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Quantitative precipitation of uranyl or plutonyl nitrate with N-(1-adamantyl)acetamide in nitric acid aqueous solution

Gaël Loubert,^a Natacha Henry,^a Christophe Volkringer,^{a,b} Sylvain Duval,^a Christelle Tamain,^c Bénédicte Arab-Chapelet,^c Thibaud Delahaye,^c Thierry Loiseau^a

Contribution from

^a*Unité de Catalyse et Chimie du Solide (UCCS) – UMR CNRS 8181, Université de Lille, Centrale Lille, Université d'Artois, F-59000 Lille, France.*

^b*Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05.*

^c*CEA, DES, ISEC, DMRC, Université de Montpellier, Marcoule, France.*

* To whom correspondence should be addressed. E-mail: thierry.loiseau@univ-lille.fr, Phone: (33) 3 20 43 41 22, Fax: (33) 3 20 43 48 95.

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Table of Content (TOC) Graphic

Table of Content (TOC) Synopsis

The N-(1-adamanty)acetamide (L) ligand is used for recovering uranyl/plutonyl species from aqueous concentrated nitric acid solution, under the form of the crystalline complex $(\text{AnO}_2)(\text{L})_2(\text{NO}_3)_2 \cdot 2(\text{L})$, with high yield (up to 99%_{An}).

ABSTRACT: The reactivity of the N-(1-adamantyl)acetamide ligand ($L = adam$) has been evaluated as precipitating agent for the hexavalent uranyl cation ($[U] = 20\text{-}60\text{ g.L}^{-1}$) in concentrated nitric acid aqueous solution ($0.5\text{-}5\text{ M}$). It results in the formation of a crystalline complex $(UO_2)(adam)_2(NO_3)_2 \cdot 2(adam)$ (**1**), in which the uranyl center is eight-fold coordinated to two chelating nitrate groups and two N-(1-adamantyl)acetamide ($= adam$) ligands through the oxygen atom of the amide function. Two other non-coordinating *adam* moieties are also observed in the crystal structure packing and interact through a hydrogen bond scheme with the uranyl-centered species. A similar molecular assembly has been obtained with the plutonyl(VI) cation, in the complex $(PuO_2)(adam)_2(NO_3)_2 \cdot 2(adam)$ (**2**). Precipitation studies indicate high $(UO_2)(adam)_2(NO_3)_2 \cdot 2(adam)$ formation yields (up to 99 %_U for L/U molecular ratio of 5/1) for HNO_3 concentration in the $0.5\text{-}5\text{ M}$ range. However, the precipitation kinetics is rather slow and the reaction is completed after several hours (3-4 h). The calcination of the resulting solid under air atmosphere led to the formation of the U_3O_8 oxide from $400\text{ }^\circ\text{C}$, through a transient phase UO_2 fluorite-type (from $200\text{ }^\circ\text{C}$).

Keywords: uranyl(VI), plutonyl(VI), N-(1-adamantyl)acetamide, precipitation study, coordination complex, single-crystal X-Ray diffraction, thermal analysis.

Introduction

The research of organic molecules for the actinides conversion into a solid form from the aqueous solution resulting from the dissolution of the spent nuclear fuel in nitric acid has been intensively investigated during the last decades. One of the current industrial process, PUREX^{1,2}, is based on the utilization of oxalate anion as a non-selective precipitating agent of actinides(III and IV). This process requires a redox adjustment before the conversion and leads to the quantitative precipitation of trivalent and/or tetravalent actinides into solid actinide oxalates used as oxide precursors (precipitation yield > 99%) but is not efficient for hexavalent uranium precipitation.³⁻⁵ Alternative reprocessing routes have been studied and based on a precipitation without redox of uranyl by new organic molecules, which chemically interact specifically with the targeted actinides. In this context, a family containing pyrrolidone derivatives has been explored for their properties as precipitating agent toward the uranyl species. Indeed, in 2000, Ikeda and co-workers⁶ described the selective

precipitation of UO_2^{2+} cation with a yield of 68 %_U by the N-cyclohexyl-2-pyrrolidone (NCP) molecule⁷ in concentrated nitric acid solutions, and opened a new investigation path for the research of novel precipitating agents with actinides. This NCP molecule has been found to be one of the most efficient ligands for the precipitation of uranyl solution and could be considered in a new process for recovering the actinides from spent nuclear fuel.⁸ The combination of a γ -butyrolactam group, with a cyclohexyl chain, is likely a good compromise that allows a good solubility of the free ligand in water and a relatively high hydrophobicity once the amide group is coordinated to metallic cations. The nature of the functionalization of the γ -butyrolactam has been examined in order to optimize the uranyl cation precipitation in concentrated nitric acid aqueous solution. These investigations gave rise to many reports of the structural characterizations of several pyrrolidone-based nitrate complexes with uranyl(VI).^{7,9,10} The reactivity of plutonyl(VI) cations has been also studied in order to analyze the formation of such pyrrolidone molecular assemblies, which may co-crystallize with the analogous uranyl(VI) element.^{11,12}

The family of the alkylamides, to which pyrrolidone belongs, has also shown a potential interest as a specific extractant of the cationic uranyl (UO_2^{2+}) and plutonium (Pu^{4+}) species for the separation of actinides from fission products.^{13,14} In this context, many investigations reported the formation of monoamide uranyl ($\text{UO}_2(\text{NO}_3)_2\text{L}_2$) complexes or diamides ($\text{UO}_2(\text{NO}_3)_2\text{L}$) complexes, in which the organic molecules L act as monodentate or polydentate ligands toward the actinide metallic center.^{15–36} The modification of the alkyl group (length and branching of the carbon chain) of the amide as well as functionalization offers the possibility to tune their extracting abilities.

