**Report:**

XAS measurements have been carried out on Am(III), Pu(III), Pu(IV), Np(IV) in presence of the DOTA in aqueous solution. Excess of DOTA ligand was chosen for this experimental setup (An/ligand ratio is 1/100) in order to take benefit of the advantageous to self-buffering effect of the DOTA ligand (pH 3) and to accelerate the An complexation by the DOTA. Three different plutonium samples was made in different conditions in order to extract the PuIII/DOTA complex and PuIV DOTA complex from distinct PuIII/PuIV ratio. Additional sample was prepared with AmIII/DTPA in order to compare this ligand to DOTA. Another DOTA sample was made starting from NpV solution and the two last samples (consisting in liquid-liquid PuIV extraction by 2 monoamide ligand) was added. The data were acquired at the An L3 edges, for each complex (17610 eV for Np, 18057 eV for Pu, and 18516 eV for Am).

1- AnIII complexes:

- Complexation of $Am^{III}$ is similar to what has been observed with $Ln^{III}$ i.e. the slow formation of a (1:1) complex. At $t_0+\varepsilon$, 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 by the UV-Vis spectra. EXAFS confirmed thanks to a DFT based fitting procedure (see Figure 1) the cation position after this complexing process: inside the cavity formed by the N-cycle and the carboxylate arms. This was observed for Am(III) with, first, shorter Am-O distances with 4 An-carboxylate distances and one water molecule and a longer Am-N distances. More particularly, these two distances in the first shell contribution with longer An-N distances and shorter An-O is the most relevant evidence of the DOTA coordination mode. Concerning the actinides affinity for nitrogen and carboxylate sites, no relevant changes was observed comparing interatomic distances to the equivalent (similar ionic radii) lanthanides (see table 1).

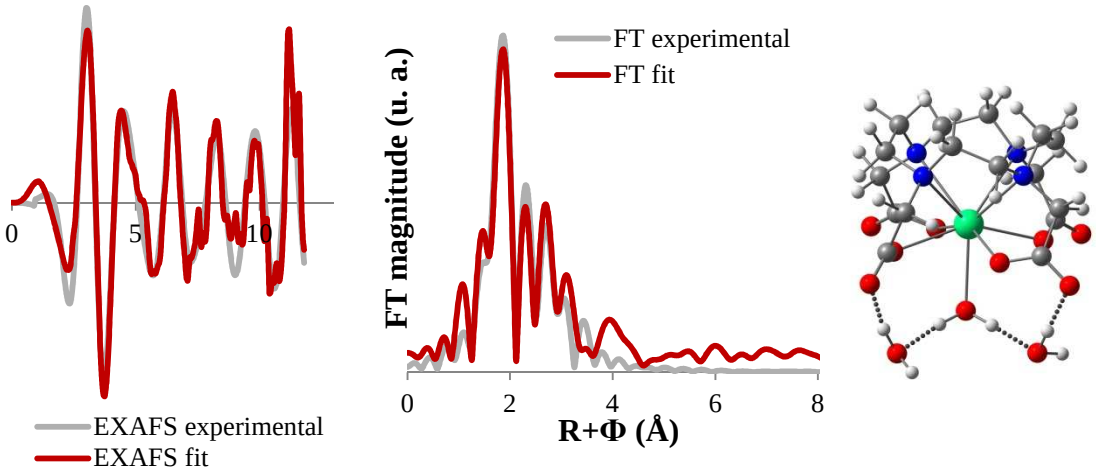


*Figure 1: Experimental and fitted EXAFS spectrum for Am(III) DOTA complex, and FT for experimental and fit results for Am(III) DOTA. Schematic representation of $Am(DOTA)(H_2O)_3^{2-}$ complexes optimizes by DFT calculation.*

For plutonium DOTA complexes, we were not able to synthetize a stable PuIII/DOTA complex but intermediate species of mixed PuIV/PuIII complexes were observed. Two different conditions were chosen to maintain as much as possible the +III oxidation state of plutonium providing two PuIV/PuIII ratio. A pure PuIV DOTA complex was also prepared. The XANES spectrum for each Pu/DOTA complexes are presented figure 2 and compared to a reference PuIII complex. Isobestic points are

present both on XANES spectra as well as in EXAFS spectrum. Electrochemical studies and UV-vis analysis provided other evidences of simple electron exchange between PuIV/DOTA complex and PuIII/DOTA. With the help of a double component analysis, a theoretical PuIII/DOTA spectrum is determined assuming that only 2 species is present in solution (PuIVDOTA/PuIIIDOTA). The resulting spectra for the XANES and EXAFS are presented figure 2 (light blue).

