

Mixed An(IV)An(III) oxalate compounds with An(IV)=Th, Np, U or Pu and An(III)=Pu or Am: Synthesis and structural characterization.

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*Actinide (IV) – Actinide (III) oxalates*

*Uranium (IV) – Lanthanide (III) mixed site*

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## Abstract

Reaction of a solution containing a tetravalent actinide An(IV), a trivalent actinide An(III) and a single-charged cation such as hydrazinium in presence of oxalic acid in acidic medium under controlled conditions, leads to the precipitation of mixed An(IV)-An(III) oxalate compounds never reported before. By varying the (An<sup>IV</sup>,An<sup>III</sup>) pair and depending on the An<sup>IV</sup>/An<sup>III</sup> ratio, two original series were obtained: (N<sub>2</sub>H<sub>5</sub>,H<sub>3</sub>O)<sub>2+x</sub>An<sup>IV</sup><sub>2-x</sub>An<sup>III</sup><sub>x</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>5.4</sub>H<sub>2</sub>O (**1**) and (N<sub>2</sub>H<sub>5</sub>,H<sub>3</sub>O)<sub>1-x</sub>[An<sup>III</sup><sub>1-x</sub>An<sup>IV</sup><sub>x</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O].4 H<sub>2</sub>O (**2**).

The crystal structures were identified from powder diffraction patterns by analogy to hydrazinium uranium (IV) lanthanide (III) oxalates whose structures were solved recently by single-crystal X-ray diffraction. Complementary investigations by UV-visible and Infra-Red spectroscopies and thermogravimetric analysis confirm the presence of both tetravalent and trivalent states of actinides in structures (**1**) and (**2**) and the role of single-charged cation and water molecules.

The originality of both structures is the existence of a mixed crystallographic site for the tetravalent actinide and the trivalent one, the charge balance being ensured by the adjustment of the single-charged ions within the structure. The main difference is that actinides are ten-coordinated in (**1**) and nine-coordinated in (**2**).

This is the first evidence of a mixed actinide(IV)-actinide(III) site in an oxalate structure.

## 1. Introduction

The oxalic precipitation of plutonium(IV) is used at an industrial scale during the reprocessing of the nuclear fuel by the PUREX process in order to convert this energetically valuable actinide into an oxide form suitable for future use, e.g. as raw material for MOX production. Oxalic acid is also a very common reagent to recover actinides from liquid waste using precipitation methods because of the very low solubility of An(IV) or An(III) oxalate compounds in acidic solutions. Chemical properties of actinide oxalates were often investigated but, surprisingly enough, only few detailed structural determinations are dedicated to these compounds<sup>1</sup>. Previous studies have been devoted to crystallographic structures of simple oxalates of actinide(IV)  $\text{An}^{\text{IV}}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}^{2,3}$  and actinide(III)  $\text{An}^{\text{III}}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}^{3,3}$  (isomorphic with  $\text{Ln}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ ; Ln = La, Ce, Pr, Nd<sup>4,5,6</sup>) and of double  $\text{M}^+ - \text{An}(\text{IV})$  ( $\text{M} = \text{K}^+, \text{H}^+, \text{An} = \text{Th}^7, \text{U}^8, \text{Np}^9$ ) oxalates, but mixed An(IV) - An(III) oxalate structures were never described up to now. Recently we published the crystal structure of new mixed  $\text{M}^+ - \text{U}(\text{IV}) - \text{Ln}(\text{III})^{10,11,12}$  oxalate compounds ( $\text{M}^+ = \text{Na}^+, \text{NH}_4^+, \text{N}_2\text{H}_5^+$ , Ln = Ce, Nd, Sm, Gd) synthesized using a crystal growth method based on a slow diffusion of metallic cations through silica gel impregnated with oxalic acid. Single crystal data acquisition led to elucidate new original mixed structures that belong to three series called triclinic, hexagonal and tetragonal. These three families of mixed U(IV) - Ln(III) oxalates are characterized by an unexpected mixed U(IV) – Ln(III) crystallographic site, where U(IV) and Ln(III) are ten-coordinated in the hexagonal structure and nine-coordinated in the triclinic and tetragonal ones. Monovalent cations equilibrate the charge in these structures depending on the  $\text{Ln}(\text{III})/(\text{U}(\text{IV}) + \text{Ln}(\text{III}))$  molar ratio. The hexagonal and triclinic compounds adopt a honeycomb type structure based on a three dimensional network of metallic and oxalate ions, whereas the tetragonal structure is built from a bidimensional arrangement of squared metal – oxalate cycles.

5f – actinides are known to exhibit similar structural behavior than 4f – lanthanides in many cases. The most obvious analogy is the similar cation size of  $\text{An}^{3+}$  and  $\text{Ln}^{3+}$  in a given coordination number<sup>13</sup>:  $\text{Ce}^{3+}$  and  $\text{Nd}^{3+}$  correspond to  $\text{Pu}^{3+}$  and  $\text{Am}^{3+}$ , respectively. Considering this analogy between  $\text{An}^{3+}$  and  $\text{Ln}^{3+}$  in coordination chemistry, structural data recently published about U(IV) – Ln(III) oxalates, can be used to identify An(IV) – An(III) co-precipitated compounds.