In the present study, we studied another relative of monoamide to be considered in conversion processes. We report the efficient precipitation of uranyl cation in nitric acid aqueous solution by an acetamide-based molecule bearing an adamantyl group called N-(1-adamantyl)acetamide. With a cyclohexyl fragment completed by two other connected cyclohexane groups in an “armchair” configuration, the nitrogen atom is still functionalized by a non polar aliphatic cycle, as for the NCP. To counter balance the increase of the molecule hydrophobicity, the butyrolactam is removed (Figure 1).

Figure 1: Schematic representation of the studied monoamide N-(1-adamantyl)acetamide (left) and N-cyclohexyl-2-pyrrolidone (right). The common carbon backbone of the two ligand types is indicated in red.

This work deals with the precipitation of uranyl(VI) cation with the N-(1-adamantyl)acetamide molecule (N-(1-adamantyl)acetamide = *adam*) in nitric acid aqueous solution. The ability of this ligand to precipitate the uranyl cation has been studied by investigating different parameters, such as molar ligand/U ratio, uranium and nitric acid concentrations and reaction time. The structure and speciation of the solid were also investigated from the synthesis and crystal structure characterization of the coordination complex of the actinyl nitrate N-(1-adamantyl)acetamide, $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$. Its analogous single-crystal structure has been investigated with plutonyl(VI) cation (compound **(2)**). Finally, the precipitating routes has been considered to recover actinides from aqueous solutions in order to elaborate actinide oxides. The thermal treatment into uranium oxide of the resulting crystalline precipitate $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**(1)**) was studied by thermogravimetric method and X-ray thermodiffraction techniques.

Experimental Section

Reagents. Caution! Uranium and plutonium precursors are radioactive and chemically toxic reactants, so precautions with suitable care and protection for handling such substances have been followed. The manipulation of plutonium reactant has been carried out at the ATALANTE facility (CEA-Marcoule, France). Because of the highly radioactive nature of plutonium, the experiments involving this element were carried out in glove box with very

restrictive protocols. Initially, Pu(IV) nitrate solution (^{239}Pu) was prepared by dissolving the corresponding oxide, PuO_2 , in a nitrofluorhydric solution (HNO_3 10 M-HF 0.05 M) followed by a purification step on a DOWEX resin. Then, the resulting Pu(IV) nitrate solution was oxidized to Pu(VI) nitrate solution by addition of silver oxide AgO (molar ratio Ag/Pu = 2/1). The reduced form of Ag^+ ion was eliminated by precipitation with one equivalent of hydrochloric acid to form AgCl. The resulting plutonyl(VI) nitrate aqueous solution was filtrated under vacuum and characterized by UV-Vis spectroscopy in order to determine the final plutonium concentration.

The other following reactants were used: uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck, 99 %), N-(1-adamantyl)acetamide ($\text{C}_{12}\text{H}_{19}\text{NO}$, noted *adam*, Alfa Aesar, 98 %), nitric acid (HNO_3 , 68 %, VWR) and deionized water. The chemical reactants were commercially available and were used without any further purification.

Compounds 1 & 2 syntheses

(UO_2)(*adam*) $_2$ (NO_3) $_2 \cdot 2$ (*adam*) (1): A mixture of 200 mg (0.4 mmol) $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 75 mg (0.4 mmol) N-(1-adamantyl)acetamide and 10 mL aqueous HNO_3 (0.5 M) was placed in a glass tube and then heated at 50°C for 24 hours. The resulting yellow crystalline powder was then filtered off, washed with water and dried at room temperature in air atmosphere. Yield reaction was 24.4 % $_{\text{U}}$ from these synthetic conditions (here, initial Ligand/U ratio of 1/1). **1** was analyzed by scanning electron microscope showing well-shaped multi-faceted bulky crystals of 10-150 μm size (Figure S1a).

(PuO_2)(*adam*) $_2$ (NO_3) $_2 \cdot 2$ (*adam*) (2): A mixture of 162 mg (0.84 mmol) N-(1-adamantyl)acetamide and 5mL plutonyl(VI) nitrate aqueous solution ($[\text{Pu}] = 0.084 \text{ M}$; $[\text{HNO}_3] = 1 \text{ M}$) was placed in a glass tube and then left at room temperature for 16 hours. Yield reaction was 49 % $_{\text{Pu}}$. **2** was analyzed by scanning electron microscope showing well-shaped multi-faceted bulky crystals of 5-50 μm size (Figure S1b). Due to the highly plutonium radiotoxicity, limited characterizations have been carried out with this element: they included single-crystal X-ray diffraction, powder X-ray diffraction (Figure S2b) and one batch of precipitation (from $[\text{Pu}] = 20\text{g.L}^{-1}$) analyses.

