

## Complexation of actinides by branched N-macrocycle DOTA Complexation des actinides par le ligand DOTA

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### Résumé :

Cette étude montre les différences de comportement des cations actinides selon leur degré d'oxydation et leur taille dans une série donnée vis-à-vis de ligands constitué d'atomes de donneurs plus ou moins durs, comme l'oxygène et l'azote. Pour le degré d'oxydation +III des actinides, le cas du plutonium et de l'américium a été choisi alors que pour les actinides au degré d'oxydation +IV, ce sont l'uranium, le neptunium et le plutonium qui ont été retenus. Le ligand DOTA, qui est très bien connu pour les cations en solution autre que les actinides, a été choisi car il présente les deux atomes donneurs : oxygène et azote.

### Summary:

This study shows the differences of behavior for the actinide (An) cations with their valence and its size in a given series versus the more or less hard donor atoms, such as oxygen and nitrogen. Plutonium(III) and americium(III) were chosen to represent the An(III) series, and for the An(+IV) series, uranium, neptunium and plutonium were selected. The DOTA ligand, which is very well known for the cations in solution other than the actinides, was chosen because it has the two donor atoms: oxygen and nitrogen.

**Keywords:** Actinide, Complexation, polyaminocarboxylate ligands, DOTA

This research deals with the study of the behavior of actinide ions in solution at oxidation states +III and +IV, with a polyaminocarboxylate ligand. This collaboration once more revealed the differences in behavior of ions according to their degree of oxidation.

Ce travail de recherche concerne l'étude du comportement en solution des ions actinides aux degrés d'oxydation +III et +IV, vis-à-vis d'un ligand polyaminocarboxylate. Cette collaboration a permis d'éclairer encore une fois les différences de comportement des ions selon leur degré d'oxydation.

## 1 Introduction

The comprehension of the actinides affinity for interest ligands has been a pivotal issue since the beginning of the nuclear fuel reprocessing. The difference in interaction between N-donors ligands and O-donor ligands is a hint on the selectivity difference between trivalent and tetravalent actinides. The study of molecules featuring both N and O-donor functions may be a way to reach a better understanding. Thus, the poly-amino-carboxylate ligands form an interesting family of f-element cations chelating agents. One specific ligand has been selected for this study: the DOTA macrocycle (1,4,7,10-tetraazacyclododecane-tetraacetic acid, Figure 1).

The DOTA macrocycle has been widely studied with lanthanides, but few investigations have been carried out with actinides [1, 2]. The main goal of this work is to extend the investigations to the

complexing behavior of DOTA with An(III) and An(IV) in aqueous solution.

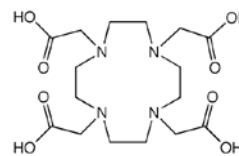


Figure 1: Developed formula of the DOTA ligand

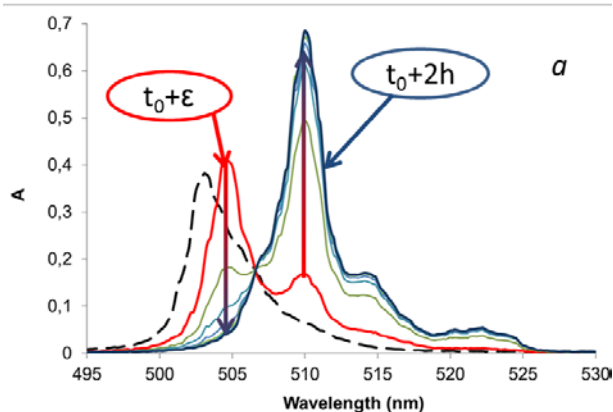
## 2 Expérimental/Méthodologie

In order to achieve this work, our methodology consists in a twofold approach, combining experimental studies with modeling calculations. Americium(III) and plutonium(III) have been selected to represent the An(III) series, while thorium(IV), neptunium(IV) and plutonium(IV) have been chosen to represent the An(IV) series. Besides the laboratory analytical techniques (UV-

Vis spectrophotometry, NMR and ESI-MS), the systems have been monitored with X-ray absorption spectroscopy (EXAFS) to confirm the stoichiometry of the complexes, identify the ligand complexing sites and probing the actinides coordination sphere using EXAFS at An L<sub>3</sub> edges. Experimental EXAFS spectra are first compared to theoretical ones based on hypothetical models obtained thanks to quantum chemistry calculations (DFT). Then the best models were used to fit the experimental spectrum with metric parameter in order to achieve the structural description of the complex. The An/DOTA coordination mode is then compared to analogous lanthanide complexes.