The silica gels method is a convenient method to promote crystal growth of oxalate compounds<sup>14,15</sup> but it exhibits major drawbacks: (i) the chemical composition of resulting crystals cannot be controlled, (ii) only few crystals are synthesized, so full characterization of

the resulting compounds using various and often destructive techniques is not possible, (iii) this method is complex to implement in confined environment such as glove-boxes: alpha self-irradiation may induce damage to the crystals during their slow growth ; isolation and conservation of sub-millimeter single crystals from the silica gel are moreover a particularly uneasy task.

Then, the present work deals with the thorough investigation of the mixed U(IV) – Ln(III) oxalates synthesized by coprecipitation methods and aims at (i) specifying the solid solution domains; (ii) investigating the transfer of metallic cations initially in solution to the co-precipitated solid, with particular attention to their redox behavior ; (iii) clarifying the role of monovalent cations taking part in the charge compensation in the structure. Finally, these co-precipitation experiments were extended to An(IV)-An(III) mixtures (An(IV)=Th, U, Np or Pu and An(III)= Pu or Am) in order to identify and structurally characterize An(IV) – An(III) co-precipitated oxalates.

## 2. Experimental

### 2.1. Reagents

Actinide(IV) and actinide(III) solutions were prepared using specific procedures, either from purified mono-metallic solutions or by dissolving mono-metallic oxides or hydroxides. Hydrazinium nitrate ( $\text{N}_2\text{H}_5^+$ ,  $\text{NO}_3^-$ ) is used as an anti-nitrous agent to stabilize the lowest oxidation states (typically IV for U and Np and III for Pu) and as source of monocharged cations. Control of the concentration, of the purity and of the oxidation state was essentially performed by UV-visible spectroscopy. Lanthanide nitrate salts (Aldrich, 99.9% Reagent Grade  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) were used when appropriate in order to prepare Ln(III) solutions to simulate An(III) solutions in pseudo-active experiments, considering the similarities between Ln(III) and An(III) ions<sup>13,43</sup>.

### 2.2. Oxalate co-precipitation experiments

The oxalate co-precipitates were prepared by mixing a solution of An(IV) and An(III) or Ln(III) (An(IV) = Th, U, Np, Pu, An(III) = Pu, Am and Ln(III) = Nd, Sm) and a concentrated  $\text{H}_2\text{C}_2\text{O}_4$  solution (with a slight excess of oxalic acid) in nitric medium<sup>16</sup>. The selected lanthanides for this work are Nd(III) and Sm(III) which both exhibit UV-visible peaks in the 350 – 900 nm spectral range.

The resulting crystallized powders, whose color depends on the elements involved, were filtered off and dried at room temperature. A series of lanthanide-uranium co-precipitates with

Ln/Ln+U molar ratios equal to 0, 10, 20, 30, 40, 50, 60 and 70% (Ln=Nd, Sm) were prepared. Beyond 70%, the co-precipitated powder is a poly-phase mixture based on the well-known lanthanide oxalate  $\text{Ln}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ <sup>44,55,66</sup>.

For An(IV)-An(III) mixtures, two molar ratios were studied : 10 and 50% in order to investigate the influence of the actinide (IV) and actinide (III) nature and that of the An(III)/(An(IV)+An(III)) molar ratio on the co-precipitate structure.

### 2.3. XRD acquisition

X-ray powder diffraction data for all mixed oxalates were obtained with an INEL CPS 120 diffractometer (curved position sensitive detector) using Cu-K $\alpha$ 1 radiation isolated by a germanium monochromator. Silicon was added to all samples as an internal standard in order to calibrate the angular positions of the observed diffraction lines. Actinides oxalates were mixed with an epoxy resin to prevent contamination spreading and their diffraction patterns were compared with the recently built M<sup>+</sup>-U(IV)-Ln(III) oxalate structures database<sup>1040,1144,12</sup> in order to detect isomorphic similitude. The lattice parameters of the mixed oxalates were refined by pattern matching using the Fullprof software<sup>17</sup>.

### 2.4. UV-Visible spectroscopic analyses

Actinides and lanthanides concentrations in solution were determined by UV-visible spectroscopy using a CINTRA 10e GBC UV spectrophotometer between 350 and 900 nm. Actinides oxidation states in the co-precipitates were investigated in glove-box using a HITACHI U-3000 spectrophotometer equipped with an integration sphere for reflexion measurements.

Hydrazinium cations were quantified by colorimetric analysis: in 1M nitric medium, hydrazinium cation reacts with dimethylamino-4-benzaldehyde to form a yellow complex that presents a peak around 455nm.

### 2.5. Infra-Red spectroscopic analyses

Infrared spectra of all samples were recorded with the NICOLET MAGNA IR 550 series II. A spectral range from 400 to 4000 cm<sup>-1</sup> was typically used.

## 2.6. Thermogravimetric analysis

Thermogravimetric analyses (TGA) were carried out with a NETZSCH STA 409C thermal analysis system with an alumina crucible up to 950°C, under argon flow and with a heating rate of 10°C min<sup>-1</sup>, in order to determine the water content of the freshly synthesized powders.