Single-crystal X-ray diffraction

Crystal of compound **1** was selected under polarizing optical microscope and glued on a glass fiber for a single-crystal X-ray diffraction experiment. X-ray intensity data were collected on

a Bruker DUO-APEX2 CCD area-detector diffractometer using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) with an optical fiber as collimator. Several sets of narrow data frames (20 s per frame) were collected with ω scans. A crystal of **2** was mounted on MicroMount patented by MiTeGen, inserted into a goniometer base. For confinement purpose, a MicroRT capillary was then drawn over the sample and onto the base, where it was sealed by adhesive. The single-crystal XRD intensities were measured on a Nonius four-circle diffractometer equipped with an Apex II detector. The instrument was equipped with a fine-focus Mo-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 1500 W. Data reduction was accomplished using SAINT V7.53a.³⁷ The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2.10³⁸) to be applied, on the basis of multiple measurements of equivalent reflections. The structure of **1** was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all data using SHELX program suites,³⁹ implemented in the OLEX2⁴⁰ interface. Crystals of compound **2** were systematically twinned (merohedral twinning) and were treated by means of the JANA2006 software suite.⁴¹ For this compound **2**, the orientation matrix for the two domains was 1 0 0; -0.1172 -1 0; -0.47 0 -1, with 49.6(7) % of domain I, and consequently 50.4(7) % of domain II.

The crystal data are given in Table 1. Supporting information is available in CIF format. CCDC numbers: 1987462 for **1**, 1987465 for **2**, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for compounds **1** & **2**.

	1	2
Formula	C ₄₈ H ₇₆ N ₆ O ₁₂ U	C ₄₈ H ₇₆ N ₆ O ₁₂ Pu
Formula weight	1167.17	1173.2
Temperature/K	296	293
Crystal type	yellow block	yellow block
Crystal size/mm	0.25 x 0.20 x 0.16	0.06 x 0.05 x 0.04
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	10.1363(3)	10.0759(3)
<i>b</i> /Å	11.5945(3)	11.5308(3)
<i>c</i> /Å	12.8737(4)	12.5976(4)
α /°	65.038(1)	65.646(1)
β /°	70.866(1)	71.250(1)
γ /°	79.406(1)	79.151(1)
Volume/Å ³	1294.05(7)	1259.99(6)

$Z, \rho_{\text{calculated}}/\text{g}\cdot\text{cm}^{-3}$	1, 1.498	1, 1.546
μ/mm^{-1}	3.200	1.374
θ range/ $^{\circ}$	1.82 - 30.50	1.84 - 29.87
Limiting indices	$-14 \leq h \leq 14$ $-16 \leq k \leq 16$ $-18 \leq l \leq 18$	$-14 \leq h \leq 13$ $-16 \leq k \leq 16$ $-16 \leq l \leq 17$
Collected reflections	34849	17665
Unique reflections	7895 [R(int) = 0.0408]	10679 [R(int) = 0.0464]
Parameters	306	305
Goodness-of-fit on F^2	1.063	1.20
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0225 wR2 = 0.0549	R1 = 0.0387 wR2 = 0.0369
R indices (all data)	R1 = 0.0228 wR2 = 0.0550	R1 = 0.0455 wR2 = 0.0381
Largest diff. peak and hole/ $\text{e}\cdot\text{\AA}^{-3}$	1.151 and -0.419	1.15 and -1.43

ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy).

The supernatant aqueous solutions after reaction of the uranyl nitrate precursor with the organic *adam* ligand have been analyzed by using a Vista-PRO VARIAN spectrometer. A fraction of the supernatant solution (10 μL) was extracted, then diluted 1000 times with deionized water. The remaining uranium concentration was then directly analyzed with the ICP-AES technique. The ICP measurement was accumulated routinely three times and then merged. The uranium contents are given with uncertainties of 5%.

Powder XRD

X-ray powder diffraction was performed on Bruker D8 Advance diffractometer (LynxEye detector) in a Bragg-Brentano θ - θ mode using $\text{Cu-K}\alpha$ radiation. Each powder pattern was recorded within an angular range of 5 - 50° in 2θ , with steps of 0.02° and counting time of 0.5 s per step.

Scanning electron microscopy

The SEM analyses of uranium compound were performed on a Hitachi-S3400N microscope, equipped with a tungsten filament (acceleration voltage = 15 kV, secondary electron mode, working distance = 5 to 10 mm). Plutonium compound was studied on a Zeiss Supra 55/55VP field-emission scanning electron microscope (acceleration voltage = 5 kV, secondary electron

mode, working distance 5 to 10 mm, diaphragm= 30 μm). Both with uranium and plutonium based samples, powders were coated with gold prior to the analysis.

Specific surface area measurement

The specific surface area was measured at 77 K by the BET method with a MICROMERITICS ASAP 2020 (surface area and porosity analyzer). About 100 mg of sample has been used and degassed at 200°C under vacuum. For surface area calculations, we used krypton gas adsorption and BET model was applied in the p/p_0 range of 0.01-0.2.

