



## Evidence for the Formation of a New Water Soluble Pu Peroxo Complex

M. Viro, E. Dalodiere, T. Dumas, C. Tamain, O. Dieste Blanco, T. Wiss, L. Venault, P. Moisy, Sergey I. Nikitenko

### ► To cite this version:

M. Viro, E. Dalodiere, T. Dumas, C. Tamain, O. Dieste Blanco, et al.. Evidence for the Formation of a New Water Soluble Pu Peroxo Complex. 4th International Workshop on Advanced Techniques in Actinide Spectroscopy (ATAS 2018), Université Côte d'Azur; CEA Marcoule; CNRS; ICN Nice, Nov 2018, Nice, France. cea-02339471

**HAL Id: cea-02339471**

**<https://cea.hal.science/cea-02339471>**

Submitted on 27 Nov 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Evidence for the Formation of a New Water Soluble Pu Peroxo Complex

M. Virot,<sup>1</sup> E. Dalodière,<sup>1</sup> T. Dumas,<sup>2</sup> C. Tamain,<sup>2</sup> O. Dieste Blanco,<sup>3</sup> T. Wiss,<sup>3</sup> L. Venault,<sup>2</sup> P. Moisy,<sup>2</sup> S. I. Nikitenko<sup>1</sup>

<sup>1</sup> Université de Montpellier, Institut de Chimie Séparative de Marcoule, UMR 5257, CEA-CNRS-UM-ENSCM, Site de Marcoule, BP17171, 30207 Bagnols sur Cèze, France

<sup>2</sup> CEA/DEN/MAR/DMRC, Nuclear Energy Division, Radiochemistry and Process Department, BP17171, 30207 Bagnols sur Cèze, France

<sup>3</sup> European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements (ITU), Postfach 2340, 76125 Karlsruhe, Germany

X oral ☐ poster

Hydrogen peroxide has been considered as an important reactant in nuclear industry for the stabilization of plutonium intermediate redox states or the precipitation of Pu peroxides used as precursors for PuO<sub>2</sub> preparation. The formation of two different Pu(IV) peroxo complexes, known as brown and red complexes, was reported to occur during the continuous addition of H<sub>2</sub>O<sub>2</sub> to Pu(IV) acid solutions.[1,2] Since the proposed structure given by Connick and W. H. McVey in 1949, only one Pu peroxo structure has been recently proposed in alkaline conditions.[1-3] The resolved peroxy-carbonate complex concerns a Pu(IV) dimeric unit coordinated by two side-on peroxide ligands.[4] In addition to the known peroxo complex of Pu(IV), the current work demonstrates that the addition of hydrogen peroxide to slightly acid Pu(IV) aqueous solutions may lead to the observation of a green solution exhibiting characteristic absorption bands at 455 and 660 nm which has, up to our knowledge, never been reported in the literature. The formation of this specie can also be observed from the sonochemical oxidation of 1 mM Pu(III) solutions under Ar/O<sub>2</sub> atmosphere (203 kHz, 250 mL, 20°C, 0.13 W mL<sup>-1</sup>). The green solution was characterized with Vis-NIR absorption spectroscopy, Raman spectroscopy, and XAFS techniques. We demonstrated the formation of a new polynuclear peroxo complex of Pu(IV) involving several Pu-O distances and at least 4 Pu atoms (Fig. 1). This water soluble complex was found to be stable for several months before it slowly converts into a Pu(IV) colloidal suspension exhibiting the characteristic absorption band at 620 nm and a strong Mie scattering in the near UV-vis range. HR-TEM and XAFS characterizations allowed to describe these colloids as monodispersed and quasi-spherical crystalline PuO<sub>2</sub> particles covered by hydrolyzed Pu(IV) moieties of approximately 2.4 nm.

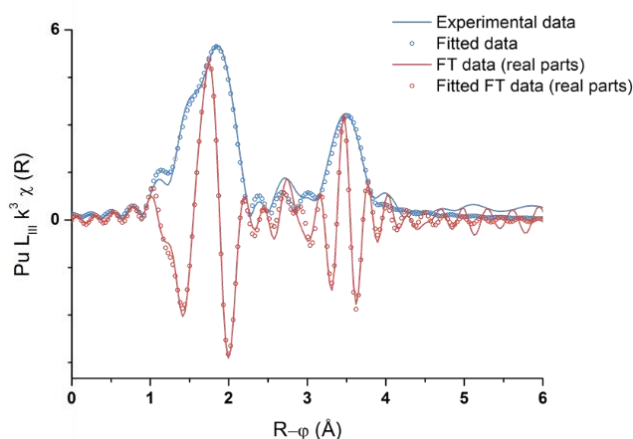


Fig. 1: Fourier transform of the k<sub>3</sub>-weighted EXAFS spectrum exhibiting two coordination spheres for the green peroxo complex.

[1] D. Clark, S. Hecker, G. Jarvinen and M. Neu, in *The Chemistry of the Actinide and Transactinide Elements*, eds. L. Morss, N. Edelstein and J. Fuger, Springer Netherlands (2011) ch. 7, pp. 813-1264.

[2] R. E. Connick and W. H. McVey, *J. Am. Chem. Soc.* (1949) 71, 1528-1533.

[3] G. A. Fugate and J. D. Navratil, in *Separations for the Nuclear Fuel Cycle in the 21st Century*, eds. G. J. Lumetta, K. L. Nash, S. B. Clark and J. I. Friese, American Chemical Society, Washington (2006) ch. 11, pp. 167-181.

[4] W. Runde, L. F. Brodnax, G. S. Goff, S. M. Peper, F. L. Taw and B. L. Scott, *Chem. Commun.* (2007) 17, 1728-1729.