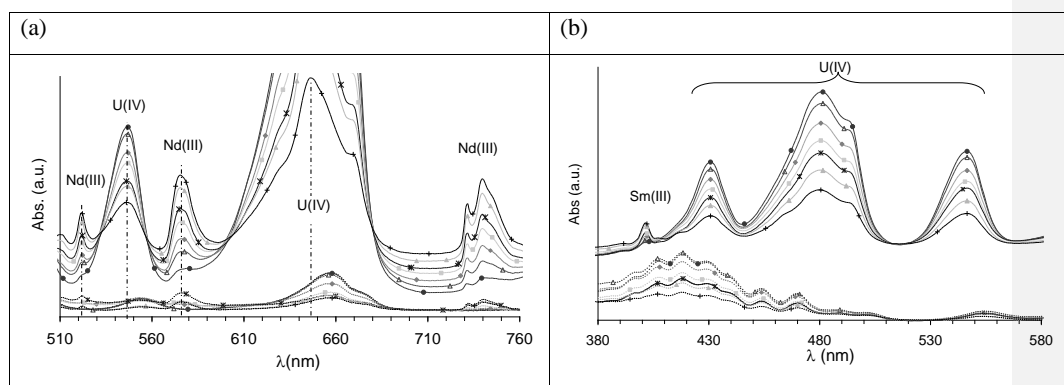
## 3. Results and discussion

The first poly-metallic systems described below are mixed uranium(IV)-lanthanide(III) (Ln = Nd, Sm) oxalates (in these experiments lanthanide(III) simulate actinide(III)), the second ones concern poly-actinides An(IV) – An(III) (An(IV) = Th, U, Np, Pu, An(III) = Pu, Am) oxalates.

### 3.1. Uranium(IV)-Lanthanide(III) system

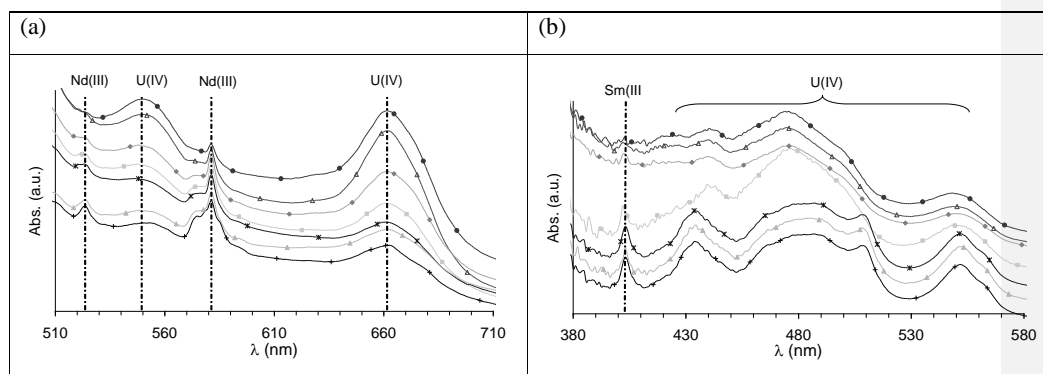
(i) Transfer of the metallic cations to the co-precipitated solid.

Using the oxalate ligand which is known to form very insoluble complex with An(IV,III) and Ln(III) in acidic media, uranium(IV) and lanthanides(III) co-precipitate quantitatively and without modification of neither the U(IV)/Ln(III) ratio nor the oxidation state of U (Figures 1 and 2). Co-precipitation yields are higher than 99% using the experimental method described above.



**Figure 1:** UV-Vis spectra of solution obtained during U(IV) – Ln(III) oxalic co-precipitation tests:  
(a) Ln = Nd; (b) Ln = Sm; ● U<sub>90</sub>Ln<sub>10</sub>; △ U<sub>80</sub>Ln<sub>20</sub>; ◆ U<sub>70</sub>Ln<sub>30</sub>; ■ U<sub>60</sub>Ln<sub>40</sub>; x U<sub>50</sub>Ln<sub>50</sub>; ▲ U<sub>40</sub>Ln<sub>60</sub>; + U<sub>30</sub>Ln<sub>70</sub>.  
Plain line: nitric solution containing U(IV) – Ln(III) mixture with a dilution factor for spectrum acquisition equal to 1:20 ; Dotted line: nitric supernatant after oxalic co-precipitation of metallic cations without any dilution for spectrum acquisition.

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**Figure 2: UV-Vis Spectra of solids obtained during U(IV) – Ln(III) oxalic co-precipitation tests showing the invariability of oxidation state during experiments: (a)  $Ln = Nd$ ; (b)  $Ln = Sm$ ; •  $U_{90}Ln_{10}$ ; △  $U_{80}Ln_{20}$ ; ♦  $U_{70}Ln_{30}$ ; ■  $U_{60}Ln_{40}$ ; x  $U_{50}Ln_{50}$ ; ▲  $U_{40}Ln_{60}$ ; +  $U_{30}Ln_{70}$ .**

#### (ii) Solid solution domains.

The previous works devoted to mixed U(IV) – Ln(III) oxalate structures<sup>10+9,11+,12</sup> indicate that two solid solutions of formula  $M_{2+x}U^{IV}_{2-x}Ln^{III}_x(C_2O_4)_5 \cdot nH_2O$  (hexagonal series) and  $M_{1-y}U^{IV}_yLn^{III}_{1-y}(C_2O_4)_2 \cdot nH_2O$  (triclinic and quadratic series) ( $M$  = monocharged cation) can be expected. The determination of the solid solution domains for the different U(IV) – Ln(III) systems requires a thorough investigation of the co-precipitate structure according to the  $Ln/(U+Ln)$  molar ratio. The Figure 3 shows the X-ray diffraction patterns of U(IV) - Ln(III) co-precipitates which were identified by comparison with the theoretical X-ray diffraction patterns of the recently built  $M^+-U(IV)-Ln(III)$  oxalate database<sup>10+9,11+,12</sup> in order to detect isomorphic similitudes.