Thermal analysis

Thermogravimetric analysis was performed on a thermoanalyzer 92 SETARAM TGA up to 800 °C, in air, with a heating rate of 5 °C.min⁻¹.

X-ray thermodiffractometry was performed under 5 l.h⁻¹ air flow in an Anton Paar HTK1200N of a D8 Advance Bruker diffractometer (θ - θ mode, CuK α radiation) equipped with a Vantec1 linear position sensitive detector (PSD). Each powder pattern was recorded in the range 5-60° (2 θ) (at intervals of 20°C up to 800°C) with a 0.5 s/step scan, corresponding to an approximate duration of 30 mn.

Visible spectroscopy

The plutonium solutions were determined by Vis spectroscopy using a spectrophotometer VARIAN CARY 6000i, the optical signal is transmitted through optical fibers (10 m length, Hellma) from the disposable UV-cuvette (PMMA, 1 cm optical path) inside the glove-box to the spectrophotometer placed outside. Solution is scanned from 350 to 900 nm with a speed of 300 nm/min, a measuring range of 1 nm and a gap width of 1.5 nm. Uncertainties of the uranium content are estimated to be 10%.

Results and discussion

Structure Description

The association of the N-(1-adamantyl)acetamide ligand with actinyl(VI) cations gives rise to the formation of a coordination complex of type (AnO₂)(adam)₂(NO₃)₂·2(adam), where An is U in **1**, and Pu in **2**. Their crystal structures are similar and composed of a molecular moiety

containing actinyl center bonded to two N-(1-adamantyl)acetamide and two bidentate nitrate groups (Figure 2). Within this discrete entity, the actinyl center sits on a special position $\frac{1}{2} \frac{1}{2} 0$ (inversion center, $1e$) and holds an eight-fold hexagonal bipyramidal coordination, with the typical double *trans* uranyl (U=O = 1.763(2) Å), or plutonyl (Pu=O = 1.736(3) Å) bondings. The two nitrate groups are placed in *trans* position within the equatorial hexagonal plane, adopting a chelating connection mode, with U-O bonding lengths of 2.514(2) and 2.536(2) Å in **1**, and Pu-O bonding lengths of 2.492(3) and 2.519(3) Å in **2**. The two remaining An-O bondings correspond to the monodentate linkage with the amide oxygen atom of the organic ligand (U-O = 2.366(1) Å; Pu-O = 2.368(2) Å). It is interesting to notice that the An-O_{nitrate} bond lengths decrease from uranyl to plutonyl as expected with the radius contraction, but the An-O_{amide} bond length is almost identical. For complex **1**, the U-O_{nitrate} (≈ 2.52 Å) and U-O_{amide} (≈ 2.36 Å) bond distances are typical for uranyl, according to the Cambridge Structural Database (Release v.5.41 November 2019). For the plutonyl complex **2**, only three compounds have been referenced in the presence of chelating nitrate groups, with the Pu-O_{nitrate} bond distances in the range 2.472-2.519 Å^{12,42,43} and Pu-O_{amide} bond distance equal to 2.377 Å,¹² close to what is observed here. Within the nitrate groups, the N-O bond distances are 1.257(3) and 1.268(3) Å, for the oxygen atoms involved with the uranyl center in **1**. The terminal N-O bonding distance is shorter, with a value of 1.215(3) Å, as expected.^{7,16} The distances within the nitrate group in **2**, are 1.270(4) Å for the oxygen atoms linked to the plutonyl center and 1.219(6) Å for the terminal N-O bonding.

Figure 2: Representations of the molecular complex of the uranyl N-(1-adamantyl)acetamide $\text{UO}_2(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1**). Yellow circle: uranium(VI); red circle: oxygen; blue circle: nitrogen; grey circle: carbon; light grey circle: hydrogen. The molecular complex of the plutonyl analog (**2**) is identical and shown in Figure S4.

The crystal structure consists of the packing of such neutral $[(\text{AnO}_2)(\text{adam})_2(\text{NO}_3)_2]$ moieties via Van der Waals and hydrogen bond interactions. Additional non-coordinating N-(1-adamantyl)acetamide molecules have been revealed from the single-crystal XRD analysis and are intercalated between the actinyl coordination complexes, along the [101] direction (Figure S3), resulting in an unexpected L/An ratio of 4 (L = N-(1-adamantyl)acetamide). One notices the difference of the carbonyl bond C=O lengths, which differs in the free state (C=O = 1.224(4) Å for **1**; 1.232(5) Å for **2**) and the coordinated state (C=O = 1.252(2) Å for **1**; C=O = 1.260(4) Å for **2**). This increase can be explained by the improved electronic delocalization from the ligand to the metallic cation combined with the conjugated nitrogen atom allowing a charge delocalization from the nitrogen doublet towards the C=O function and towards the cation. The phenomenon is also responsible for the slight shorten of the C-N bond (Table 2) of the monoamide with 1.320(3) Å for **1**, and 1.321(5) Å for **2** for the coordinating molecule, and 1.336(3) Å and 1.345(5) Å for **1** and **2**, respectively for the non-coordinating ligand. The free N-(1-adamantyl)acetamide species interacts through hydrogen bonds between its N-H group and the terminal oxygen atom of the nitrate group (≈ 2.21 Å) as well as the C=O group with the N-H group (≈ 2.03 Å) from an adjacent linked N-(1-adamantyl)acetamide molecule (Figure 3).

