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## Neodymium uranyl peroxide synthesis by ion exchange on ammonium uranyl peroxide nanoclusters

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**This study demonstrates the ammonium uranyl peroxide nanoclusters U<sub>32R</sub>-NH<sub>4</sub> ability to undergo exchanges in between NH<sub>4</sub><sup>+</sup> and trivalent (Nd<sup>3+</sup>) or tetravalent (Th<sup>4+</sup>) cations in the solid state. It paves the way of promising new routes for the synthesis of mixed uranyl peroxides. The exchange ability may also be considered for solution decontamination and synthesis of new mixed actinides-oxides precursors. Both of these applications could be used in the nuclear industry.**

Uranium peroxides play an important role in the nuclear fuel cycle and waste management. Up today the applications are essentially limited to studtite, (UO<sub>2</sub>)(O<sub>2</sub>)·4H<sub>2</sub>O, and metastudtite, (UO<sub>2</sub>)(O<sub>2</sub>)·2H<sub>2</sub>O, which can also form as alteration products of spent nuclear fuel (SNF)<sup>1</sup> by reaction between UO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> produced by alpha-radiolysis of water. The formation of these peroxides under different dissolution conditions and their implication in the storage of SNF motivated several studies in recent years<sup>2</sup>. Precipitation of uranium as studtite is performed at several steps in the front and the back end of the fuel cycle: (i) during the extraction-transformation of uranium ores, the uranium ores are ground, mashed and dissolved in concentrated sulfuric acid<sup>3</sup>, and uranium is precipitated as uranyl peroxide by using hydrogen peroxide in some mining sites, (ii) during the reprocessing of the spent nuclear fuel (SNF), at the end of the PUREX process, uranium is also precipitated as uranyl peroxide by adding H<sub>2</sub>O<sub>2</sub> to the solution purified from fission products plutonium and minor actinides. In each case, uranyl peroxide is transformed into U<sub>3</sub>O<sub>8</sub>, the most stable uranium oxide, to avoid alteration, particularly hydration, during the transport and/or storage of uranium compounds.

The family of peroxides was recently enlarged by the discovery of actinyl peroxide nanospheres by the research group of P.C. Burns in 2005<sup>4</sup>. This work raised a real emphasis on this beautiful and exciting new classes of materials<sup>5,6</sup>. A topic of general interest is the use of uranyl peroxide to prepare precursors of uranium oxides for nuclear fuel fabrication<sup>7</sup>. Our work aims to extend the applications of uranyl peroxides to the fabrication of mixed oxides nuclear fuel (MOX). Currently, the so-called French MOX fuel (for Mixed Oxides) is prepared by mixing depleted uranium dioxide and plutonium dioxide resulting from the calcination of plutonium oxalate precipitated from a nitric solution containing Pu (PUREX process). After sintering into pellets, the MOX can be used as fuel in some Pressurized Water Reactors. In the future, reactors would be completely powered by MOX. Homogeneity of the actinides repartition in the MOX fuel pellets can be increased by using a mixed actinides solid-solution such as oxalate compounds<sup>8</sup>, or alternatively uranyl peroxide clusters with another actinide as counter-cation as potential mixed oxide precursors<sup>9</sup>. Other applications in the nuclear industry may concern the waste management and contamination remediation by transfer of radionuclides from contaminated environments towards the uranyl nano-clusters. From an academic point of view, our work can be seen as a route for the synthesis of uranyl peroxide nanoclusters containing various di-, tri-, tetra-, ... valent metals which have not been prepared by direct synthesis up to date.

