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Stereo- and Regiochemical Effect of *N,N*-Dialkylamide Extractants on the Speciation of Pu Complexes

David Lemire,^[a] Thomas Dumas,^[b] Cécile Marie,^[b] Fabrice Giusti,^[a] Guilhem Arrachart,^[a] Sandrine Dourdain,^{*[a]} and Stephane Pellet-Rostaing^[a]

The relationship between extractant stereochemistry and their extraction performance has only poorly been established. In order to address a part of this concern, we investigated the Pu(IV) liquid-liquid extraction (LLE) by using the *N,N*-di-(2-ethylhexyl)butyramide (DEHBA), as well as those of its position isomers. DEHBA ($\beta\beta$ -isomer) and *N*-(2-ethylhexyl)-*N*-(oct-3-yl)butyramide (EHOBA or $\alpha\beta$ -isomer) were synthesized as a mixture of stereoisomer or stereoenriched (*R,S*)- and (*S,S*)-diastereoisomers, and were all assessed for Pu^{IV} LLE. The results showed that both the position and the stereoisomerism of the aliphatic substituents affect Pu^{IV} complexation and extraction. We found that Pu extraction is lowered by factor 2 to 4 when

the ethyl branching group is closer to the complexing site. UV-vis spectroscopy showed that this extraction decrease was affected by steric hindrance inducing a deprivation of Pu inner sphere complex. Effect of stereoisomerism is highlighted for branching closer to the complexing site (α -position). Enantiopure DEHBA stereoisomers provided similar Pu extraction, whereas a slight decrease could be noticed for the more cluttered stereoenriched ($\alpha\beta$)-isomers, which was also concomitant with a smaller population of inner sphere complex. In contrast, the stereoisomers mixture led to a strong decrease of Pu extraction because of an antagonistic association in the mixed complexes.

Introduction

Liquid-liquid extraction (LLE) is a widely used method for metal separation in hydrometallurgy and for purification processes applied to produce pure chemical compounds. Liquid-liquid extraction consists in the transfer of a desired compound to a second phase immiscible with the first one. It is generally applied with the use of extractant molecules solubilized in the organic phase, that are able to selectively complex the desired solute. The choice of the extractant is determinant and can be fixed according to many parameters. Effect of the nature of its chelation site (also called polar head),^[1-5] the length and branching of its alkyl chains,^[6-12] its interactions with the chosen diluent^[5,13-19] as well as the effect of the aqueous phase composition on its extraction performances^[5,12,20-24] are for instance extensively studied. A comprehensive knowledge of these parameters is important because the proper tuning of these latter is the key to reach high performance and selectivity

of extraction. The performance of an extractant is quantified with the distribution coefficient (*D*). The distribution coefficient is given by Equation (1).

$$D_M = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \quad (1)$$

Where $[M]_{\text{org}}$ is the concentration of the metal *M* in the organic layer and $[M]_{\text{aq}}$ is the concentration of the metal *M* in the aqueous phase.

Extractants stereoisomerism has also been shown to be a very promising parameter to finely adjust extraction efficiency or selectivity. For instance, it has been studied for the extraction of organic molecules that usually exhibit chiral sites such as drugs^[25] and amino acids.^[26-29] However, effect of extractants stereochemistry observed on the separation of non-chiral inorganic molecules such as metal cations, remained sparsely reported during the last five decades. Herein only few examples are presented. Lemaire *et al.* reported the *cis-syn-cis*- and the *cis-anti-cis*-isomer of the dicyclohexano-18-crown-6 ether (DCH 18C6) as substituent of tributylphosphate (TBP) for nuclear fuel reprocessing, and put the emphasis on the higher selectivity of the *cis-syn-cis*-isomer towards Pu(IV) ($D_{\text{syn}}/D_{\text{anti}} = 3.5$).^[30] Moreover, Wilden *et al.* observed a high effect of chirality on the separation of f-elements achieved with some *N,N,N',N'*-tetraoctyldiglycolamide derivative methylated on each methylene bridge (Me₂-TODGA).^[31] A marked difference of distribution ratios between (*R,S*)- and (*S,S*)-Me₂-TODGA diastereoisomers was observed for every metal (all lanthanides with americium and curium) that was submitted to LLE in the presence of one of the two isomers. The maximum difference was reached for holmium with a factor of 94 in the favor of the (*R,S*)-isomer. The authors showed that these differences resulted from the

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orientation of the backbone methyl groups which caused a structural change in the nitrate coordination of the metal-(Me₂-TODGA-NO₃)₃ complexes, the generated methyl-nitrate steric hindrance being more pronounced for the (*S,S*)-isomer. Weßling *et al.* explained the difference of extraction of the *N,N,N',N'*-tetradecyldiglycolamide Me₂-TDDGA by observing the effect of the stereoisomerism on the stability of the resulting europium and curium complexes. For the most efficient (*R,S*)-diastereoisomer, they observed 1 : 3 complexes in the organic phase whereas for the (*R,R*)-diastereoisomer they found a mixture of 1 : 2 and 1 : 3 complexes^[32] which indicated that the orientation of alkyl groups influenced greatly the formation of the main metal-extractant complex in organic solvents. While the effect of stereoisomerism on extraction has been shown to be very promising, its effect on the underlying solvent extraction mechanisms remains only partly described.

The stereochemistry of the extractant can indeed influence the nature of the metal complexes during the separation process; it is an important parameter to consider while developing new chiral center-bearing extractant molecules for the separation of metals. It therefore remains of high interest to determine how such conformational effects may affect the complexation mechanisms by investigating in more details the microstructure of the complexes.

In a previous work, we studied the effect of stereochemistry of some monoamide ligands on the complexation of plutonium in extraction conditions (see Felines *et al.*^[33]). Optically pure diastereoisomers of the *N,N*-di(2-ethylhexyl)butyramide (DEHBA) extractant were synthesized and the effect of their stereoisomerism on uranium and plutonium coextraction were investigated at two different acidities.^[33] It was found that the stereoisomerism had no significant effect on the extraction of uranium, whereas the plutonium extraction was greatly influenced: the (*R,S*)-DEHBA diastereoisomer provided lower distribution ratio of plutonium at high and low acidity than the (*S,S*)-DEHBA diastereoisomer.