Table 2: Summary of the interatomic bond distances related to the C-N length within the organic ligand, for the compounds **1** & **2**.

C-N bond length (Å)	Bounded monoamide	Free monoamide
U(VI)-adam (1)	1.320(3)	1.336(3)
Pu(VI)-adam (2)	1.321(5)	1.345(5)

Figure 3: View of the hydrogen bond network (dotted red line) in compound $\text{AnO}_2(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1-2**), with the connection modes between free N-(1-adamantyl)acetamide molecules and the coordination molecular complex $[\text{AnO}_2(\text{adam})_2(\text{NO}_3)_2]$ via $\text{N-H} \cdots \text{O}_{\text{nitrate}}$ and $\text{N-H} \cdots \text{O-C}$ bonding. Yellow circle: uranium(VI) or plutonium(VI); red circle: oxygen; blue circle: nitrogen; grey/black circle: carbon; light grey circle: hydrogen.

Precipitation study of the actinyl N-(1-adamantyl)alkylamide nitrate complexes

The precipitation yield of uranyl nitrate with N-(1-adamantyl)acetamide (L) was firstly investigated in nitric acid aqueous solution. The initial uranium and nitric acid concentrations were adjusted to 20 g.L^{-1} and 0.5 M , respectively. The molar ratio of amide over uranium concentrations L/U range from 0.25 to 6. The precipitation process followed the synthetic route described in the experimental section for the preparation of complex **1** under static conditions (without magnetic stirring), after heating at 50°C for 24 hours. The supernatant solution at the end of the precipitation was separated from the solid and analyzed by ICP-AES to measure the concentration of non-converted uranyl species, and thus the quantitative yield of the precipitation reaction for the formation of complex **1**. For each synthesis, the

composition of the solid was analyzed by powder X-Ray diffraction to ensure it is single-phased. One example of the comparison of the experimental XRD pattern to the calculated one (from the single-crystal study) is given Figure S2a of the supporting information. The solid was also analyzed by IR spectroscopy (see Figure S8 of the supporting information). Figure 4 indicates the evolution of the yield of the formation of $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1**) precipitate as a function of L/U molar ratio. It shows a linear increase of the yield between $\text{L}/\text{U} = 0.25$ and $\text{L}/\text{U} = 4$ (yield reaction 92 %_U), and then a slight increase for $\text{L}/\text{U} > 4$, 96 % and 99 %_U for $\text{L}/\text{U} = 5$ and 6 respectively. The optimum ratio $\text{L}/\text{U} = 4$ is expected since it is directly related to that of the stoichiometry observed in the crystal structure of complex **1**. For the $\text{U}/\text{L} = 6$ ratio value, the remaining uranium concentration in the supernatant solution is lower than 0.2 g.L^{-1} .

Figure 4: Yields of the formation of $(\text{AnO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (U (**1**): red lozenge; Pu (**2**): blue triangles) precipitates as a function of L/U molar ratio in HNO_3 0.5 M for uranyl aqueous solution and HNO_3 (1 M) for plutonyl aqueous solution ($[\text{U}] = [\text{Pu}] = 20 \text{ g.L}^{-1}$).

Due to the structural similarities observed for the complex $(\text{AnO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ involving uranium(VI) (**1**) or plutonium(VI) (**2**), the same experiment has been performed from an aqueous solution containing plutonyl nitrate species with a concentration of 20 g.L^{-1} at ambient temperature. For safety reasons, it was not possible to carry out the experiment at 50°C as for uranium. Moreover, the nitric acid concentration was set to 1 M to preclude plutonium hydrolysis reaction. The molar ratio of the N-(1-adamantyl)acetamide (L) over Pu contents was ranging from 1 to 5, and the mixture was left static for 16 hours. The comparison of the experimental XRD pattern to the calculated one (from the single-crystal study) given Figure S2b of the supporting information indicates the formation of the same phase as the one

described previously. The reaction yield for the formation of complex $(\text{PuO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**2**) was estimated on the basis of the concentration of plutonium remaining in the aqueous solution, by using UV-Vis spectroscopy. The evolution of the plutonium precipitation yield is alike the uranyl one: linear progression between $\text{L}/\text{Pu} = 1$ and $\text{L}/\text{Pu} = 4$ ratios (Figure 4), with a upper value up to 88 %_{Pu} with a slight increase for higher ratio than stoichiometry ($\text{L}/\text{Pu} = 5$, 95 %_{Pu}).

For the formation of the uranyl N-(1-adamantyl)acetamide nitrate complex (**1**), the influence of the acidity of the aqueous solution has been then examined for nitric acid concentrations ranging from 0 to 5 M with L/U molar ratio of 5 (after reaction at 50°C for 24 hours). Without HNO_3 , the precipitation yield is found to be about 88 %_U. The addition of nitric acid favors the crystallization of compound **1** resulting in increasing acidity, and by providing an excess of nitrate anion to the reaction medium. An increase of the precipitation yield up to 99 %_U for HNO_3 above 1 M, (Figure 5). This result as well as the conservation of the XRD patterns indicate that such uranyl N-(1-adamantyl)acetamide nitrate complex (**1**) exhibits a very good stability toward nitric acidity, as it is required in the actinide recycling process.