Our interest was initially focused on the synthesis of a neodymium uranyl peroxide, neodymium being used as analog of actinides (III). We report here the isolation and characterization of a uranyl peroxide based on the U<sub>32R</sub> crown cluster containing neodymium as counter-cation. The synthetic method was then applied to the synthesis of uranyl peroxide with an actinide (IV), thorium, on the one hand, and with strontium, on the other hand. Direct synthesis of such materials containing lanthanide (III) or actinides (III) and (IV) is not favorable due to strong hydrolysis of these cations under alkaline conditions. Our synthetic route using an uranyl peroxide with a monovalent cation as counter ion takes advantage of the exchange ability of this cation in crystals containing the clusters with lanthanide or actinide ions in solution. Ammonium uranyl peroxide, U<sub>32R</sub>-NH<sub>4</sub>,

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$(\text{NH}_4)_{40}[(\text{UO}_2)_{32}(\text{O}_2(\text{OH})_2)_{52}] \cdot n\text{H}_2\text{O}$ , containing the  $\text{U}_{32\text{R}}$  cluster, was chosen as starting material because (i) its crown structure presents large apertures favorable to ion exchange (ii) it contains only one type of cation that stabilizes both pentagonal and hexagonal rings<sup>7,10</sup>, (iii) it can be easily synthesized with high yields (>80%), (iv) any residual ammonium ions, thermally labile, will be eliminated during the heat treatment and the conversion of the mixed peroxide into a mixed oxide.

After thirty minutes contact between the  $\text{U}_{32\text{R}}\text{-NH}_4$  crystals, prepared by using a route adapted from the previously described<sup>7,10</sup> and a solution of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in water, UV-vis analysis showed that the resulting compound contains neodymium (Figure S4). The structure of the exchanged compound, hereafter denoted  $\text{U}_{32\text{R}}\text{-Nd}$ , determined from single crystal X-ray data, is very similar to that of the parent compound  $\text{U}_{32\text{R}}\text{-NH}_4$  and is built from the same  $\text{U}_{32\text{R}}$  crown cluster. However instead of ammonium ions templating the hexagonal and pentagonal uranyl polyhedra rings, neodymium ions are located within and all around the crown cluster in different positions. Nd(3) and Nd(4) half occupy sites forming a regular octagon (Figure 1a) and are coordinated to three oxygen atoms of uranyl ions, denoted  $\text{O}_{\text{vi}}$  oxygens, of the hexagonal rings (Figure 2) in a manner similar to Li in the  $\text{H}_2(\text{Li})$  mode evidenced by a theoretical study<sup>11</sup>. No atom was located at the center of the crown cluster. However a neodymium atom Nd(6) partially occupies a (16o) site forming squares at the bottom and the top free spaces of the cluster (Figure 1b) and is connected to two oxygens of a non-shared peroxide and one  $\text{O}_{\text{vi}}$  oxygen (Figure 2). The stabilizing effect of internal counter-ion on both pentagonal and hexagonal rings is known to be necessary to form uranyl nano-clusters<sup>12</sup> but in  $\text{U}_{32\text{R}}\text{-Nd}$  no atom stabilizes the pentagonal and hexagonal rings. It is a supplementary reason explaining why no direct synthesis of uranyl nano-cluster with lanthanide atoms as counter-ions has been reported up to now. Connection between the clusters is ensured by neodymium atoms *via*  $\text{O}_{\text{vi}}$  atoms for Nd(1) and Nd(5), and *via* peroxide bridges for Nd(2) (Figure 2). All the neodymium atoms, except Nd(2), are connected to uranyl ions through so-called cationation interactions (CCIs). CCIs discovered by Sullivan<sup>13</sup> involved two actinide centers where an  $\text{O}_{\text{vi}}$  atom of one actinyl bonds the actinide center of another actinyl ion. Such CCIs were evidenced in Np(V) compounds and to a lesser extend in U(VI) compounds and discussed in several papers<sup>14</sup>. The use of the term CCI was more recently extended to the interaction between an  $\text{O}_{\text{vi}}$  of an actinyl or even a vanadyl and another cation<sup>15</sup>. In CCIs, the  $\text{U} = \text{O}_{\text{vi}}$  distance for the shared  $\text{O}_{\text{vi}}$  oxygen is increased. Considering the fully occupied Nd(1) site, it is connected to one  $\text{U}(2)\text{O}(21)_2^{2+}$  and two  $\text{U}(5)\text{O}(23)_2^{2+}$  actinyl ions through O(21) and O(23) oxygen atoms respectively, the  $\text{U}(2) - \text{O}(21)$  and  $\text{U}(5) - \text{O}(23)$  distances increase from 1.819(39) and 1.755(28) Å in  $\text{U}_{32\text{R}}\text{-NH}_4$  to 1.863(24) and 1.861(18) Å in  $\text{U}_{32\text{R}}\text{-Nd}$ .