In an attempt of understanding the origin of stereochemical effect on these systems, the present study proposes to compare extraction performance and complexes structures of various stereoisomers. We synthesized the (*R,S*)-, (*S,S*)- and the mixture of stereoisomer of DEHBA as well as the stereoisomers of an analogue of DEHBA, namely the *N*-(2-ethylhexyl)-*N*-(octan-3-yl)butyramide, (EHOBA), for which one ethyl side chain is closer to the complexing amide function (Scheme 1). For the sake of simplicity, DEHBA **1** and EHOBA **2** are respectively named $\beta\beta$

and $\alpha\beta$ in the following, according to the position of their alkyl (ethyl moiety) branching. The $\alpha\beta$ is interesting for this study since one of the chiral sites is closer to the complexing site. This proximity is expected to increase the influence of the chirality on the extraction properties of this ligand. As the branching groups are identical for each isomer, a reliable assessment of the steric hindrance contribution could be achieved.

This study will therefore focus on the synthesis of the mixture of stereoisomers and stereochemically pure (or enriched) (*R,S*)- and (*S,S*)-forms of two extractants $\beta\beta$ and $\alpha\beta$, and on their Pu extraction performances.

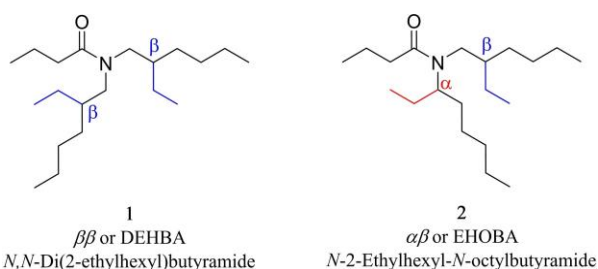
In the last part of this study, the speciation of the plutonium complexes are studied by ultraviolet-visible (UV-vis) spectroscopy to investigate the origin of the observed stereo- and regiochemical effects on extraction. Using the plutonium complexes signature described in the literature, UV-vis spectra were compared to differentiate the plutonium complexes in the different organic phases.

Results and Discussion

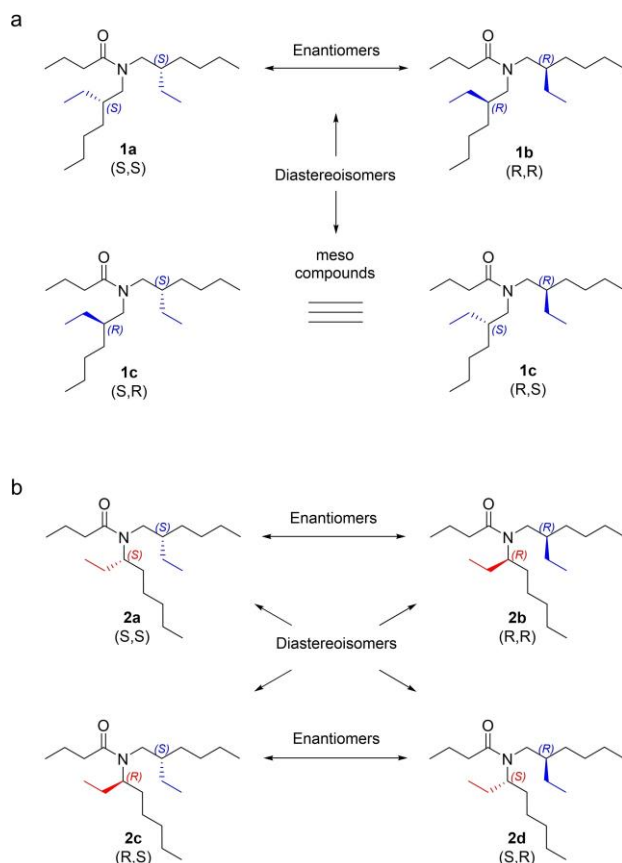
Synthesis of the mixture and diastereopure isomers of $\beta\beta$ and $\alpha\beta$

The first part of this work concerned the synthesis of a mixture of stereoisomers and of stereochemically pure (*R,S*)- and (*S,S*)-forms of two isomers, namely $\beta\beta$ and the $\alpha\beta$, whose structure are presented in Scheme 2. Both isomers contain two chiral carbons carried by the alkyl substituents of the amide function. If the mixture of EHOBA stereoisomers is, as expected, an equimolar mixture of two pairs of enantiomers (see Scheme 2b), the $\beta\beta$ is a 25 : 25 : 50 mixture of only three different stereoisomers which are two enantiomers and one meso-isomer. The optically inactive meso form results from the observable plan of symmetry in both the (*R,S*)- and (*S,R*)-isomers (Scheme 2a).

The mixture of diastereoisomers (mix $\beta\beta$) **1** was easily obtained in 97 % yield by condensing the commercially available *N,N*-bis(2-ethylhexyl)amine with the butanoic acid in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 1-hydroxybenzotriazole (HOBt) as coupling reagents in the dichloromethane (DCM). Every amidation was performed under the same reaction conditions as these used for the mix $\beta\beta$. The synthesis of stereochemically pure (*R,S*)- $\beta\beta$ **1 c** and (*S,S*)- $\beta\beta$ **1 a** was performed as described in the literature (Scheme 3).^[33] Briefly, the 2-ethylhexanoic acid **3** was stereo-enriched to an enantiomeric excess (ee) higher than 96 % by diastereoselective recrystallization in acetonitrile (CH₃CN) of the salt formed with (*R*)-methylbenzylamine **4 b**. The enantiopure (*S*)-2-ethylhexanoic acid **3 a** (32 %) was reduced to the (*S*)-2-ethylhexan-1-ol **5 a** with 97 % yield, using lithium aluminum hydride (LiAlH₄) in refluxed diethyl ether (Et₂O) and, to perform further steps, the ee was kept over a minimum of 92 % which was measured by chiral GC. The enantiopure (*S*)-2-ethylhexan-1-ol **5 a** was mesylated with methanesulfonyl chloride (MsCl) in the presence of triethylamine (NEt₃) to lead to **6 a** (100 %) then the later was converted to the enantiopure (*S*)-1-bromo-2-



Scheme 1. Structure of $\beta\beta$ and $\alpha\beta$.