From 0 to 50% of neodymium substitution rate, the precipitate is a single-phase oxalate (solid solution) isomorphic to the ammonium uranium(IV) oxalate  $(NH_4)_2U_2(C_2O_4)_5 \cdot 0.7H_2O$ , previously described<sup>10+9</sup> and which adopts a hexagonal structure (Figure 3-a). This single-phase oxalate is characterized by a three-dimensional arrangement of U-centered polyhedra linked through bis-bidentate oxalate groups. The U(IV) atom is ten-fold coordinated by oxygen atoms from five bidentate oxalate groups, but astonishingly U(IV) can be partially substituted by Nd(III) in the same crystallographic site, the deficit of charge being compensated by additional monovalent ions. This partial substitution  $U(IV) \rightarrow Nd(III) + M^+$  do not modify the crystallographic structure of the co-precipitated compound. It can occur because the ionic radii of U(IV) and Nd(III) are close, 1.05 and 1.163 Å respectively

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(Coordination Number = IX<sup>18</sup>) and because both ions can exhibit the same type of coordination sphere, for instance, 10 oxygen atoms from five bidentate oxalate ligands. Beyond 50% of substitution, precipitates are composed by a mixture of hexagonal mixed oxalate and neodymium(III) oxalate Nd<sup>III</sup><sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O. The linear evolution of the unit cell parameters with the Nd/(U+Nd) ratio confirms the existence of a hexagonal solid solution of general formula M<sub>2+x</sub>U<sup>IV</sup><sub>2-x</sub>Ln<sup>III</sup><sub>x</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>5</sub>·nH<sub>2</sub>O which is stable within a large domain of composition (0 ≤ Nd/(U+Nd) ≤ 50%, Figure 4) and also magnificantly illustrates the presence within the structure of a mixed U(IV)-Nd(III) crystallographic site.

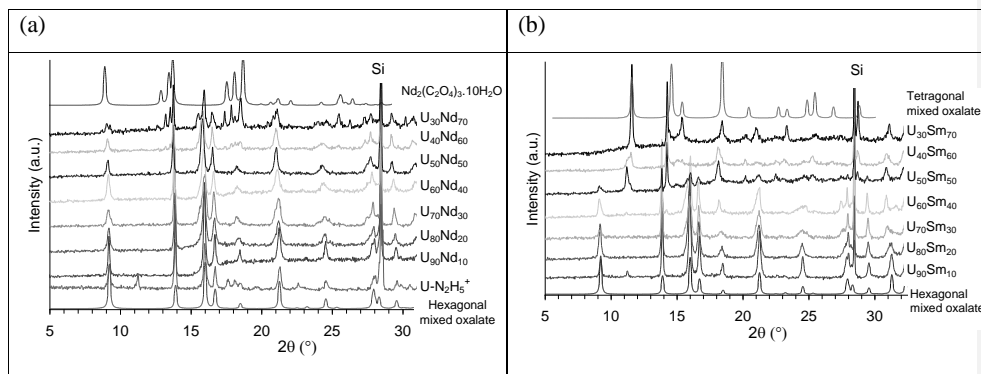


Figure 3: X-ray diffraction patterns of U(IV) – Ln(III) oxalic co-precipitates : (a)  $Ln = Nd$  ; (b)  $Ln = Sm$ .

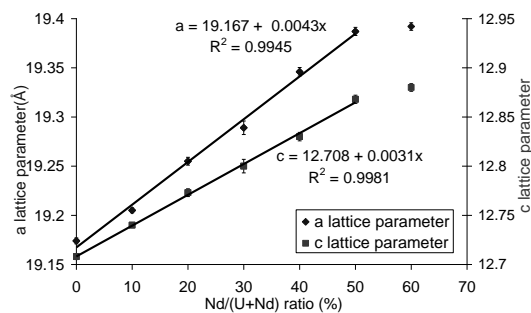


Figure 4: Determination of the Vegard's Law for U(IV) – Nd(III) hexagonal solid solution confirming the existence of a large solid solution domain.



