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

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## Introduction

Hydrogen peroxide has been considered as an important reagent for actinide chemistry because of its redox, acido-basic and complexing properties. Particularly, H<sub>2</sub>O<sub>2</sub> has been used for redox control of plutonium ions and Pu(IV) precipitation in acid media.<sup>1</sup> 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 H<sub>2</sub>O<sub>2</sub> leads to green precipitates of Pu(IV) peroxides that crystallizes in the hexagonal or cubic form.<sup>1</sup> 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 H<sub>2</sub> gas and H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> in solution.<sup>2</sup> 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/O<sub>2</sub> atmosphere. The investigations revealed a strong decrease of H<sub>2</sub>O<sub>2</sub> 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.

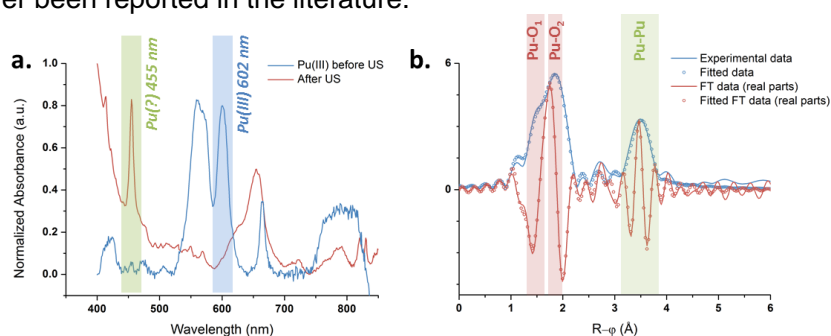


Figure 1: (a.) UV-Vis absorption spectra of the sonicated Pu(III) solution and the formed Pu(IV) cluster, (b.) Fourier transform of the k<sub>3</sub>-weighted EXAFS spectrum of the cluster

## References

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