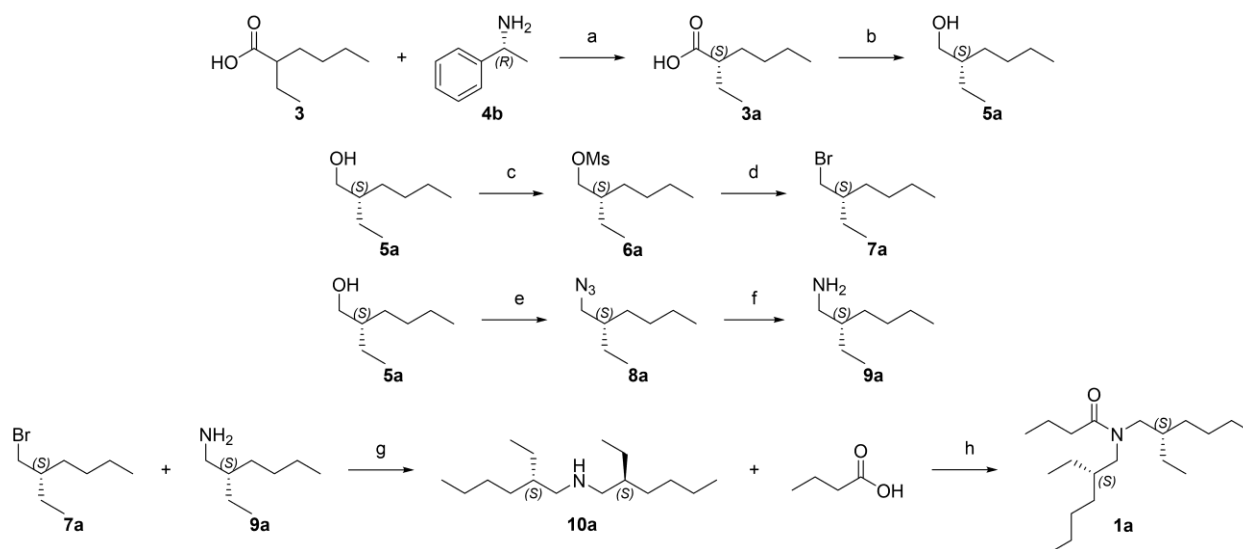


Scheme 2. Structure of the different stereoisomers a) $\beta\beta$ and b) $\alpha\beta$.

ethylhexane **7 a** in 83 % yield via a substitution reaction performed in acetone in the presence of lithium bromide (LiBr). The enantiopure (*S*)-2-ethylhexan-1-ol **5 a** was also used to synthesize the enantiopure (*S*)-2-ethylhexylamine **9 a** in two

steps. **5 a** was first converted to the azide **8 a** (85 %) through the Mitsunobu reaction involving treatment by diphenylphosphorylazide (DPPA) and diisopropylazo-dicarboxylate (DIAD) then **8 a** was reduced to the amine **9 a** (75 %) with LiAlH_4 . The *N*-alkylation of the enantiopure (*S*)-2-ethylhexylamine **9 a** with enantiopure (*S*)-1-bromo-2-ethylhexane **7 a** was performed under microwave at 120 °C in acetonitrile in the presence of potassium carbonate (K_2CO_3) to obtain the diastereopure (*S*)-bis(*S*)-2-ethylhexylamine **10 a** in 64 % yield. The same procedure was used for the synthesis of (*S*)-2-ethyl-*N*-((*R*)-2-ethylhexyl)hexan-1-amine **10 c** (see SI.1) starting from enantiopure (*S*)-2-ethylhexylamine **9 a** with enantiopure (*R*)-3-(bromomethyl)heptane **7 b**. **10 a** and **10 c** were used to synthesize the diastereopure $\beta\beta$ using the same procedure as that providing the mix $\beta\beta$ **1** presented above. The diastereopure (*R,S*)- $\beta\beta$ and (*S,S*)- $\beta\beta$ were obtained with a global yield of 20 % (see Scheme 3).

The synthesis of $\alpha\beta$ **2** was performed with a similar synthetic pathway as described for $\beta\beta$ **1**. The mixture of stereoisomer $\alpha\beta$ **2** or diastereoenriched (**2 a** and **2 c**) monoamides were obtained in 60 % yield after condensation of butanoic acid with the $\alpha\beta$ dialkylamine precursor. The later could be obtained via two reciprocal pathways which are *i*) *N*-alkylation of the 2-ethylhexylamine with 3-octyl halide or *ii*) *N*-alkylation of the 3-octylamine with the 3-(halomethyl)heptane. Only the first strategy was explored in this work. Therefore, *N*-alkylation involved a secondary halide (3-bromooctane) put in reaction in an aprotic polar solvent (acetonitrile) and undoubtedly proceeded via a competition between the $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ mechanisms. Thus, because of likely partial (or complete) racemization of the chiral center of the 3-octyl chain, only the racemic bromide **13** was used. The racemic (**14**) and the (2*S*,3'*R*)-form (*N*-((*S*)-2-ethylhex-1-yl)octan-3-amine **14***) of $\alpha\beta$ dialkylamine were obtained with a 50 % average yield from the



Scheme 3. Synthesis of (2*S*,2'*S*)-stereopure $\beta\beta$; [a]: 1) CH_3CN 2) HCl 0.5 M, 32%; [b]: LiAlH_4 , Et_2O , reflux, 1 h, 97%; [c]: MsCl , NEt_3 , CH_2Cl_2 , 16 h, 100%; [d]: LiBr , Acetone, reflux, 18 h, 83%; [e]: PPh_3 , DIAD, DPPA, THF, 20 h, 85%; [f]: LiAlH_4 , Et_2O , 5 h, 75%; [g]: K_2CO_3 , CH_3CN , μ -wave 120 °C, 5 h, 64%; [h]: EDC, HOBt, *N*-methylmorpholine, DCM, 16 h, 68%. Performing the racemic resolution (first step) with the *S*-enantiomer of **4 a** allowed the synthesis of the *R*-enantiomer of **5 a** from which was derived **7 b** (See details in Supporting Information).

N-alkylation of either the racemic (**9**) or the enantiopure (*S*)-2-ethylhexylamine **9 a** respectively. The bromide **13** was synthesized with 91 % yield via conversion of the mesylated intermediate **12**, itself yielded (100 %) from the mesylation of 3-octanol **11**. Conditions for mesylation and subsequent bromination were the same as these used for the synthesis of the $\beta\beta$ derivatives (see above & Scheme 4 below).

