



HAL
open science

Chronicles of peroxide plutonium species: structural characterization of new Pu(IV) green peroxide

Julien Margate, Matthieu Viro, Simon Bayle, Denis Menut, Thomas Dumas, Elodie Dalodiere, Christelle Tamain, Paul Estevenon, Philippe Moisy, Sergey I. Nikitenko

► To cite this version:

Julien Margate, Matthieu Viro, Simon Bayle, Denis Menut, Thomas Dumas, et al.. Chronicles of peroxide plutonium species: structural characterization of new Pu(IV) green peroxide. ATALANTE 2024 – Nuclear Chemistry for Sustainable Fuel Cycles, Sep 2024, Avignon, France. hal-04766140

HAL Id: hal-04766140

<https://hal.science/hal-04766140v1>

Submitted on 4 Nov 2024

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.

Chronicles of peroxide plutonium species: structural characterization of new Pu(IV) green peroxide

J. Margate [1], M. Virost [1], S. Bayle [1], D. Menut [3] T. Dumas [2], E. Dalodière [1], C. Tamain [2], P. Estevenon [2], P. Moisy [2], S. I. Nikitenko [1]

[1] ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France

[2] CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France

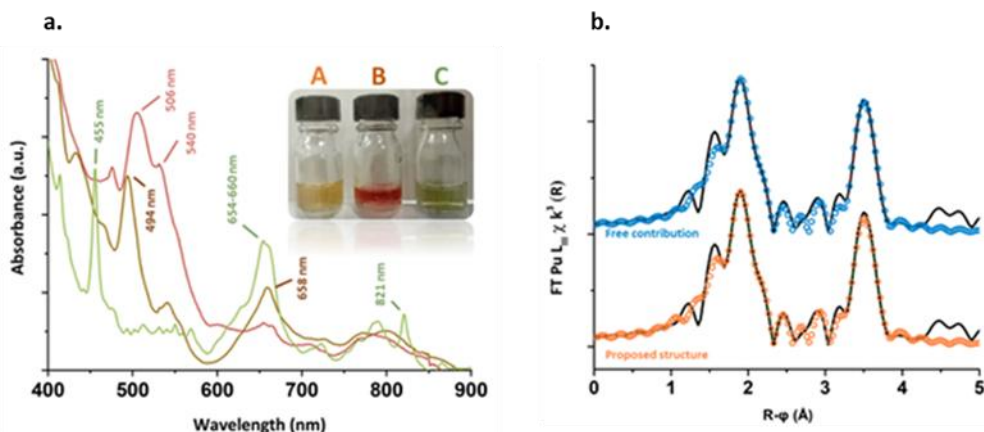
[3] Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, France

matthieu.virost@cea.fr

Over fifty years ago, the description of plutonium peroxy complexes started with the addition of hydrogen peroxide to acidic Pu(IV) solutions, forming colored species in solution. The solutions were reported to transition from the brown to the red color as H₂O₂ concentration increased. Several structures have been postulated.[1] The excessive addition of H₂O₂ to Pu(IV) acidic solutions was reported to form green precipitates, used as precursors for the purification of Pu solutions prior to PuO₂ synthesis or for nuclear spent fuel waste management.[2] Nowadays, the literature surprisingly offers only one resolved structure for Pu peroxy compounds: a dimeric peroxy carbonato compound exhibiting bridging $\mu_2\text{-}\eta^2\text{:}\eta^2\text{O}_2$ ligands [3].

In this study, we synthesized a new peroxy compound of tetravalent plutonium by diluting Pu(IV) acidic aliquots into highly concentrated solutions of H₂O₂ ($n(\text{H}_2\text{O}_2)/n(\text{Pu})$ ratio > 10) at a pH of 1-2. Such a procedure resulted in the formation of a stable green solution devoid of any precipitate. The solution displayed distinct absorption bands at 455 nm and 820 nm with a broader one located in the 654-660 nm region (Fig. 1.a). Upon drying, the solid precipitated as a green compound exhibiting an absorption spectra identical to the stable green species observed in solution. This observation, in combination to laboratory and synchrotron characterization techniques, allowed to clarify the coordination sphere of the Pu atoms and the presence and nature of the peroxy ligands in the structure (Fig. 1.b). The approach allowed us to propose a relevant polynuclear structure agreeing with the clues acquired from the different techniques.

Figure 1(a) Vis-NIR absorption spectra acquired in solution for the (A) brown (495, 541 and 658 nm), (B) red (510 and 530 nm) and (C) green (455, 654-660 and 821 nm) peroxy complexes or compounds of Pu(IV) in nitric media. Insert: photography of the respective solutions (b) FT of the experimental k^3 -weighted EXAFS spectrum (black) measured on the green peroxy complex in solution (5 mM). Blue and orange circles stand for the fits.



[1] R.E. Connick et al., J. Am. Chem. Soc. 71 (1949)

[2] J.A. Leary et al. Ind. Eng. Chem. 51 (1959) 27–31

[3] W. Runde et al. Chem. Commun. (2007) 1728.