Figure 5: Yield of the formation of $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1**) precipitate as a function of the HNO_3 concentration for L/U molar ratio 5/1.

The concentration of uranium in aqueous solution with nitric acid 0.5 M was then studied for 20, 40 and 60 g.L⁻¹. For the L/U ratio of 5, the precipitation yield remains approximately stable even if it slightly increases with the uranium concentration, from 96 up to 98 %_U (Figure S5).

Precipitation kinetics of the uranyl N-(1-adamantyl)acetamide nitrate complex (**1**)

The kinetics of the precipitation of the complex **1** was analyzed for three uranium concentrations, 20, 40 and 60 g.L⁻¹ in HNO₃ 0.5 M. The ligand was added at t=0 to the uranyl nitrate aqueous solution and then a 10 µL sample of supernatant liquid was withdrawn at different times in order to measure by ICP the remaining uranium concentration in the liquid phase. The Avrami-Erofe'ev equation^{42,44} involving an exponential evolution of type $\alpha = 1 - \exp[-(kt)^n]$ was used to help rationalize the data. For this model, α is the reaction rate (in our case, related to the precipitation yield of uranyl complex **1**), k is a kinetics constant and n is an Avrami coefficient. Although this kinetics model was initially used for the specific case of solid-solid transitions, it is now widely used to describe the crystalline formation of different types of materials (for instance: zeolites,^{45,46} organically templated metal phosphates,⁴⁷⁻⁴⁹ coordination polymers, metal-organic frameworks,⁵⁰⁻⁵²...). The expression is quite convenient to extract kinetics constants of the formation of crystalline products. However, the significance of the fitted Avrami parameter could be questionable and then considered with caution, if one considers the heterogeneous crystallization from a solution to a solid, as it occurs in our precipitation experiment of uranyl N-(1-adamantyl)acetamide nitrate complex. The fit accuracy of kinetics curves has been evaluated using the Sharp-Hancock method,⁵³ corresponding to the linear transformation of the Avrami-Erofe'ev equation, as $\ln[-\ln(1 - \alpha)] = n\ln(k) + n\ln(t)$. The kinetics parameters obtained for the different precipitations with various conditions (static/stirring; [U] varying from 20 to 60 g.L⁻¹) are summarized in the Table 3. The Avrami-Erofe'ev and Sharp-Hancock plots are presented in the Figure 6 only for [U] = 20 g.L⁻¹. Other kinetics curves for [U] = 40 and 60 g.L⁻¹, are given in the Supplementary Information (Figures S6 & S7).

At [U] = 20 g.L⁻¹, under static condition (without magnetic stirring; Figure 6), the maximum precipitation yield is not reached after 10 hours, since only 87% of uranium crystallized. The corresponding fitted values k and n are 0.0049(3) min⁻¹ and 0.71(5), respectively. The influence of stirring the aqueous solution mixture has been evaluated by means of rotating magnet (rotation speed: 750 rpm). The precipitation kinetics increases drastically under magnetic stirring reaching the maximum yield value of 99%_U after 4 hours of reaction at 50°C. The corresponding k and n values are 0.0168(7) min⁻¹ and 0.99(7), respectively. The effect of stirring increases the precipitation kinetics by a factor ≈ 3.5 in these conditions. The

same behavior is observed for higher uranium concentrations, but less contrasted. The k parameters are $0.0101(4) \text{ min}^{-1}$ (static) and $0.0203(6) \text{ min}^{-1}$ (stirring) for $[U] = 40 \text{ g.L}^{-1}$, and are a factor of ≈ 2 . They are $0.0214(7) \text{ min}^{-1}$ (static) and $0.0230(8) \text{ min}^{-1}$ (stirring) for $[U] = 60 \text{ g.L}^{-1}$, and are only a factor of ≈ 1.07 . For the latter, the influence of the magnetic stirring is quite limited, since the kinetics gain is about 7%. The kinetics of the precipitation is thus directly correlated to the concentration of uranium in the aqueous nitric acid solution. Without stirring, this result is not surprising as for a greater concentration, the reagent put in touch is less limited by diffusion. The maximum precipitation yield ($99\%_{\text{U}}$) is reached after ≈ 3 hours for $[U] = 40$ and 60 g.L^{-1} , under stirring conditions. However, we notice that the kinetics of precipitation remains quite slow and requires a reaction time of 3-4 hours for getting the maximal yield.

Figure 6: (top) Kinetics curve of formation of the $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1**) precipitate for U concentration at 20 g.L^{-1} under static conditions (red) and magnetic stirring (blue) in HNO_3 0.5 M (at 50°C), with molar ratio ligand/U ≈ 5 . (bottom) Sharp-Hancock plot from linear regression of the Avrami-Erofe'ev equation ($\ln[-\ln(1-\alpha)] = n\ln(k) + n\ln(t)$).

