



HAL
open science

Preparation of a water soluble plutonium (IV) cluster: A preliminary study

E. Dalodiere, M. Viro, T. Dumas, P. Moisy, Si. Nikitenko

► **To cite this version:**

E. Dalodiere, M. Viro, T. Dumas, P. Moisy, Si. Nikitenko. Preparation of a water soluble plutonium (IV) cluster: A preliminary study. Actinide 2017, Jul 2017, Sendai, Japan. hal-02433877

HAL Id: hal-02433877

<https://hal.science/hal-02433877v1>

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.

Preparation of a Water Soluble Plutonium (IV) Cluster: A preliminary Study

E. Dalodière¹, M. Viro^{1*}, T. Dumas², P. Moisy², S. I. Nikitenko¹

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

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

*e-mail: matthieu.virot@cea.fr

Introduction

Hydrogen peroxide has been considered as an important reagent for actinide chemistry because of its redox, acido-basic and complexing properties. Particularly, H₂O₂ has been used for redox control of plutonium ions and Pu(IV) precipitation in acid media.¹ The addition of hydrogen peroxide to Pu(IV) solutions may lead to brown and red peroxy complexes absorbing respectively at 495 and 540 nm, and 513 nm, respectively. Further addition of H₂O₂ leads to green precipitates of Pu(IV) peroxides that crystallizes in the hexagonal or cubic form.¹ Other related complexes or polynuclear Pu species involving peroxy ligands are really scarce. It has long been known that sonication of aqueous solutions may generate H₂ gas and H₂O₂ that accumulates in solution. Previous investigations showed for instance that the 20 kHz sonication of aqueous nitric solutions (with anti-nitrous reagent) of Pu(III) or Pu(IV) allows redox processes through the accumulation of H₂O₂ in solution.² Nevertheless, such process has never been investigated in near neutral conditions.

Results and Discussion

This work deals with the sonication of Pu(III) in weakly acid aqueous solutions. Several parameters were studied including the concentration of Pu, the acoustic frequency, and the saturating atmosphere. The sonicated Pu(III) can be totally converted into a new Pu complex absorbing at 455 and 660 nm which was found to be stable for several months (Figure 1.a.). The kinetics related to this specie accumulation can be dramatically enhanced under high frequency ultrasound and Ar/O₂ atmosphere. The investigations revealed a strong decrease of H₂O₂ accumulation rate in the presence of Pu(III) demonstrating its contribution to the process. XAS investigations at the Pu LIII edge confirmed the presence of Pu(IV) (XANES) and evidenced the formation a polynuclear cluster characterized by several coordination spheres (EXAFS) indicating the presence of several Pu-O distances and at least 4 Pu atoms (Figure 1.b.). Most probably, hydrogen peroxide and nitrate can contribute to the complex stabilization. This water soluble Pu(IV) cluster has, to the best of our knowledge, never been reported in the literature.

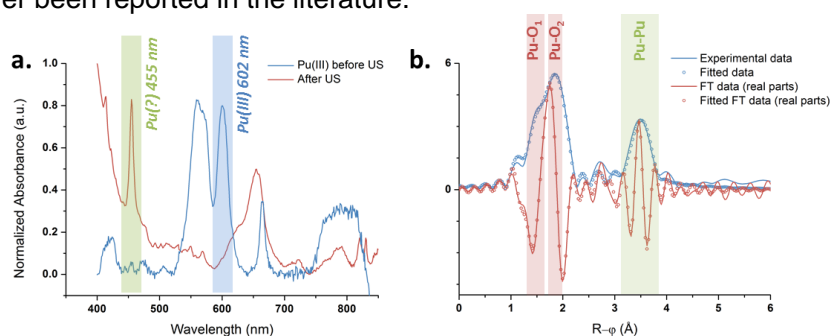


Figure 1: (a.) UV-Vis absorption spectra of the sonicated Pu(III) solution and the formed Pu(IV) cluster, (b.) Fourier transform of the k₃-weighted EXAFS spectrum of the cluster

References

1. D.L. Clark, S.S. Hecker, G.D. Jarvinen, M.P. Neu, The chemistry of the actinide and transactinide elements, Chapter seven, 2006.
2. M. Viro, L. Venault, P. Moisy, S.I. Nikitenko, Sonochemical redox reactions of Pu(III) and Pu(IV) in aqueous nitric solutions, Dalton Trans. **44**, 2567-2574 (2015)