The stereochemical enrichment of each (2*S*,3*S*)- and (2*S*,3*R*)- $\alpha\beta$ diastereoisomer was achieved via flash-chromatography separation (see SI.2) of their *N*-benzyl derivatives, namely and respectively, **15 a** and **15 c**. *N*-benzylation was achieved in 91 % yield by allowing the diastereoisomers mixture **14*** to react with benzyl bromide (BnBr) in refluxed acetonitrile in the presence of K_2CO_3 for 16 h. Benzylation allowed to easily monitor the diastereoisomers separation by UV-detection. A total of 91 % of the *N*-benzyl-*N*-((*S*)-2-ethylhexyl)octan-3-amine **15** was recovered after separation where stereo-enriched compounds were retrieved as 27 % of the (*S*)-*N*-benzyl-*N*-((*S*)-2-ethylhexyl)octan-3-amine **15 a** and 64 % of the (*R*)-*N*-benzyl-*N*-((*S*)-2-ethylhexyl)octan-3-amine **15 c**. The benzyl group of both **15 a** and **15 c** compounds was then removed by palladium-catalyzed hydrogenolysis, leading to the formation in quantitative (> 95 %) yield of the (*S*,*S*)- and (*S*,*R*)-stereo-enriched **14 a** and **14 c** isomers mixture respectively. Although the separation of *N*-benzyl-*N*-((*S*)-2-ethylhexyl)octan-3-amine diastereoisomers **15** was performed on high-resolution purification (HP) columns, the efficiency of these columns was not sufficient to afford a high diastereomeric ratio (dr) of the octyl chain. No separation of the diastereoisomers was obtained by GC analysis, thus the dr was calculated from specific rotation (see SI.3). A maximum of 72 % dr was obtained for the octyl chain. However, the diastereoenrichment was assumed as sufficient to induce, if it did so, observable differences of LLE properties between each

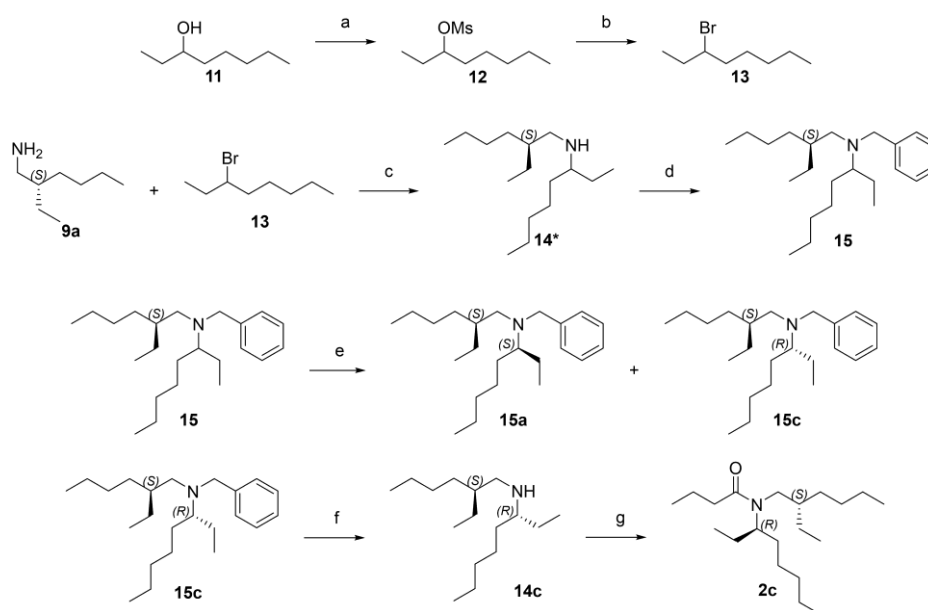
diastereoenriched mixture, thus, these dialkylamines were all converted to the $\alpha\beta$ monoamides **2**, **2 a** and **2 c** that were assessed in Pu LLE experiments as planned with $\beta\beta$ compounds.

The dialkylamines **14**, **14 a** and **14 c** were converted to the mix, the (*S*,*S*)- or the (*R*,*S*)- $\alpha\beta$, respectively, by using butanoic acid and coupling reagents such as EDC and HOBt with the same procedure as described for $\beta\beta$. The resulting $\alpha\beta$ was used as a stereochemically enriched compound whose dr could be estimated at 72% since amidation was not expected here to induce racemization of the final product.

Finally, the syntheses performed in this work led to six distinguishable monoamides, namely, the $\beta\beta$ stereoisomeric mixture, its optically pure (*R*,*S*)- and (*S*,*S*)-diastereoisomers, the $\alpha\beta$ stereoisomeric mixture and its stereo-enriched (*R*,*S*)- and (*S*,*S*)-diastereoisomers. Herein, these six compounds were used as extractant for the extraction of plutonium in nitric acid solutions.

Pu extraction and comparison between $\beta\beta$ and $\alpha\beta$

The two *N,N*-dialkylamide ($\beta\beta$ and $\alpha\beta$) were used for Pu(IV) extraction in hydrogenated tetrapropylene (TPH) to compare two distinct effects. First, the effect of ethyl orientation on extraction is compared for each extractant between the stereoisomeric mixtures and the (*R*,*S*)- and (*S*,*S*)-diastereoisomers. Second, the effect of the position of the ethyl group is compared between the two extractants ($\beta\beta$ and $\alpha\beta$). Extraction experiments were performed at two different nitric acid concentrations (4 mol·L⁻¹ and 0.5 mol·L⁻¹). This allows to evaluate the performance of the different isomers under typical extraction conditions (4 mol·L⁻¹) and under typical stripping conditions (0.5 mol·L⁻¹).^[21,34]



Scheme 4. Synthesis of stereo-enriched $\alpha\beta$; [a]: $MsCl$, NEt_3 , CH_2Cl_2 , 16 h, 100 %; [b]: $LiBr$, Acetone, reflux, 18 h, 91 %; [c]: K_2CO_3 , CH_3CN , μ -wave 120 °C, 5 h, 52 %; [d]: $BnBr$, K_2CO_3 , CH_3CN , reflux, 18 h; [e]: separation of the diastereoisomers were performed on a 15 μm silica gel column (detailed in SI); [f]: H_2 (6 bar), Pd/C , $EtOH$ 18 h; [g]: EDC , $HOBt$, *N*-methylmorpholine, CH_2Cl_2 , 16 h, 68 %.