Concerning the U(IV) – Sm(III) system (Figure 3-b), the identification of the X-ray diffraction patterns of oxalate co-precipitates thanks to the structural data base is more complex: from 0 to 10% of substitution, precipitate is a mixture of uranium(IV) oxalate  $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  and U(IV) – Sm(III) hexagonal mixed oxalate, for  $10 < \text{Sm}/(\text{U}+\text{Sm}) \leq 30\%$ , there is a hexagonal single-phase compound, for  $30 < \text{Sm}/(\text{U}+\text{Sm}) \leq 50\%$ , resulting powders correspond to a mixture of hexagonal and tetragonal mixed oxalate phases. This tetragonal mixed oxalate is built from a bi-dimensional arrangement of metal – oxalate squared cycles. In this structure, U(IV) and Sm(III) occupy the same crystallographic site and this mixed site is nine-fold coordinated by oxygen atoms from four bidentate oxalate ligands and one water molecule. For  $50 < \text{Sm}/(\text{U}+\text{Sm}) \leq 70\%$ , precipitates are tetragonal single-phase oxalates and finally beyond 70%, there is a mixture of samarium(III) oxalate and U(IV) – Sm(III) tetragonal mixed oxalate.

The comparison of these structural results with those obtained previously for the U(IV) – Nd(III) system, highlights the evolution of the solid solution domains along the lanthanide series.

The lattice parameters refinement of the U(IV)-Sm(III) mixed oxalate was more complex because few Sm/(U+Sm) ratios lead to single-phase precipitate. However, for Sm/(U+Sm) = 20, 30 and 60%, the lattice parameters were refined by pattern matching (Table 1). The decrease of the lattice parameters of the hexagonal U(IV)-Ln(III) mixed oxalate (Ln=Nd or Sm) from Nd(III) substituted compounds to Sm(III) ones is in agreement with the decrease of the ionic radii along the lanthanide series ( $r_{\text{Nd(III)}} = 1.163 \text{ \AA}$  and  $r_{\text{Sm(III)}} = 1.132 \text{ \AA}$  in nine-coordination<sup>18</sup>)

**Table 1 : Lattice parameters of mixed U(IV) – Sm(III) oxalates.**

Sm/(U+Sm) (%)	Structure	a (Å)	c (Å)
0	Hexagonal	19.174(3)	12.707(3)
20	Hexagonal	19.217(6)	12.747(5)
30	Hexagonal	19.245(6)	12.761(5)
60	Tetragonal	8.798(3)	7.874(4)

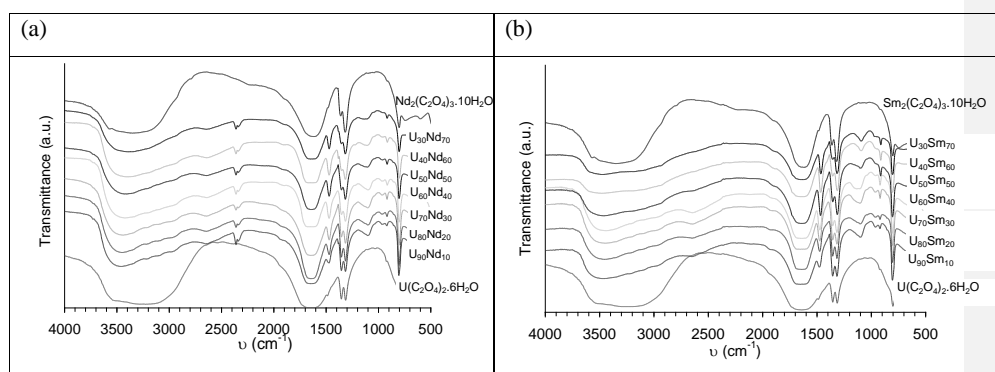
(iii) Identification of monovalent cations.

The Infrared spectra of U(IV)–Ln(III) co-precipitates presented on Figure 5 are characteristic of oxalate compounds. Infrared bands at 1650, 1485, 1360, 1320 and 805  $\text{cm}^{-1}$  are characteristic of a tetradentate oxalate ligand<sup>19,20</sup>. However, the comparison of these IR spectra with those of lanthanide oxalate  $\text{Ln}^{\text{III}}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  and uranium oxalate

$\text{U}^{\text{IV}}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  indicates the presence of two additional bands located at 960 and 930  $\text{cm}^{-1}$  which could be assigned to the N-N stretching vibrations of the hydrazinium cation  $\text{N}_2\text{H}_5^{+20,21}$ . The large absorption band between 3000 and 3600  $\text{cm}^{-1}$  has been attributed to  $\nu_{\text{O-H}}$  of water molecule.

Consequently, the charge compensation in the structure is partially ensured by hydrazinium cations  $\text{N}_2\text{H}_5^+$  located inside the cavities of the crystal network.

Chemical composition analysis (spectrophotometric titration of  $\text{N}_2\text{H}_5^+$  cations) together with TGA to determine the water content for each composition led to formula  $(\text{N}_2\text{H}_5)(\text{H}_3\text{O})_{1+x}\text{U}^{\text{IV}}_{2-x}\text{Ln}^{\text{III}}_x(\text{C}_2\text{O}_4)_5 \sim 4\text{H}_2\text{O}$  for the hexagonal mixed U(IV) – Ln(III) oxalates and to formula  $(\text{N}_2\text{H}_5, \text{H}_3\text{O})_{1-y}\text{U}^{\text{IV}}_y\text{Ln}^{\text{III}}_{1-y}(\text{C}_2\text{O}_4)_2 \sim 4\text{H}_2\text{O}$  for the tetragonal one. For the hexagonal mixed oxalate compounds, considering the substitution scheme  $\text{U(IV)} \rightarrow \text{Ln(III)} + \text{M}^+$ , the charge balance is ensured by  $\text{H}_3\text{O}^+$  cations starting from the  $\text{U}_2(\text{H}_3\text{O}^+)(\text{N}_2\text{H}_5^+)(\text{C}_2\text{O}_4)_5 \sim 4\text{H}_2\text{O}$  oxalate compound. For the tetragonal system complementary investigations are needed to clarify the role of  $\text{H}_3\text{O}^+$  and  $\text{N}_2\text{H}_5^+$  in the charge balance.