$\text{U}_{32\text{R}}\text{-NH}_4$  and  $\text{U}_{32\text{R}}\text{-Nd}$  solids were characterized by Infra-Red and Raman spectroscopy (Figures S5 and S6). On the IR spectra (Figure S5) two bands corresponding to the antisymmetric ( $\nu_3$ ) and symmetric stretching ( $\nu_1$ ) vibrations of  $\text{U} = \text{O}_{\text{vi}}$ , are observed within the range [900-850]  $\text{cm}^{-1}$ . The Raman spectrum of  $\text{U}_{32\text{R}}\text{-NH}_4$  (Figure S6) reveals two bands at 803 and 841  $\text{cm}^{-1}$  assigned to the symmetric stretching vibration mode,  $\nu_1$ , of the uranyl ions and to the symmetric stretching mode of the peroxo ligands respectively, according to the assignment in studtite<sup>16</sup> and in uranyl peroxide

cage clusters<sup>17</sup>. The two wavenumbers of the  $\text{U}_{32\text{R}}\text{-HH4}$  Raman spectrum fit quite well with the relationship between the uranyl symmetric stretching mode and the peroxide symmetric stretching mode established by McGrail *et al.*<sup>17</sup> In the Raman spectrum of  $\text{U}_{32\text{R}}\text{-Nd}$  (Figure S6) the two bands overlap with maxima located at 811 and 823  $\text{cm}^{-1}$ . The decrease of the wavenumber of the symmetric stretching mode of the peroxo ligands was attributed to the coordination of some neodymium atoms by peroxide ligands since the geometrical parameters of the structure remain unaffected by the substitution (the average  $\text{U}-\text{O}_2-\text{U}$  dihedral angles are 142.7 and 141.4° for  $\text{U}_{32\text{R}}\text{-NH}_4$  and  $\text{U}_{32\text{R}}\text{-Nd}$  respectively). The  $\text{U} = \text{O}_{\text{vi}}$  bond lengths in  $\text{U}_{32\text{R}}\text{-Nd}$  were calculated by means of the following empirical laws<sup>18</sup> using the [ $\nu_1(\text{UO}_2^{2+})$ ] and [ $\nu_3(\text{UO}_2^{2+})$ ] vibration band wavenumbers provided by the spectroscopic data (Raman and IR respectively)<sup>19</sup>.

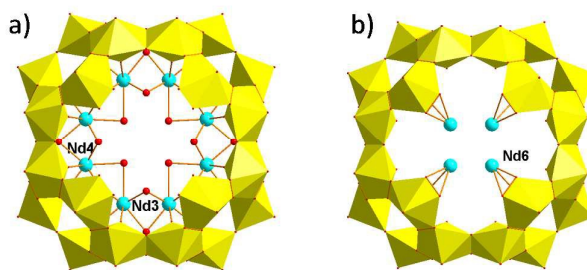
$$R_{\text{U}=\text{O}}(\text{pm}) = 10650 \times [\nu_1(\text{UO}_2^{2+})(\text{cm}^{-1})]^{-2/3} + 57.5$$

And

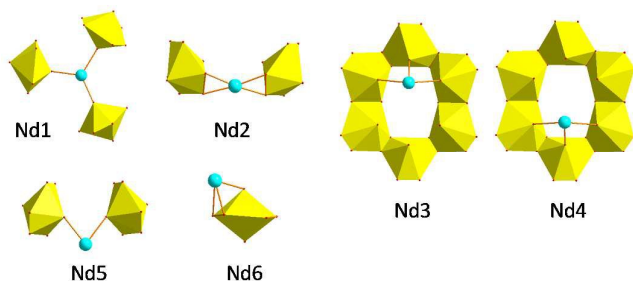
$$R_{\text{U}=\text{O}}(\text{pm}) = 9141 \times [\nu_3(\text{UO}_2^{2+})(\text{cm}^{-1})]^{-2/3} + 80.4$$