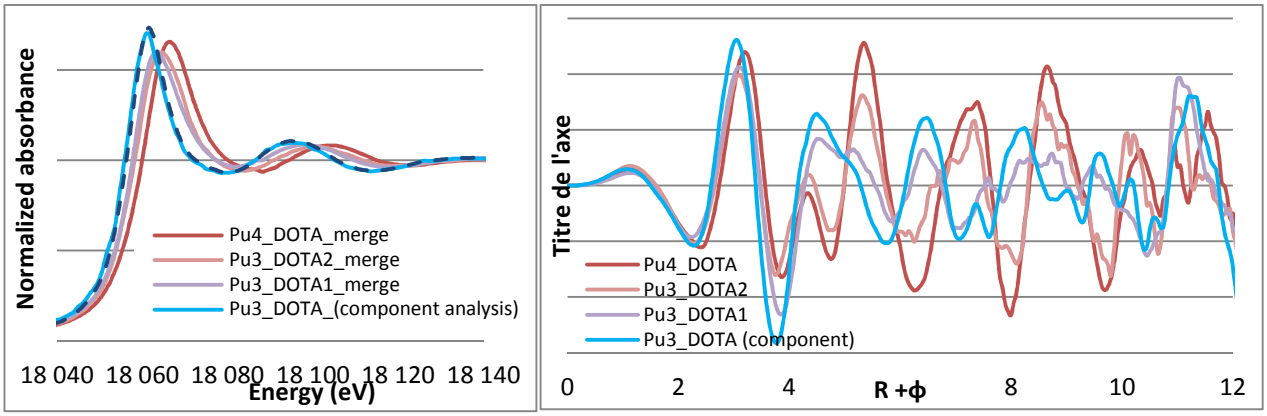


*Figure 2: Experimental XANES spectrum for PuIII/DOTA complexes synthetized with two different route and comparison to PuIVDOTA complex and reference PuIII. Right figure is the corresponding EXAFS spectrum.*

This procedure allowed us to perform a PuIII/DOTA fit as made for AmIII/DOTA. The two 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-DOTA systems. Table 1 shows the fitted data for our systems are in agreement with what was previously obtained with lanthanides of equivalent ionic radii. This observation once more illustrates the actinides(III) behave exactly with the lanthanides(III) when they are being complexed by DOTA. A publication on this topic is under redaction and will be submitted this semester : Structural characterisation of DOTA complexes with $Am^{3+}$ and $Pu^{3+}$

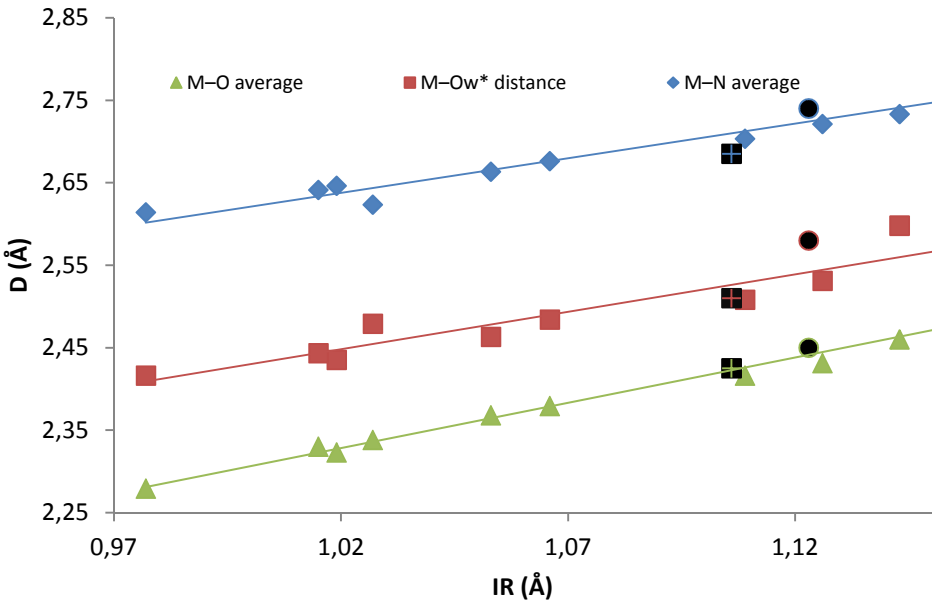


*Table 1: Fitted EXAFS bond lengths in AmIIIDOTA and extracted PuIIIDOTA complex compared to lanthanides data as a function of ionic radii.*