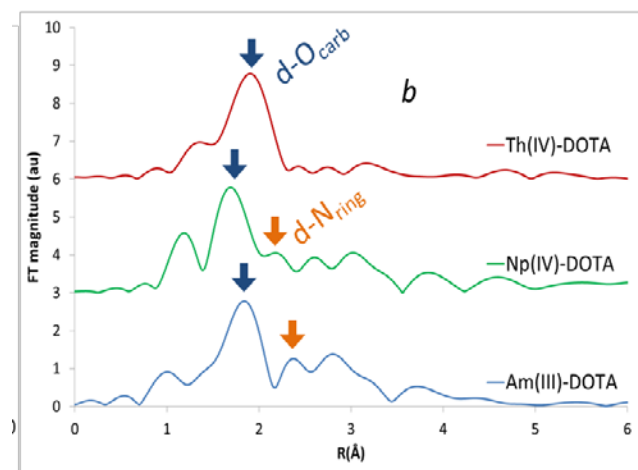
### 3 Résultats

The experiments proved DOTA forms complexes with both An(III) and An(IV) (Figure 2). Complexation of An(III) is similar to what has been observed with Ln(III) i.e. the slow formation of a (1:1) complex. At  $t_0 + \epsilon$ , the reaction first leads to the formation of an intermediate species where the cation is complexed by the carboxylate arms only. Then, the system slowly evolves towards the final species, as shown on the UV-Vis spectra (Figure 2a). The cation eventually gets inside the cage formed by the N-cycle and the carboxylate arms (Figure 2b).



**Figure 2:** a: UV-Vis kinetic follow-up of the complexation of  $1 \times 10^{-3} \text{ M Am}^{3+}$  by 0.1M DOTA at  $\text{pH} = 3 \pm 0,3$  and  $\theta = 25 \text{ }^\circ\text{C}$  in aqueous solution. Dashed black line:  $\text{Am}^{3+}$  in absence of ligand.  $t_0$ : addition of the metal to the ligand solution.

The differences in coordination mode regarding the An(III)-DOTA and An(IV)-DOTA systems will be discussed: stoichiometry, participation of the complexing sites and distances to the metallic center [3, 4]. The evolution of the formed species will be considered.



**Figure 2:** b: Fourier Transform of the EXAFS spectra of Am-DOTA ( $[\text{Am}] = 10^{-3} \text{ M}$ ,  $[\text{DOTA}] = 0.1 \text{ M}$ ), Np-DOTA and Th-DOTA systems ( $[\text{Np}] = [\text{Th}] = 2.10^{-3} \text{ M}$ ,  $[\text{DOTA}] = 0.2 \text{ M}$ ). All measurements were done at  $\text{pH} = 3 \pm 0,3$  and  $\theta = 25 \text{ }^\circ\text{C}$ .

For the actinides +III, the calculated kinetic constant shows the C1  $\rightarrow$  C2 transition for both  $\text{Pu}^{3+}$  and  $\text{Am}^{3+}$  are of the same order of magnitude, which is not surprising considering the similarity in ionic radii of the two ions (for CN9). The two An(III) systems moreover end up with the formation of a (1:1) complex only, as proved by the EXAFS experiments. The fitted theoretical structures match the experimental data, leading to the conclusion the final complex is the (1:1) species, where the cation is bonded to the nitrogens of the ring, the four carboxylate arms and a water molecule is completing the coordination sphere, as what has been previously observed with Gd(III)-DOTA systems.

Within the An(IV) series, U(IV), Np(IV) and Pu(IV) seem to behave exactly as the An(III), although to the complexation is slower to complete. However, the EXAFS experiments (Figure 2b) the complexation of Th(IV) doesn't end up with the formation of a (1:1) complex involving the nitrogen atoms of the ring. Several configurations, such as a (1:2) species may then be considered.

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