The calculated values ( $R_{\text{U}=\text{O}} = 1.84$  and  $1.86$  Å) are in good agreement with the structural data of  $\text{U}_{32\text{R}}\text{-Nd}$  but the comparison between the spectroscopic data of  $\text{U}_{32\text{R}}\text{-Nd}$  and  $\text{U}_{32\text{R}}\text{-NH}_4$  doesn't provide evidence of an increase of some uranyl bonds.

The sum of the refined occupancies of the Nd sites (11.55 Nd by  $\text{U}_{32\text{R}}$  cluster, see Table S2) is close to the value calculated for neutrality (13.33). The almost total exchange of neodymium for ammonium is confirmed by EDS and ICP-AES analyses with Nd/U values of 0.416(8) and 0.40(3), respectively, giving a  $\text{U}_{32\text{R}}\text{-Nd}$  compound with formula close to  $\text{Nd}_{13.33}[(\text{UO}_2)_{32}(\text{O}_2(\text{OH})_2)_{52}] \cdot n\text{H}_2\text{O}$ . From  $\text{U}_{32\text{R}}\text{-NH}_4$  to  $\text{U}_{32\text{R}}\text{-Nd}$  infrared spectra, the band observed at 1420-1410  $\text{cm}^{-1}$ , corresponding to the N-H vibrations, decreases accordingly to an exchange of ammonium by neodymium ions. Furthermore, electron microprobe maps realized on a pellet of crushed crystals shows a homogeneous repartition of Nd and U (Figure S8).



**Figure 1.** Position of the internal neodymium atoms Nd3 and Nd4 (a) and Nd6 (b) in  $\text{U}_{32\text{R}}\text{-Nd}$ .



**Figure 2.** Connection of the neodymium atoms to the uranyl hexagonal bipyramids *via*  $O_{VI}$  oxygens (Nd1, Nd3, Nd4, Nd5) and *via* peroxide ions non-shared to form the  $U_{32R}$  cluster (Nd2). Nd6 is connected *via* both an  $O_{VI}$  oxygen and a peroxide ion.

The first application of the nano-cluster exchange ability and the formation of a neodymium uranyl peroxide is to model the fabrication of MOX combustible by this new route,  $Nd^{3+}$  being used as analog of  $Pu^{3+}$ . Thus the study of the thermal decomposition of the double peroxide is essential. Firstly, the thermal decomposition of  $U_{32R}-NH_4$  was studied. The temperature dependent X-ray diffraction studies show the formation of  $\alpha-UO_3$  at 550°C and its transformation into  $\alpha'-U_3O_8$  at 600°C in air (Figure S9) and the formation of  $\alpha-UO_3$  at 425°C and its transformation into  $UO_2$  at 500°C in  $N_2/H_2$  (3%) with a refined unit cell parameter  $a = 5.4676(1)$  Å (Figure S10). The thermal behavior of  $U_{32R}-Nd$  is different. In air, the formation of  $\alpha-UO_3$  at 575°C is accompanied with that of a fluorite-structure phase whose proportion increases with temperature (Figure S11). The calcination of the sample at 1400°C gives a pure fluorite-type oxide with  $a = 5.4356(7)$  Å close to the value of the solid solution term  $Nd_{0.3}U_{0.7}O_{2+x}^{20}$ . In a reducing flow (Figure S12) a pure fluorite-structure phase is obtained from 475°C with  $a = 5.4484(4)$  Å corresponding to a reduced solid solution  $Nd_{0.3}U_{0.7}O_{2-x}$ . The rod-like morphology is kept after the thermal decomposition of  $U_{32R}-Nd$  into the fluorite-type oxide both in air at 1400°C and in  $N_2/H_2$  (3%) at 800°C (Figure S13). The Nd/U ratio determined on the oxide by EDS (0.445(7)) is close to that of the  $U_{32R}-Nd$  precursor. The use of this peroxide precursor presents the advantage, compared with the other methods such as oxalate coconversion<sup>8</sup>, to be a non-carbon route and to form only water and oxygen during calcination.