**Figure 5 : Infrared Spectra of U(IV) – Ln(III) oxalic co-precipitates : (a)  $\text{Ln} = \text{Nd}$  ; (b)  $\text{Ln} = \text{Sm}$ .**

### 3.2. Actinide(IV)-Actinide(III) system

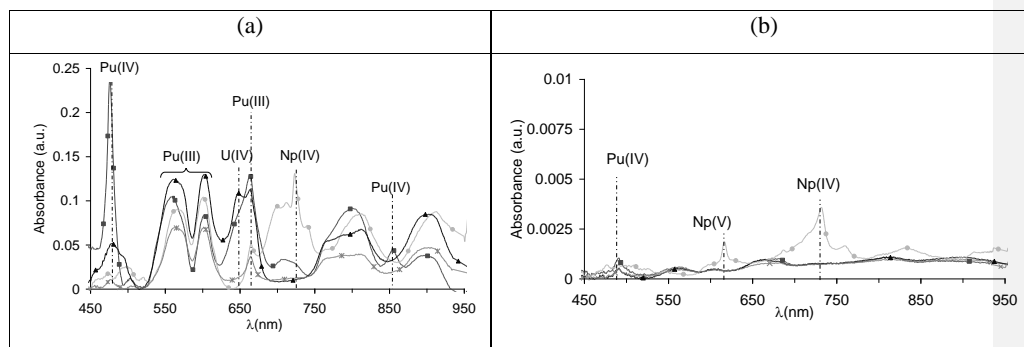
(i) Transfer of the metallic cations to the co-precipitated solid.

Investigations by UV-Visible spectroscopy confirm the simultaneous oxalic co-precipitation of all the An(IV) and An(III) involved ( $\text{An(IV)} = \text{Th, U, Np or Pu}$  and  $\text{An(III)} = \text{Pu or Am}$ ) without modification of neither the  $\text{An(IV)}/(\text{An(III)}+\text{An(IV)})$  ratio nor the oxidation state (Figures 6 and 7). The UV-Visible spectra of the different precipitated solids confirm the

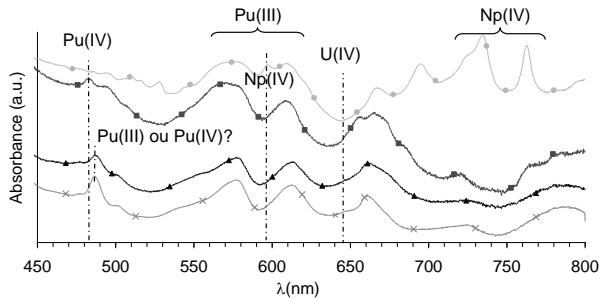
stabilization of a mixture of actinide(III) and (IV) within the same compound. This result is undoubtedly original and more interesting for the Pu(IV)-Pu(III) mixed oxalate in which the two oxidation states of plutonium are stabilized within the same solid phase.

Except for the Np(IV)-Pu(III) experiment, actinides concentrations in the nitric supernatant after oxalic co-precipitation are very weak (10-30 mg/L). Under controlled conditions, these concentrations are comparable even lower than the values published for the different  $An^{IV}(C_2O_4)_2 \cdot 6H_2O$ <sup>22</sup> and  $An^{III}_2(C_2O_4)_3 \cdot 10H_2O$  oxalates. Thus, for Th(IV)-Pu(III), U(IV)-Pu(III), Pu(IV)-Pu(III) (Figure 6) and U(IV) – Am(III) pairs, oxalic co-precipitation yields are higher than 99%.

Concerning the Np(IV)-Pu(III) system, even if the co-precipitation yield remains very high ( $\approx 92\%$ ), the neptunium(IV) concentration (90 – 100 mg/L) in the nitric supernatant is significant and curiously higher than the solubility of  $Np^{IV}(C_2O_4)_2 \cdot 6H_2O$  oxalate<sup>23</sup>. In fact, this result can be explained by the presence of Np(V) ( $\approx 5\%$ ) in the Np(IV) solution. Np(V) is totally found in the oxalic supernatant, where it reacts slowly with Pu(III) traces according to the redox reaction :  $Pu^{3+} + NpO_2^+ + 4H^+ \rightarrow Pu^{4+} + Np^{4+} + 2H_2O$ . The Pu(IV) produced by this reaction is subsequently reduced in Pu(III) by hydrazinium nitrate contained in the medium, leading to the reduction of the majority of the Np(V) initially present.