Extraction results obtained in the high acidity conditions ($[\text{HNO}_3] = 4 \text{ mol}\cdot\text{L}^{-1}$) are presented in Figure 1. For $\beta\beta$, only very slight differences are observed between the mixture and the stereoisomers, with a higher extraction for the mixture of stereoisomers. This apparent contradictory result (when compared to U/Pu extraction obtained by Felines *et al.*^[33]) turned out to be due to the presence of oxalates in the primary aqueous solution studied by Felines *et al.* (see SI.4 for more details). Oxalates are indeed expected to greatly influence the distribution coefficient for the extraction of plutonium (D_{Pu}) as they are conventionally applied to induce precipitation of plutonium followed by calcination to obtain the plutonium oxide (PuO_2).^[35,36]

Pu extraction obtained with the $\alpha\beta$ shows different behaviors. First, the impact of the ethyl position was enlightened as D_{Pu} was decreased by a factor of 2 to 4 when compared to that obtained with the $\beta\beta$. Moreover, an effect of stereoisomerism can be observed with an antagonistic effect of the mixture of stereoisomers on plutonium extraction compared to the diastereoenriched $\alpha\beta$ stereoisomers. A small difference of efficiency occurred also between the enriched stereoisomers with a higher D_{Pu} for the (R,S)-isomer.

Same experiment was performed with a low nitric acid concentration in the aqueous phase to estimate the potential Pu stripping with these extractants. Results are presented in Figure 2. Under this low nitric acid condition ($[\text{HNO}_3] = 0.5 \text{ mol}\cdot\text{L}^{-1}$), distribution coefficients below 1 were obtained for

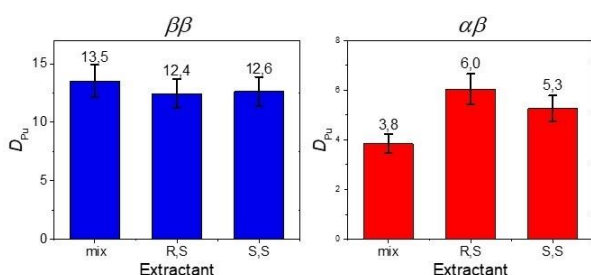


Figure 1. Distribution ratios of plutonium (D_{Pu}) for the (R,S)- and (S,S)- $\beta\beta$ (blue) or $\alpha\beta$ (red) stereoisomers compared with the corresponding stereoisomeric mixture. Experimental conditions: $[\text{Pu}^{\text{IV}}]_{\text{aq,ini}} = 22.3 \text{ mmol}\cdot\text{L}^{-1}$; $[\text{HNO}_3]_{\text{aq,ini}} = 4 \text{ mol}\cdot\text{L}^{-1}$; $[\text{Ligand}] = 1.2 \text{ mol}\cdot\text{L}^{-1}$ in TPH, $V_{\text{org}}/V_{\text{aq}} = 1/4$, $T = 25^\circ\text{C}$.

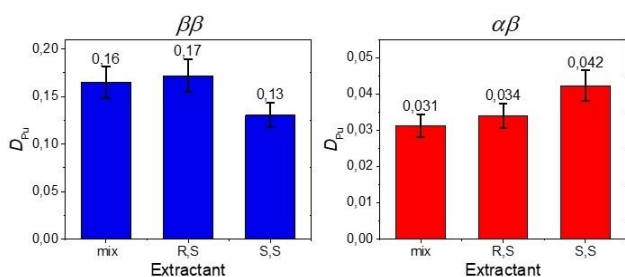


Figure 2. Distribution ratios of plutonium (D_{Pu}) for the (S,S)- and (R,S)- $\beta\beta$ (blue) or $\alpha\beta$ (red) stereoisomers compared with the corresponding stereoisomeric mixture at low nitric acid concentration. Experimental conditions: $[\text{Pu}^{\text{IV}}]_{\text{aq,ini}} = 60.2 \text{ mmol}\cdot\text{L}^{-1}$ for $\beta\beta$ and $74.0 \text{ mmol}\cdot\text{L}^{-1}$ for $\alpha\beta$; $[\text{HNO}_3]_{\text{aq,ini}} = 0.5 \text{ mol}\cdot\text{L}^{-1}$; $[\text{Ligand}] = 1.2 \text{ mol}\cdot\text{L}^{-1}$ in TPH, $V_{\text{org}}/V_{\text{aq}} = 1/5$, $T = 25^\circ\text{C}$.

all the extractants, which confirms that Pu can be stripped efficiently from these extractants in such acidity conditions.

It is to note that the distribution coefficients of the $\alpha\beta$ extractants are 3 to 5 times lower than those of the $\beta\beta$, thus underlining a better ability of the $\alpha\beta$ derivatives for the stripping of the plutonium at low nitric acid concentration. At variance with the (S,S)-stereoisomers, no significant differences in the stripping properties were observed between the mixture of stereoisomers and the (R,S)-stereoisomers of a same extractant. Moreover, it is noteworthy that the effect promoted by the (S,S) configuration for the $\beta\beta$ is the opposite of that observed for the $\alpha\beta$.

UV-vis spectroscopy and linear combination

Regarding these extraction results, UV-vis spectroscopy was applied to identify and quantify the Pu-N,N-dialkylamides complexes in the organic solution in order to evaluate if the speciation of the plutonium complexes is influenced by the stereopurity of the ligands.

