

Reagents

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. $^{239,240}\text{Pu(IV)}$ 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 $7\text{ mol.L}^{-1}\text{ HNO}_3$ and elution with $0.5\text{ mol.L}^{-1}\text{ HNO}_3$. Oxidation state and concentration of the actinide solutions were checked by Vis-NIR spectrophotometry. **DEHBA** *N,N*-dialkyl amides were synthesized by Pharmasynthese (France). DODECANE is purchased from Aldrich.

Sample preparation

The **DEHBA** samples were prepared by liquid-liquid extraction at 25°C . Nitric acid aqueous phases ($[\text{HNO}_3] = 3\text{ mol.L}^{-1}$ and 11 mol.L^{-1}), containing the Pu(IV) were contacted for 15 minutes by means of an automatic vortex shaker with organic solutions (aqueous phase volume over organic phase volume ratio: $\text{Vaq/Vorg} = 1$) containing the ligand. Before the extraction, the organic phase was pre-equilibrated with the targeted nitric acid ($\text{Vaq/Vorg} = 3$) for 30 min at 25°C . The phases were separated after centrifugation. Plutonium concentrations in the organic phase were determined by alpha-spectroscopy. The evolution of Pu(IV) was monitored with Vis-NIR spectrophotometry during several days corresponding to the delay between the samples preparation and their analysis at the Synchrotron.

Table 1. Compositions of **DEHBA** solutions used in EXAFS and vis-NIR measurements.

	$C^{\text{aq}}_{\text{HNO}_3}$	$C^{\text{org}}_{\text{HNO}_3}{}^{\text{b}}$	$[\text{Ligand}]_{\text{org}}$ (mol.L^{-1}) ^a	$[\text{Pu}]_{\text{org}}$ (mmol.L^{-1})	Measurements
Pu-DEHBA 2.8M	2.8 M	0.7	1.2	2.2 ^c	vis-NIR
Pu-DEHBA 3.3M	3.3 M	0.8	1.2	2.2 ^d	EXAFS, vis-NIR
Pu-DEHBA 5M	5 M	1.9	2.7	2.2 ^c	vis-NIR
Pu-DEHBA 8M	8 M	3.4	2.7	2.2 ^c	vis-NIR
Pu-DEHBA 11M	11M	4.2	2.7	2.2 ^d	EXAFS, vis-NIR

^a Amide concentration in the organic phase. ^b HNO_3 concentration in the organic phase estimated values from ref [20] and [24] of the main manuscript. ^c Pu(IV) concentration in the organic phase estimated values from ref [20] and [24] of the main manuscript. ^d Alfa spectroscopy measurements.

EXAFS data acquisition and treatment

EXAFS spectra were recorded at Synchrotron SOLEIL (Saint-Aubin, France) (2.75 GeV at 450 mA), at the MARS beamline. MARS is equipped with a water-cooled Si(220) double crystal horizontal focusing monochromator (DCM). Beam vertical collimation/focusing and rejection of higher-order harmonics were achieved with two Ptcoated mirrors before and after the DCM. A 13-element HPGe solid state detector (ORTEC) was used for data collection in fluorescence mode. Monochromator energy calibration was carried out at zirconium K-edge. All measurements were performed at room temperature in 200 μL double-layered cells specifically designed for radioactive samples. All spectra were recorded at the plutonium L_3 edge (18057 eV for Pu). The data represent averages of 4 scans. Data processing was carried out with the Athena code.¹ After energy calibration, the $e0$ energy was set at the maximum of the absorption edge. For all the samples, the maximum energy of the absorption edge confirms the redox state +IV for plutonium (18068.2 eV).^{2,3} The EXAFS signal was extracted by subtracting a linear pre-edge background and a combination of cubic spline functions for atomic absorption background and then normalized by the Lengeler-Eisenberg procedure. Pseudo-radial distribution functions (PRDF) were obtained by Fourier transform in $k^3\chi(k)$ using the ATHENA code between 1.5 and 12.5 \AA^{-1} . For EXAFS data analysis, no fitting procedure is applied. Theoretical scattering phases and amplitudes were calculated by the FEFF9.^{4,5} from computational methods.

Computational details

The geometry and frequency calculations have been performed with Gaussian 09⁶ at the DFT level of theory with the PBE0 functional.⁷ A small core quasi-relativistic effective core potential (RECP – 60 electrons)^{8,9} by the Stuttgart-Cologne group and its corresponding TZ-valence basis set have been used for Pu¹⁰ and the def-TZVP¹¹ basis sets for the other atoms. Solvent effects have been taken into account with a polarizable continuum model (IEFPCM) corresponding to *n*-dodecane.⁶ The *ab initio* DW factors have been calculated at 300 K for each scattering path from the dynamical matrix extracted from the DFT frequency calculation with the DMDW module of FEFF9.^{4,5} The EXAFS spectra have then been simulated with FEFF9 considering this *ab initio* DW factors, and all multiple-scattering paths up to a half-path length of 6 Å. The scattering potentials were calculated using a self-consistent loop. The amplitude factor S_0^2 was fixed to 1. The shift of the photoelectron energy origin ΔE_0 is the only parameter adjusted in the EXAFS simulation and has been taken so that the first amplitudes of the simulated spectra are in phase with the experimental ones.

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