The Avrami parameters are in the range 0.7-1.1 (Table 3), with higher values for the stirring conditions (in the range 0.9-1.1) and lower values for the static conditions (in the range 0.7-0.9). According to previous data from literature,^{44,54} the crystallization mechanisms would be controlled by the diffusion of species for an Avrami exponent in the range 0.6-0.8, whereas it is controlled for reaction of species on the crystal surface if the Avrami exponent is in the range 1.0-1.1. This study confirms these two mechanisms: under static conditions, the kinetics of precipitation would be limited by a diffusion-controlled mechanism, and under stirring conditions, it would be limited by phase-boundary-controlled reaction.

Table 3: Kinetics parameters extracted from the curve fits from the Avrami-Erofe'ev equation and Sharp-Hancock plots describing the crystallization of $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1**). The fitting was performed using Kaleidagraph 4.5.

	[U] = 20 g.L ⁻¹		[U] = 40 g.L ⁻¹		[U] = 60 g.L ⁻¹	
<i>Avrami-Erofe'ev</i>	no stirring	stirring	no stirring	stirring	no stirring	stirring
<i>k</i> (min ⁻¹)	0.0049(3)	0.0168(7)	0.0101(4)	0.0203(6)	0.0214(7)	0.0230(8)
<i>n</i>	0.71(5)	0.99(7)	0.71(4)	1.00(5)	0.88(4)	1.08(7)
* <i>R</i> ²	0.970	0.988	0.986	0.994	0.993	0.989
<i>Sharp-Hancock</i>	no stirring	stirring	no stirring	stirring	no stirring	stirring
<i>k</i> (min ⁻¹)	0.0049(5)	0.0168(3)	0.0109(6)	0.0219(5)	0.02286(5)	0.0242(7)
<i>n</i>	0.71(4)	1.10(4)	0.77(4)	1.05(6)	0.93(4)	0.90(5)
* <i>R</i> ²	0.966	0.989	0.963	0.969	0.976	0.966

**R*²: correlation coefficient from the kinetics curves fittings.

This study shows that the acetamide bearing an adamantyl group (i.e N-(1-adamantyl)acetamide) could be a good candidate for precipitating uranyl nitrate from highly acidic nitric acid aqueous solutions. When the *adam*/U ratio reaches to 5/1, one observes high yields for uranium precipitation with values in the range 96-99%_U for nitric acid concentrations 1-5M. It is well-known that the classical precipitating agent used in the spent nuclear fuel recycling is the oxalic acid molecule, which is very efficient for its rapid reaction with tetravalent actinide, such as plutonium(IV) with very high yields (>99%_{Pu}). Unfortunately, in the case of uranyl nitrate aqueous solution, the precipitation yield was observed to decrease drastically. For instance, previous investigations,⁵⁵ have shown the formation of a powdered product of hydrated uranyl oxalate type $(\text{UO}_2[\text{C}_2\text{O}_4](\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O})$ after mixing oxalic acid in a nitric acid aqueous solution containing uranyl nitrate. Optimal

precipitation yield was found to be less than 83%_U (remaining [U] = 4.0 g.L⁻¹), from an uranyl nitrate concentration [23.8 g.L⁻¹] in HNO₃ (2M) aqueous solution at ambient temperature. If the precipitation of UO₂[C₂O₄](H₂O)·2H₂O appeared after a few minutes, the maximal yield is obtained after several hours.⁵⁵ By comparison, our study indicates a precipitation of uranyl nitrate complex within roughly the same reaction time but, with a better precipitation yield (up to 99%_U).

Nevertheless, this slow precipitation kinetics drawback is not reported when using N-cyclohexyl-2-pyrrolidone (NCP), for which a pioneering work describes the formation of an uranyl nitrate coordination complex UO₂(NO₃)₂(NCP)₂ with reaction yield of 68 %_U, from an initial NCP/U = 3.6 and [U] = 50 g.L⁻¹.⁷ Further investigations on this NCP-U(VI) system have shown a robust precipitation route since high specifications with reaction yields > 99%_U have been described from highly concentrated uranyl nitrate solution, i.e 238 g.L⁻¹, NCP/U ratio >3 in HNO₃ 3M.⁵⁶ The main difference is the kinetics of the precipitation of uranyl cation between the NCP and *adam* systems. Indeed, the precipitation of the NCP uranyl nitrate complex is complete after a few minutes at room temperature only,⁵⁶ but requires a reaction time for several hours for the production of the complex **1** with *adam* ligand from solutions containing [U] = 40 or 60 g.L⁻¹ at 50°C (with HNO₃ 0.5M). The solubility of the organic complexing agent in water might be considered for explaining such different kinetic reactivities. The NCP molecule is a viscous liquid, which possesses a high miscibility with water,⁹ whereas oxalic acid and N-(1-adamantyl)acetamide) reactants are powdered compounds. The water solubility of oxalic acid is known to be quite high (90-100 g.L⁻¹ at room temperature) and we estimated that of N-(1-adamantyl)acetamide), which was found to be very low (≈ 1-2 g.L⁻¹ at room temperature). These ligand solubility considerations may thus control the slow formation of the (UO₂)(*adam*)₂(NO₃)₂·2(*adam*) (**1**) complex, compared to that of the NCP uranyl complex. This drastic kinetics difference strongly limits the potential use of the N-(1-adamantyl)acetamide molecule as precipitating agent for industrial applications.