For this, we used a methodology based on linear combinations of pure Pu-DEHBA UV-Vis spectra as reported by Acher *et al.*^[37] In their study, the authors showed that the speciation of the Pu-DEHBA complexes is dependent of nitric acid concentration. Thanks to UV-vis and extended X-ray absorption fine structure (EXAFS) measurements coupled to density functional theory (DFT) calculations, they identified two main complexes: $\text{Pu}(\text{NO}_3)_4\text{L}_2$ and $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$ for 2.8 and 11 $\text{mol}\cdot\text{L}^{-1}$ nitric acid concentration respectively (see structure of the complexes in Figure 3). For the sake of simplification, DFT computation was performed for Pu-N,N-diethylpropylamide (DEPA) complexes.^[38]

The $\text{Pu}(\text{NO}_3)_4\text{L}_2$ complex (Figure 3a), also named inner sphere complex, contains 2 monodentate amide ligands and 4 bidentate nitrates in the inner sphere of the complex. It was shown to be the preponderant complex at low acidities. The $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$ complex (Figure 3b), named outer sphere complex, is mostly present at high nitric acid concentrations. The plutonium is surrounded by six bidentate nitrate and the ligand is protonated (HL^+) in the cation outer coordination sphere. The protonated amide is thus bound to a nitrate via a hydrogen

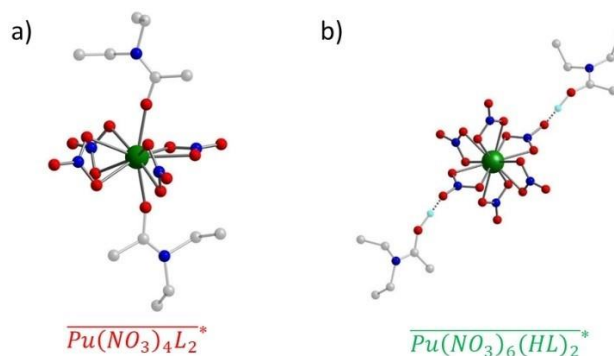


Figure 3. Representation of a) $\text{Pu}(\text{NO}_3)_4\text{L}_2$ and b) $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$ based on DFT-optimized geometries of the plutonium complexes with L = DEPA from the literature.^[37,38]

bond of the protonated amide function. Thanks to a linear combination of reference outer sphere and inner sphere UV-vis spectra, Acher *et al.* further evaluated the proportion of these two complexes at intermediate acidities.^[10,37]

In the present study we applied a similar methodology to evaluate if the similar or different Pu extraction measured with the mixture (mix), the (*R,S*)- and (*S,S*)-ligands can be related to similar or different speciation of the Pu complexes.

UV-vis spectra measured for the $\beta\beta$ and $\alpha\beta$, (*R,S*), (*S,S*) and mix after being engaged in an extraction with a Pu aqueous phase at 4 mol·L⁻¹ nitric acid are presented in Figure 4a. Linear combination of outer/inner sphere complexes spectra were applied to further fit for the experimental spectra. The resulting fit spectra are plotted in dashed lines in Figure 4a. The ratios of each complexes were derived from these linear combinations (see Table S1) and exploited to evaluate individual distribution coefficients corresponding to the two Pu-complexes identified by spectroscopy. The resulting *D* values are presented in Figure 4b for all the tested molecules.

This representation shows that Pu extraction is mainly driven by the formation of inner sphere complexes for both $\alpha\beta$ and $\beta\beta$ extractants. For $\beta\beta$ extractants ~85 % of the plutonium is present as a Pu(NO₃)₄L₂ inner sphere complex whose corresponding *D*_{Pu} are approximately 10.5, 10.8 and 11.9 for the (*R,S*)-, (*S,S*)- and mix extractants, respectively.

In the case of the $\alpha\beta$, the lower Pu extraction is concomitant with a decrease of inner sphere complex Pu(NO₃)₄L₂ from ~85 % to 65 %, corresponding to distribution coefficients decreasing from ~11 for the $\beta\beta$ molecules, to 4.0, 2.8 and 2.6 for (*R,S*)-, (*S,S*)- and mix $\alpha\beta$ respectively. This result can be assigned to the larger $\alpha\beta$ steric hindrance of the oct-3-yl chain which disadvan-

tages the formation of inner sphere complex Pu(NO₃)₄L₂. Failali *et al.* indeed showed that steric hindrance of a monoamide destabilizes the complex Pu(NO₃)₄L₂ when the acyl chain was branched.^[39] By rendering the inner spheres complexes formation less favorable, this steric hindrance would therefore be responsible of the Pu extraction decrease.

A higher distribution coefficient of the outer sphere complex Pu(NO₃)₆(HL)₂ is observed for stereo-enriched $\alpha\beta$ compared to their $\beta\beta$ counterpart. Distribution coefficient of ca. 1.85 for the (*R,S*)- and (*S,S*)- $\beta\beta$ is increased to 2.1, and 2.5 for (*R,S*)- and (*S,S*)- $\alpha\beta$. This significant increase of distribution coefficient of the outer sphere complex indicates that this complex is more favored for the stereo-enriched $\alpha\beta$ ligand. Those results show that steric hindrance does not only demote the inner sphere complex but also seems to favor the outer sphere complex (at least in the stereo-enriched cases). It is also interesting to notice that the difference of distribution coefficient due to outer sphere complex cannot be explained by the fact that more free ligands are available for the formation of plutonium complex since i) in the organic phase, the plutonium concentration goes from 0.017 to 0.022 mol·L⁻¹ whereas that of $\alpha\beta$ or $\beta\beta$ extractant is 1.2 mol·L⁻¹, ii) the mix $\alpha\beta$ shows the lowest complex formation for both type of complexes. It can be estimated that there are more than 50 free ligands per plutonium complex in the organic solutions.

Looking at the effect of stereoisomerism for the $\beta\beta$ ligands on Pu extraction with (*R,S*), (*S,S*) and mix, it can be observed that Pu extraction evolves with the same trend as the *D*_{Pu} due to inner sphere complexes. The slightly higher Pu extraction obtained for the mixture of stereoisomers can be attributed to an entropic effect due to the greater number of possible complexes configurations with the mixture, and to the fact that all these configurations are favorable.

Effect of stereoisomerism is more important with $\alpha\beta$ ligands. Looking at the distribution coefficient due to inner and outer sphere complexes, we observe that the (*S,S*)-extractant forms less inner sphere complex (ca. 52.8 % of the whole complexes amount with *D*_{Pu,inner} = 2.8) than the (*R,S*) (ca. 65.6 % of the whole spheres amount with *D*_{Pu,inner} = 4.0). Here again, the intrinsic steric hindrance of the (*S,S*)-diastereoisomer may induce that this latter forms less inner sphere complexes, and consequently extracts less Pu than (*R,S*) (*D*_{Pu} 6.0 versus *D*_{Pu} 5.2).