**Figure 6: UV-Vis spectra of solutions obtained during  $An(IV)$  –  $Pu(III)$  oxalic co-precipitation experiments: (a) nitric solution containing  $An(IV)$  –  $Pu(III)$  mixture with a dilution factor for spectrum acquisition equal to 1:20; (b) nitric supernatant after oxalic co-precipitation of metallic cations without any dilution for spectrum acquisition: •  $Np(IV)_{50}Pu(III)_{50}$ ; ■  $Pu(IV)_{50}Pu(III)_{50}$ ; ▲  $U(IV)_{50}Pu(III)_{50}$ ; x  $Th(IV)_{50}Pu(III)_{50}$ .**



**Figure 7: UV-Vis Spectra of solids obtained during An(IV) – Pu(III) oxalic co-precipitation tests showing the invariability of oxidation state during experiments : ● Np(IV)<sub>50</sub>Pu(III)<sub>50</sub>; ■ Pu(IV)<sub>50</sub>Pu(III)<sub>50</sub>; ▲ U(IV)<sub>50</sub>Pu(III)<sub>50</sub>; x Th(IV)<sub>50</sub>Pu(III)<sub>50</sub>.**

(ii) Solid solution domains.

The new mixed An(IV)-An(III) (An(IV)=Th, U, Np or Pu and An(III)=Pu or Am) single-phase co-precipitates obtained by oxalic co-conversion, were characterized from powder diffraction patterns by analogy to uranium(IV)-lanthanide(III) oxalates whose structures were recently solved from single-crystal X-ray diffraction data<sup>10,11,12</sup>. By varying the (An<sup>IV</sup>,An<sup>III</sup>) pair and depending on the An<sup>IV</sup>/An<sup>III</sup> ratio, two original series were identified, M<sub>2+x</sub>An<sup>IV</sup><sub>2-x</sub>An<sup>III</sup><sub>x</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>5</sub>nH<sub>2</sub>O (**1**) and M<sub>1-x</sub>[An<sup>III</sup><sub>1-x</sub>An<sup>IV</sup><sub>x</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O]<sub>n</sub>H<sub>2</sub>O (**2**) (M = single charged cation), with hexagonal or tetragonal symmetry, respectively. Thus, considering the An(IV) – Pu(III) pairs (An(IV)= Th, U, Np, Pu) and a Pu(III)/(An(IV)+Pu(III)) ratio close to 50%, an evolution of the structure of the precipitate is observed along the actinides series (Figure 8). For An(IV)=Th or U, the precipitate is characterized by the hexagonal structure whereas for An(IV) = Np or Pu, the solid compound crystallizes mainly in the tetragonal system.

At the same time, the influence of the An(III) nature (An(III)=Pu or Am) on An(III)-U(IV) precipitates structure was investigated. For a ratio An(III)/(U(IV)+An(III)) (An(III) = Am or Pu) close to 10%, whatever the actinide(III) considered, the mixed An(III)-U(IV) oxalate adopts an hexagonal structure.

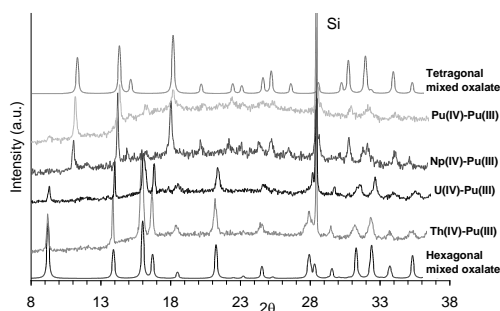
The sample preparation and the partial radiolysis induced by some isotopes were responsible for the low signal-background ratio which makes the lattice parameters refinement difficult. However, the unit cell parameters of An(IV) – An(III) mixed oxalate compounds were quite accurately refined by pattern matching using the Fullprof software<sup>1747</sup>. Only the lattice parameters of the U(IV)<sub>90</sub>-Pu(III)<sub>10</sub> compound was not refined because of the weak crystallinity of the sample: the comparison with the theoretical X-ray pattern of the hexagonal structure indicates on the same that the precipitate corresponds to a hexagonal mixed oxalate.

The decrease of the lattice parameters from Th(IV) to U(IV) for the hexagonal structure and from Np(IV) to Pu(IV) for the tetragonal one is in agreement with the decrease of the ionic radii along the actinides series<sup>1848</sup> (Table 2).

The An(IV) – An(III) crystallographic mixed site is responsible for the homogeneous distribution of actinides (solid solution) in the precipitates which are thus relevant mixed oxide precursors.