In presence of nitrate ions as in the PUREX process, plutonium(III) is oxidized into plutonium(IV), so the exchange between  $NH_4^+$  and a tetravalent actinide is also challenging. A preliminary study was realized by using thorium(IV) as an actinide(IV). The X-ray diffraction study of a single crystal obtained by putting in contact  $U_{32R}-NH_4$  crystals with a thorium nitrate solution revealed the presence of thorium atoms both into and outside the  $U_{32R}$  clusters. In fact Th(3) and Th(4) occupy similar positions in the  $U_{32R}$  cluster than Nd(3) and Nd(4) in  $U_{32R}-Nd$  (Table S2). Th(1), Th(2) and Th(5) connect the  $U_{32R}$  crowns as Nd(1), Nd(2) and Nd(5). Th(6) also connects  $U_{32R}$  crowns *via* two  $O_{VI}$  oxygens. The sum of the refined occupancies of the Th sites (8.61 Th by  $U_{32R}$  cluster) is lower to the value calculated for neutrality (10 Th by  $U_{32R}$  cluster) and indicates a non-complete exchange. In fact, the crystals of  $U_{32R}-Th$  are

accompanied by a powder of uranyl peroxide ( $UO_2(O_2) \cdot 4H_2O$ ). The formation of this peroxide is due to the low pH of the thorium nitrate solution (pH 2.35 for  $[Th^{4+}] = 0.05M$ ), resulting to the hydrolysis of  $Th^{4+}$  and a partial dissolution of  $U_{32R}-NH_4$ . Starting from a thorium complex to avoid hydrolysis is under study. However this approach clearly demonstrates the possibility to prepare double actinide(IV) uranyl peroxides by ion exchange.

The ion exchange properties of uranyl peroxides are also potentially important for both waste management and contamination remediation in the nuclear industry. A preliminary study shows that fission products with lower oxidation states than lanthanides (III), such as strontium, can exchange the ammonium ions contained in the  $U_{32R}-NH_4$  crystals. After short contact between  $U_{32R}-NH_4$  crystals and a solution of strontium nitrate, X-ray diffraction study of a resulting single crystal revealed the presence of strontium atoms in the  $U_{32R}$  cluster in the same positions than Nd(3) and Nd(4) (Table S2). Other strontium atoms connect the  $U_{32R}$  crowns. The sum of the refined occupancies of the Sr sites (14.2 Sr by  $U_{32R}$  cluster) is lower to the value calculated for neutrality (20 Sr by  $U_{32R}$  cluster) and indicates a non-complete exchange in the used experimental conditions.

Finally the exchange is possible with other uranyl clusters. After contact of  $U_{28}-NH_4$  powder with a solution of  $Nd^{3+}$ , an amorphous fine powder is obtained (Figure S3). UV-Vis. spectroscopy (Figure S7) shows the presence of Nd and ICP-AES analysis gives a Nd/U value (0.36) in agreement with the theoretical one considering a complete exchange ( $Nd/U = 0.33$ ).

In conclusion, by exchanging monovalent cations in the uranyl peroxide cage-clusters in the solid state, it is possible to obtain double lanthanide(III) uranyl peroxides and double actinide(IV) uranyl peroxide not obtained by direct synthesis. These double peroxides can be seen precursors of mixed oxides for fabrication of advanced nuclear fuel. The exchange properties also open a new route for synthesis uranyl peroxides nanoclusters with divalent, trivalent, tetravalent... metals and for contamination remediation of solutions containing radioactive elements.

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