Thermal analysis

The thermal treatment under air atmosphere has been analyzed, only for the complex **1**, in order to study the thermal transition of this uranyl complex under its oxide form. The thermal decomposition of complex **1** has been characterized by in-situ powder X-ray diffraction (Figure 7). This experiment shows multiple phase transformation steps. Bragg peaks of the phase **1** persist up to 200°C. At this temperature, a new transient crystalline product (red

diffraction patterns – Figure 7) appeared with a new set of peaks located at $d = 10.03$, 8.96 , 6.67 and 7.62 Å, for the lowest angle values. This structural transformation is related to a first weight loss of 3 %, after heating up to 170°C , reported on the thermogravimetric curve (Figure S9). Between 200 and 400°C , new broad Bragg peaks (blue diffraction patterns – Figure 7) are visible with $d = 3.33$, 2.86 and 1.99 Å, indicating the crystallization of a second badly crystalline product, related to the formation of UO_2 fluorite type compound (Figure S11). A remarkable and unexpected transient reduction of the uranium is observed during the decomposition of the coordination organic-inorganic complex. Indeed, previous thermal decompositions have been reported for some uranyl coordination complexes, such as uranyl terephthalate,⁵⁷ uranyl pyromellitates⁵⁸ or uranyl mellitate,⁵⁹ for instance. The thermal transformation of these initial complexes went directly to the formation of the uranium oxide U_3O_8 under air atmosphere, without through the generation of a transient UO_2 phase. For the present study, the appearance of the UO_2 oxide could be correlated to the air combustion of the organic part (which is present with a larger L/U ratio compared to the previous examples),^{57–59} likely into transient CO species, inducing high concentration of these evacuating gases and provoking the temporary reduction of uranium, crystallizing with the fluorite structure. This intermediate uranium reduction during thermal treatment is therefore quite specific of the degradation of compound **1**. The fluorite phase is then classically transformed when further heating under air into the U_3O_8 form.⁶⁰ Indeed, from 400°C , the crystallization of $\alpha\text{-U}_3\text{O}_8$ is clearly observed with peaks intensity increasing with temperature. The thermogravimetric curve of this complex (Figure S9) presents weight loss events between 120 and 500°C . The remaining weight value is 24.1 %, in good agreement with the expected one (24.0 % wt.), for U_3O_8 as final phase at 800°C .

BET surface area (using krypton adsorption) of the resulting uranium oxide after heating at 800°C , was measured at $3.9 (\pm 0.5) \text{ m}^2.\text{g}^{-1}$. This value strongly depends on the calcination conditions but seems to be a bit high compared to previous studies on U_3O_8 compounds.^{61,62} Scanning electron microscopy of the calcined complex **1** at 800°C indicates the preservation of large blocks ($50 \mu\text{m}$), but cracks and holes are visible, due to the gaseous evacuation of the degradation products from the organic ligand (Figure S10).

Figure 7: Evolution of the powder XRD patterns as a function of temperature for the $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1**) (heating rate $5^\circ\text{C} \cdot \text{min}^{-1}$ and scans collected every 50°C , air atmosphere). XRD patterns in green: $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ (**1**) phase; red: unknown phase; blue: transient fluorite-like UO_2 phase; black: $\alpha\text{-U}_3\text{O}_8$ phase.

Conclusion

In summary, the ability of the N-(1-adamantyl)acetamide molecule to precipitate the uranyl cation has been examined in the view of a general actinide recycling process. In a wide range of highly concentrated nitric acid solutions (0.5-5 M), this organic species is able to react with the actinyl cation, to form a crystalline coordination complex, $(\text{AnO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ ($\text{An} = \text{U}(\mathbf{1})$ or $\text{Pu}(\mathbf{2})$), obtained with high yield (up to 99% An , when L/An ratio is 5). The kinetics investigations have shown that the precipitation reaction is rather slow and completed after several hours (3-4 h) for the compound **1** even under stirring. This could be related to the rather weak solubility of the powdered N-(1-adamantyl)acetamide molecule in water, which inhibits the rapid reaction with the uranyl cations. The thermal degradation of the $(\text{UO}_2)(\text{adam})_2(\text{NO}_3)_2 \cdot 2(\text{adam})$ compound (**1**) showed a decomposition in three steps with the transient formation of an crystalline unidentified phase, followed by a reduction process from 200°C , with the crystallization of fluorite-type UO_2 , and finally transformed into uranium oxide U_3O_8 from 400°C , under air atmosphere.

The N-(1-adamantyl)acetamide ligand has thus showed interesting properties for the quantitative precipitation of uranyl(VI) cation in nitric acid, which can be extended to the use of the analogous element, plutonyl(VI) cation (**2**). This chemical reactivity have been restricted to the use of hexavalent state of actinide and further investigations will be required in order to examine the precipitation behavior with tetravalent actinide elements.

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Associated Content

Supporting Information

Supplementary data (powder XRD pattern, thermogravimetric curves, IR spectra) associated with this article can be found in the online version.

Accession Codes

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1987462 for **1**, 1987465 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336-033; e-mail: data_request@ccdc.cam.ac.uk).

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