In contrast, the mix is clearly unfavorable to Pu extraction for $\alpha\beta$ (3.8 for mix against 5.2 and 6.0 for (*S,S*) and (*R,S*)). The origin of this behavior appears different in this case, as it cannot be related to a higher extraction of Pu due to a higher proportion of inner sphere complexes (69 % for the mix and 66 % for (*R,S*)). It should be considered here that the mixture can statistically form 10 different complexes, among which 4 are stereopure complexes (composed of two identical diastereoisomers). The 6 other complexes are mixed complexes composed of a couple of ligands such as [(*R,S*);(*S,S*)], [(*R,S*);(*S,R*)], etc. The lower extraction obtained with the mixture of all these complexes may result therefore from the fact that the mixed complexes are less efficient in extracting plutonium, even if they present a greater proportion of internal species when compared to the (*S,S*)-diastereoisomers. It can be assumed that

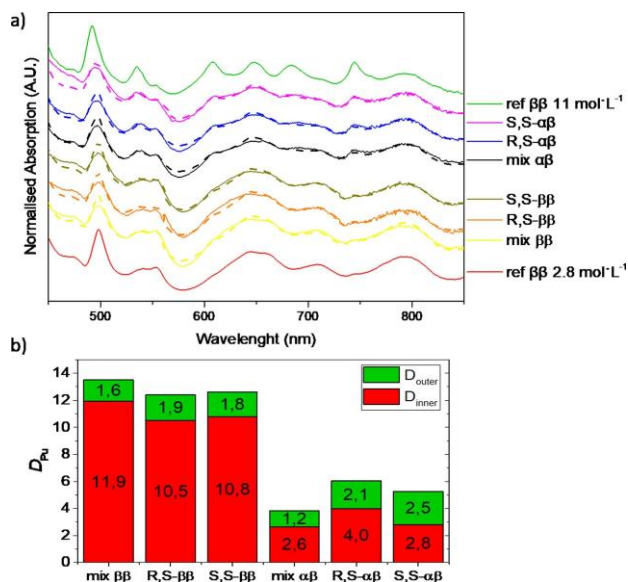


Figure 4. a) Vis-NIR absorption spectra of organic solution from Pu-dialkylamide solvent extraction, dashed line = linear combination, plain line = experimental data. All experiments were performed at 4 mol·L⁻¹ nitric acid. Red (bottom) and green (top) reference curves were yielded by Acher *et al.*^[37] at 2.8 and 11 mol·L⁻¹ HNO₃, respectively. b) Distribution coefficient of each Pu complex: Pu(NO₃)₄L₂ in red and Pu(NO₃)₆(HL)₂ in green for the given extractant.

the antagonist effect of the mixture of stereoisomer may be caused by a competition between the four different ligands (*SS*, *RR*, *RS*, *SR*) to generate the complexes $\text{Pu}(\text{NO}_3)_4\text{L}_2$ and $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$. This suggests that the optical purity of the ligands is important for the evaluation of new ligand for extraction.

Overall it is interesting to consider that the spatial interaction leading to different Pu extraction can be due to *i*) steric effect close to the metal which can hamper the formation of complex, or to *ii*) effect on the supramolecular layout of the complexes.

To our knowledge, the speciation of the plutonium-*N,N*-dialkylamide complexes at low concentration of nitric acid has never been described in literature. Therefore, we performed UV-vis spectroscopy on the organic phases of extraction achieved with $0.5 \text{ mol}\cdot\text{L}^{-1}$ of nitric acid (see Figure S.2). As previously, the ratios of $\text{Pu}(\text{NO}_3)_4\text{L}_2$ and $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$ complexes were determined. As expected, UV-Vis spectra indicate that the outer sphere complex $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$ is not present and that the inner sphere $\text{Pu}(\text{NO}_3)_4\text{L}_2$ complex is the major complex at $0.5 \text{ mol}\cdot\text{L}^{-1}$. It is however interesting to notice that the spectra of the organic phases do not perfectly fit with the reference of the inner sphere complex ($\text{Pu}(\text{NO}_3)_4\text{L}_2$). The differences with the reference may indicate the presence of a third uncharacterized species of complex which would be present in diluted acidic solutions. We assume that the uncharacterized complex may be a $\text{Pu}(\text{NO}_3)_4\text{L}_3$ complex as already observed by De Sio *et al.* at low acidity in the case of TBP.^[40] Condamines *et al.* also observed a slope of 3 for DEHBA and 4 for *N,N*-di(2-ethylhexyl)isobutanamide (DEHiBA) in the bilogarithmic plot of the distribution coefficients as a function of the amide concentration (at $[\text{HNO}_3] = 1 \text{ mol}\cdot\text{L}^{-1}$ for $[\text{L}] \ll 0.1 \text{ mol}\cdot\text{L}^{-1}$), which indicated a stoichiometry of 3 ligands per plutonium.^[12] Because of the very low concentration of Pu in these conditions, a low signal to noise ratio prevented us to determine the ratio of this unknown complex. Complementary experiments including for instance X-ray absorption spectroscopy would be helpful to conclude on this point.

Conclusions

Aiming at probing the impact of the stereochemistry of *N,N*-dialkylmonoamide ligands on their extraction properties in the PUREX context, we developed a series of mixture (mix) and stereoenriched diastereoisomers (*(R,S)* or *(S,S)*) form of DEHBA ($\beta\beta$) and of one of its regioisomer, namely the EHOBA ($\alpha\beta$), which differ from the position of one ethyl branching. Diastereoisomers of DEHBA were obtained as diastereopure whereas those of EHOBA were only stereoenriched versions. Plutonium LLE experiments have been performed with the mix, *(R,S)*- and *(S,S)*-stereoisomers for both $\alpha\beta$ and $\beta\beta$. These experiments allowed to distinguish two different effects of the ethyl branching on the extraction of plutonium which could be related to different speciation of the plutonium complexes: *i*) the position of the branching affected significantly plutonium extraction as well as the formation of the inner sphere complex; *ii*) the stereoisomerism of the ligands showed an impact on

extraction which was more significant for the $\alpha\beta$ extractant as the branching is closer (α position) to the complexing site. These results showed that inner sphere Pu complexes are demoted by steric hindrance while outer sphere Pu complexes are promoted by steric hindrance. The cases of the stereoisomers mixtures are also interesting since an antagonist effect was observed for the $\alpha\beta$ while a small synergic effect was observed for the $\beta\beta$.

