55 ±0.1	5.85 ±0.05	7.5 ±0.2	6.7 ±0.1

The magnitude of stability constants measured with Np(V) was not usual, but such property has already been described with specific preorganized molecules, like bicyclic malonamides in aqueous medium [10]. Further studies are planned to confirm the structure in such medium.

The new family based on preorganized dipyrindylphenanthroline units gives higher stability constants than amidoterpyridines, this property is consistent with extraction data and confirms the potential utility of the family.

Within each group (one or two amido-pyridine), the substitution of one ethyl chain by a phenyl group increases slightly the complex strength (from 0.1 to 0.7 units in logarithmic scale) which was also observed with lipophilic molecules but with a higher effect. Additional studies are in progress to better describe this effect.

Whereas no Am/Ln selectivity was observed with amido-terpyridine compounds, the phenanthroline ligands have a higher affinity for Am(III), with a ratio β_{Am}/β_{Eu} of 22 to 30, consistent with data obtained in extraction mode with more lipophilic molecules. These experimental data are consistent with first additional calculations performed by DFT to evaluate the free energy exchange between aquo ions and complexes 1-1 as presented in the following equilibrium:



The difference of energy, ($\Delta(\Delta G)$ -16 kJ/mol, was in favor of Am(III)-complexes.

Conclusion

In this study we have reported that new bitopic molecules, N,N,N',N'-tetraalkyl-6,6'-([1,10]-phenanthroline-2,9-diyl)-pyridin-2-ylidamide (named di(amidopyridine)phenanthrolines) (d(deapy)-phen and d(ephapy)-phen), can extract actinides in different oxidation states from 3 M HNO₃ with good selectivity towards Eu(III). First comprehensive studies about the protonation and the complexation in homogeneous mixed methanol-water solution with four representative molecules have been also described.

The interest to graft amide functions on polynitrogen cycles to reduce the basicity of such molecules and to increase the metal-ligand affinity was confirmed. Moreover, introduction of a phenyl substituent on the amide group instead of an alkyl group allows higher metal-ligand affinity without increasing its basicity. The replacement of terpyridine by the preorganized dipyrindyl phenanthroline unit and the increase of N-donor atoms led to better properties. Complexation of actinides and lanthanides is indeed stronger with those ligands and Am(III)/Ln(III) selectivity is confirmed in homogeneous solution. The experimental results have been confirmed by DFT calculations. Behavior of the neptunyl cations is rather different probably due to steric hindrance. Structural investigations are currently in progress.

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