AmDTPA:

On the contrary to DOTA complexes, we were not able to distinguish two distances in the first shell contribution on the experimental EXAFS spectrum obtain for the Am/DTPA sample. The EXAFS oscillations only consist in a single contribution in the first coordination sphere corresponding to nine O/N atoms. This result disagrees with theoretical calculation (DFT) as observed on figure 3 and result most likely of a non complexed americium cation in water in the choosen conditions.

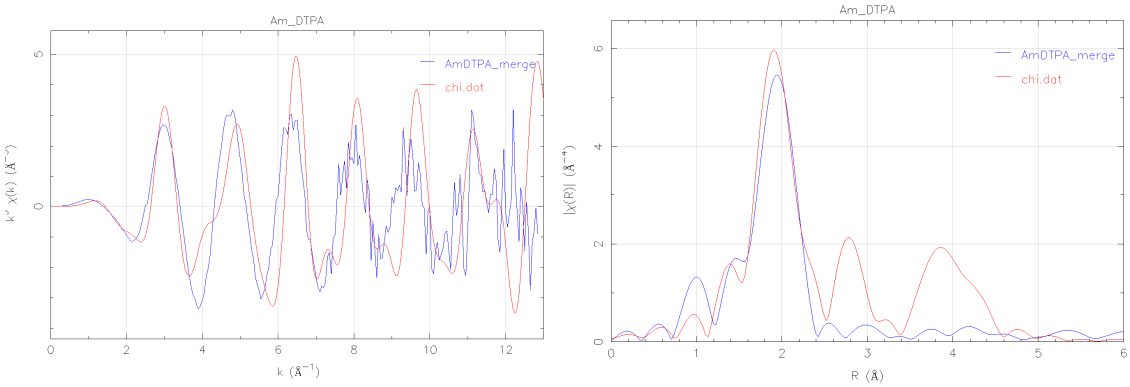


*Figure 3: Experimental EXAFS spectrum for AmIII/DTPA complexes(blue) compared to theoretical spectrum from a complexed Am/DTPA (red).*

2- AnIV complexes:

- In equivalent chemical conditions, Np(IV) and a pure Pu(IV) compound behaves as the AmIII : the cation also ends up inside the cage. Actinides IV complexation remains more unknown since no lanthanides analogs was determined yet. Even if NpIV and PuIV seem to be identical to AmIII complementary analyses are required to confirm its coordination mode. Unfortunately to this date, no significant data was recorded for the Ce(IV)DOTA ligand due to the rapid reduction to Ce(III). This experiment must be implemented in more oxidative conditions or under a fixed potential (electrochemical cell?). EXAFS data analysis was performed again with the help of theoretical calculation (DFT) for the Np/Pu(IV)DOTA sample (figure 3).