**Table 2 : Lattice parameters of An(IV) – An(III) mixed oxalate compounds**

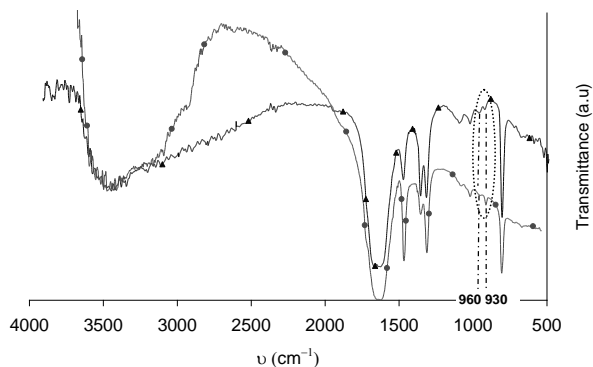
System	Structure	a (Å)	c (Å)
Th <sub>50</sub> (IV)-Pu <sub>50</sub> (III)	Hexagonal	19.176(4)	12.735(5)
U <sub>50</sub> (IV)-Pu <sub>50</sub> (III)	Hexagonal	19.115(7)	12.664(5)
Np <sub>50</sub> (IV)-Pu <sub>50</sub> (III)	Tetragonal	8.792(2)	8.018(3)
Pu <sub>50</sub> (IV)-Pu <sub>50</sub> (III)	Tetragonal	8.813(7)	7.97(1)
U <sub>90</sub> (IV)-Am <sub>10</sub> (III)	Hexagonal	19.203(8)	12.74(1)



**Figure 8: X-ray diffraction patterns of An(IV) – Pu(III) oxalic co-precipitates (An(IV) = Th, U, Np, Pu)**

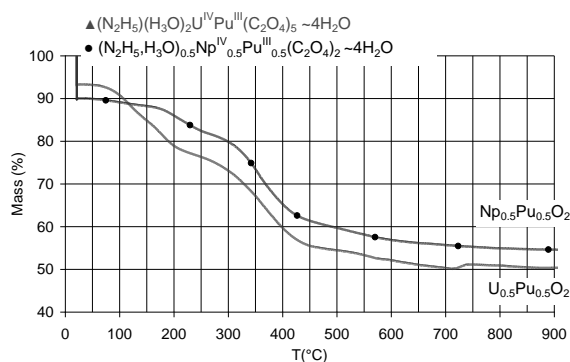
(iii) Identification of monovalent cations.

As in the previous case of mixed U(IV)-Ln(III) oxalates, infrared spectra of An(IV) – An(III) co-precipitates are characteristic of oxalate compounds. Moreover, the presence of the two additional bands at 960 and 930 cm<sup>-1</sup> assigned to N-N stretching vibrations confirms the presence of hydrazinium cations within the structure (Figure 9).



**Figure 9 : Infrared Spectra of An(IV) – An(III) oxalic co-precipitates : ▲ An(IV)-An(III) hexagonal mixed oxalate; ● An(IV)-An(III) tetragonal mixed oxalate.**

Results of hydrazinium cation titrations in mixed An(IV)-An(III) oxalates are in agreement with those obtained for U(IV)-Ln(III) compounds. In the hexagonal structure, the hydrazinium cation content is quasi constant and independent of the An(III)/(An(IV)+An(III)) ratio and the charge balance is ensured by  $\text{H}_3\text{O}^+$  cations whereas in the tetragonal compound, it seems that both cations,  $\text{H}_3\text{O}^+$  and  $\text{N}_2\text{H}_5^+$ , take part in the electroneutrality of the structure. Thermogravimetric experiments were carried out on the different mixed An(IV)-An(III) compounds and led to the determination of the water molecule content for each precipitate and consequently for each type of oxalate series (hexagonal or tetragonal).



**Figure 10: TG plot starting from a An(IV)-An(III) mixed oxalates under Ar.**

#### 4. Conclusion

These thorough investigations of the mixed U(IV) – Ln(III) oxalates synthesized by a co-precipitating method complete the structural data recently acquired on these compounds from single crystals obtained by the gel growth method. This work confirms the existence of two types of U(IV)-Ln(III) oxalate solid solutions (one adopting a hexagonal structure and the other a tetragonal one) and also illustrates the presence within the structure of an original mixed U(IV)-Ln(III) crystallographic site.

The extension of this structural study to actinides systems, leads to the preparation and characterization of homeotype single-phase mixed An(IV) – An(III) oxalates. A range of mixed-valent uranium compounds<sup>24,25,26,27,28</sup> have previously been reported with different inorganic and/or organic ligands and different pairs of oxidation states (IV-V; IV-VI or V-VI). In most of these mixed-valent compounds, the environment of uranium atoms depends on the oxidation state. Hexavalent uranium, for instance, adopts a specific environment: it is always axially bonded to two oxygen atoms forming a uranyl unit with an O=U=O bond angle close to 180°. On the contrary, in the oxalates described in this paper, the tetravalent actinide and the trivalent one can adopt the same type of coordination sphere (nine or ten oxygen atoms from bidentate oxalate ligands and/or water molecules) and then can be disordered on the same crystallographic site. Thus, original oxalate solid solutions formulated  $(\text{N}_2\text{H}_5\text{H}_3\text{O})_{2+x}\text{An}^{\text{IV}}_{2-x}\text{An}^{\text{III}}_x(\text{C}_2\text{O}_4)_5 \cdot 4\text{H}_2\text{O}$  and  $(\text{N}_2\text{H}_5\text{H}_3\text{O})_{1-x}[\text{An}^{\text{III}}_{1-x}\text{An}^{\text{IV}}_x(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}$  are obtained. Finally, other types of An(IV)-An(III) mixtures and other  $\text{An}^{\text{III}}/(\text{An}^{\text{IV}}+\text{An}^{\text{III}})$  ratios are being investigated in order to determine precisely the solid solution domains for each An(IV) –An(III) pairs.

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