This study shows therefore that with an experiment as simple as UV-vis spectroscopy, it is possible to discriminate finely the various complexes that are formed with molecules which only differ stereochemically. To go further, more spatial interaction should be considered such as *i*) steric effect near the metal which may cause a diminution of complex formation or *ii*) effect on the supramolecular layout of the complexes. To answer these hypothesis extended X-ray absorption fine structure (EXAFS) and small-angle X-ray scattering (SAXS) will be performed. EXAFS study would allow to observe if there is a difference in the distance between the oxygen of the dialkylamide and the plutonium (Pu-O_L) depending on the involved stereoisomer. The SAXS study would allow to assess if reverse micelles are formed with such extractants, and if they might be affected by the optical purity of the extractant in the case of plutonium extraction.

Experimental Section

Chemicals

Hydrogenated tetrapropylene (TPH) is a diluent used in the reprocessing plant of ORANO (France) and was purchased from Novasep. Anhydrous solvents (AcroSeal) were purchased from Acros. All other chemicals were analytically pure (Sigma-Aldrich, Acros or ABCR) and used without further purification.

The enantiomeric excess (ee) was determined after separation of the 2-ethylhexan-1-ol enantiomers (compounds **5 a** and **5 b**) by Gas Chromatography coupled to Mass Spectrometry (GC-MS: Shimadzu GC-2010- Shimadzu GCS-QP2010S), on a chiral stationary phase Supelco β -DEX120 from SUPELCO. Experimental conditions: The analyses were performed at a constant temperature (80 °C) for 45 min using Helium as the carrier gas.

The purity of compounds was assessed by GC-MS (Waters GCT high-resolution time-of-flight (TOF) mass spectrometer). Runs were performed on a nonpolar column containing a 100 % dimethylpolysiloxane (PDMS), CP-Sil 5 CB (LxID: 25 m \times 0.25 mm, df 0.25 μm) from Agilent. Prior treatment of the monoamides with DIAZALD® in ethyl acetate (AcOEt), allowed the methylation of the suspected contaminants such as carboxylic acid or acidic alcohol (*i. e.* phenol) in order to observe them more easily by the GC analysis. The following time-temperature program was used for the analysis: 60 °C (1 min); 60-150 °C at 10 °C/min, 150-175 °C at 5 °C/min, 175 °C (10 min) 175-250 °C at 20 °C/min, 250 °C (5 min) using Helium as the carrier gas.

The *N,N*-dialkylamide used for the extraction were certified with a purity of 98% or more.

Pu extraction procedure

Pu solution. Caution! Plutonium present radiotoxicity hazards. All experiments on transuranium elements were conducted in the Atalante facility (CEA Marcoule, France), in a laboratory dedicated to these highly radioactive elements. All experiments were carried out with approved safety operating procedures in negative pressure glove box.

$^{239, 240}\text{Pu}^{\text{IV}}$ solution was prepared by dissolving the corresponding oxide, PuO_2 , with concentrated HNO_3 in a glove box. It was then purified by fixation on a DOWEX anion exchange resin at $7 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 and elution with $0.5 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 . Oxidation state and concentration of the actinide solutions were checked by Vis-NIR spectrophotometry.

Organic phases. The organic phases containing the ligand diluted at $1.2 \text{ mol}\cdot\text{L}^{-1}$ in TPH were prepared by liquid-liquid extraction at 25°C in Eppendorf vials. The organic layers were pre-equilibrated with nitric acid at the corresponding acidity (aqueous layer volume over organic layer volume ratio: $V_{\text{aq}}/V_{\text{org}} = 2$) for 5 min at 25°C twice successively. The phases were separated after centrifugation.

Aqueous phase. Initial aqueous phases concentrations were (i) $C_{\text{HNO}_3}^{\text{aq,ini}} = 4 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{Pu(IV)}}^{\text{aq,ini}} = 22.3 \text{ mmol}\cdot\text{L}^{-1}$; (ii) $C_{\text{HNO}_3}^{\text{aq,ini}} = 0.5 \text{ mol}\cdot\text{L}^{-1}$ $C_{\text{Pu(IV)}}^{\text{aq,ini}} = 60.2 \text{ mmol}\cdot\text{L}^{-1}$ ($C_{\text{Pu(IV)}}^{\text{aq,ini}} = 74.0 \text{ mmol}\cdot\text{L}^{-1}$ for $\alpha\beta$).

Extraction. Aqueous phases containing plutonium and nitric acid were contacted for 30 min by means of an automatic vortex shaker with organic solutions (i) $V_{\text{aq}}/V_{\text{org}} = 1$, (ii) $V_{\text{aq}}/V_{\text{org}} = 1.5$) containing the pre-equilibrated organic phases.

$^{239, 240}\text{Pu}$ activities in each phase were determined by α -spectrometry at 5157 MeV (Model 7401, Canberra).

The concentration of the ligand in the organic layer was deduced from the titration of an aliquot diluted in acetic anhydride solution using perchloric acid ($0.1 \text{ mol}\cdot\text{L}^{-1}$). The pH of the solution was monitored with a Metrohm titroprocessor.

The concentration of nitric acid of the plutonium solution was deduced from the titration of an aliquot diluted in a saturated solution of ammonium oxalate with $0.1 \text{ mol}\cdot\text{L}^{-1}$ of sodium hydroxide (NaOH). The pH of the solution was monitored with a Metrohm titroprocessor.

UV-vis spectroscopy

UV-vis spectroscopy was measured in 8 mm vials containing $70 \mu\text{L}$ of the organic phase after plutonium extraction. The baseline was measured with the respective mixture of diastereoisomers at $1.2 \text{ mol}\cdot\text{L}^{-1}$ brought into contact with an aqueous phase containing only nitric acid at the same acidity as that of the plutonium samples.

Supporting Information

Completed general information, full synthesis and extensive characterization of *N,N*-dialkylamides. Supplementary UV-vis spectra and linear combination results are reported.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: diastereoisomers • liquid-liquid extraction • *N,N*-dialkylamide • plutonium • UV/Vis spectroscopy

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