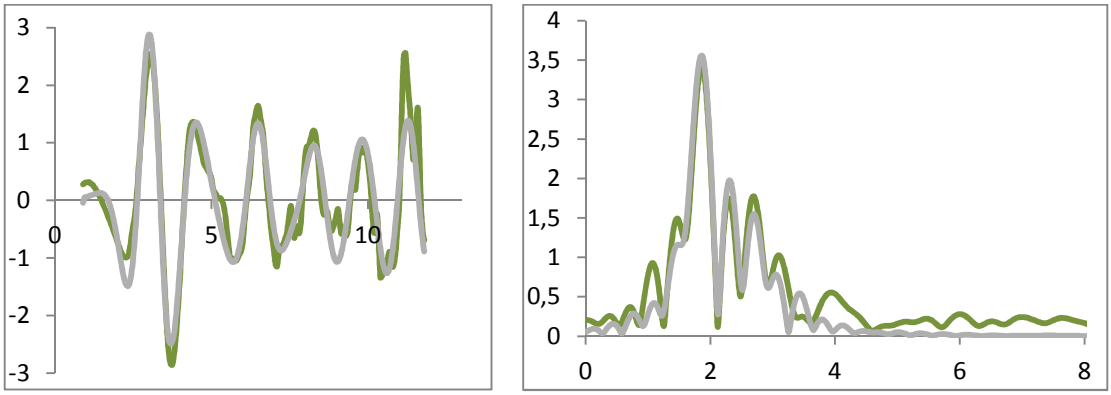

*Figure 3 : Experimental and fitted EXAFS spectrum for Np(IV)DOTA complex and FT for experimental and fit results.*

3- AnV complexes:

For the NpV samples the $NpO_2^{2+}$ sterical enhance hinder the DOTA complexation process. On the EXAFS spectrum only the shorter $O_{yle}$ contribution and a single $O_{eq}$ shell are clearly observed. Np-$O_{eq}$ distances might correspond to carboxylate group or to water molecule. Efforts to distinguish the two

type of ligand are under progress with the help of ESI-MS (electrospray induced mass spectroscopy) studies to determine the NpV/DOTA and NpV/$DOTA_2$ complexes stability.

4- PuIV monoamide complexes.

*N*,*N*-dialkylamides RCONR'R'' have been proposed since 1960 as alternative to TBP (tributylphosphate, $(C_4H_9O)_3$ PO) for the reprocessing of nuclear fuel (the PUREX process). A better description of the bond between the amide group and metal ion as well as a co extracted anions is expected from X-absorption measurements. The relationship between *N*,*N*-dialkylamides ligands geometry (nature of the R, R' and R'' substituent) and affinity toward actinides and extraction properties and selectivity must be probed. To reach this aim two PuIV samples extracted by 2 monoamides ligand in dodecane has been analyzed. The two monoamides were chosen for their ability to extract UVI and PuIV and their different selectivity toward these uranium and plutonium cation. Alkyl substituent on the carboxylate group (R) is modified from a linear butyl chain to an isobutyl group, supposedly rising the steric enhance in the plutonium coordination sphere. Fourier transform obtained for these samples is presented figure 4.

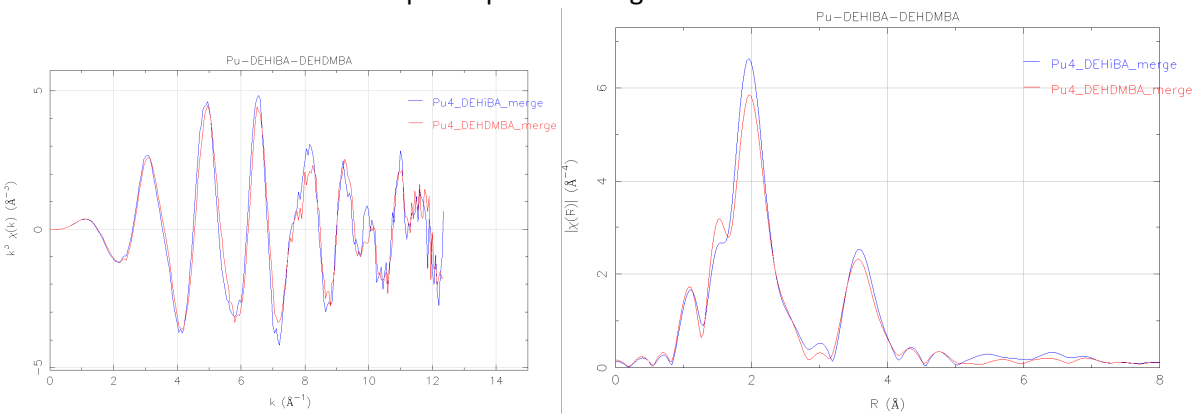


Figure 4: EXAFS spectrum and fourier transform of the two Pu/monoamide complexes.

During this experiment, no clear change was observed in coordination number for plutonium first and second coordination This data will be then fitted with the help of theoretical model provided both by quantum chemistry (DFT) and molecular dynamics simulation to include more precisely the complex coordination mode distribution (An-ligand 1:2 and 1:3 ration?).