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Preparation of a New Water Soluble Polynuclear Peroxide Complex of Pu(IV)

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Introduction

Due to its acido-basic, complexing and redox properties, hydrogen peroxide has been widely used in nuclear research and industry. Particularly, this salt-free reagent has been highly considered for the stabilization of Pu(IV) in acid conditions and the precipitation of Pu peroxides as precursors for PuO₂ preparation. The addition of H₂O₂ to Pu(VI) acid solutions allows its conversion into Pu(V) which disproportionates and allows the accumulation of Pu(IV).[1] Further addition of H₂O₂ may lead to Pu(III), or a mixture of Pu(IV) and Pu(III), through the generation of a Pu(IV) peroxy complex which decompose in acid conditions.[1,2] The continuous addition of H₂O₂ to Pu(IV) acid solutions leads to the progressive formation of a brown peroxy complex which turns red before insoluble plutonium peroxide precipitate.[2,3] The structure of these complexes which have been postulated in 1949 still remains under debate. Since, only one Pu peroxy structure has been recently proposed and concerned a dimeric molecular compound prepared in alkaline conditions.[4] The current study focuses on the behavior of Pu(IV) aqueous solutions in slightly acid conditions in the presence of hydrogen peroxide. We particularly describe the first observation of a water soluble polynuclear peroxy complex of Pu(IV) which has, up to our knowledge, never been reported in the literature.

Results and Discussion

While the dispersion in pure water of Pu(IV) previously stabilized in nitric media leads to its hydrolysis and the generation of stable Pu(IV) colloid suspensions, the dispersion of a similar solution in dilute aqueous solutions of H₂O₂ leads to different phenomena. For molar ratios of Pu(IV) to H₂O₂ equal to 0.5, an absorption band standing at 495 nm can be observed on Vis-NIR absorption spectra which can be attributed to the brown Pu(IV) peroxide complex described by Connick and McVey in 1949.[2] This solution is found to be rapidly reduced to Pu(III) with a characteristic absorption band standing at 602 nm. The dispersion of Pu(IV) solutions in more concentrated aqueous solutions of H₂O₂ leads to the formation of a green Pu solution absorbing at 455 and 660 nm which has, up to our knowledge, never been reported in the literature (Fig. 1.a.). Sonication at high frequency (203 kHz, 250 mL, 20°C, 0.13 W mL⁻¹) of a 1 mM Pu(III) solution under Ar/O₂ atmosphere also lead to green and pure solutions having similar absorption spectra. The oxidation and formation of Pu(III) was attributed to the consumption of the sonochemically generated hydrogen peroxide.

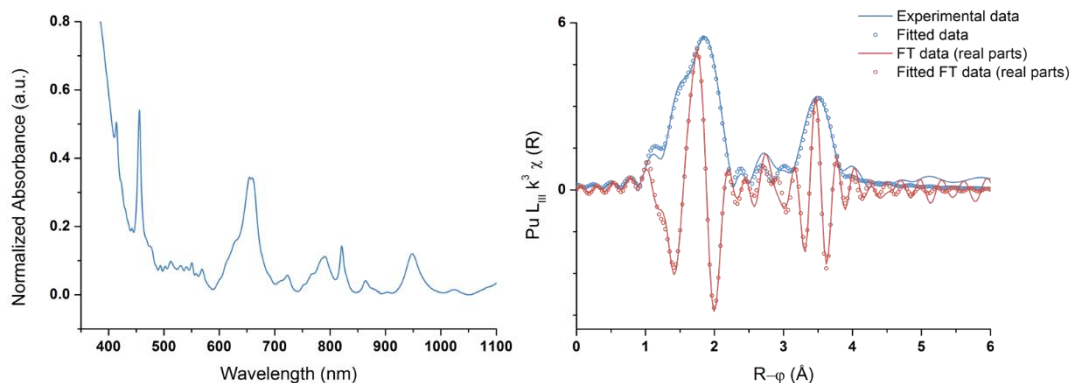


Figure 1: (a.) Vis-NIR absorption spectra of the formed Pu(IV) polynuclear complex, (b.) Fourier transform of the k^3 -weighted EXAFS spectrum exhibiting two coordination spheres for the green peroxy complex.

Raman spectroscopy of this green solution allowed the observation of a vibration band standing at 833 cm^{-1} that can be attributed to the O-O symmetric stretching mode of the $\mu:\eta^2-\eta^2$ peroxy ligand in agreement with the literature.[5] XAFS investigations evidenced the formation of a polynuclear assembly made out of Pu(IV) and characterized by several Pu-O distances and at least 4 Pu atoms (Fig. 1.b.). The as-prepared solutions were found to be stable for several months before they slowly convert into a Pu(IV) colloid suspension characterized by an absorption band standing at 620 nm and a strong absorption in the near-UV range (Mie scattering). These colloids were compared to “classical” colloid suspensions obtained by controlled dilution in pure water of Pu(IV) previously stabilized in nitric media. UV-vis spectroscopy, XAFS and HR-TEM experiments showed that colloidal suspensions obtained from Pu green peroxy complex were composed of monodispersed and spherical crystalline PuO_2 particles having a smaller size (ca. 2.4 nm, Fig. 2) than what reported for “conventional” chemistry (ca. 2.9 nm).

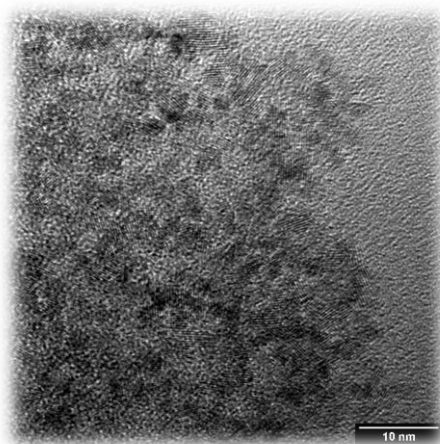


Figure 2: HR-TEM observation of a Pu colloid obtained from the new Pu peroxy complex.

Conclusion

This study shows that the dispersion of Pu(IV) in concentrated aqueous solutions of H_2O_2 leads to the observation of a green and water soluble peroxy complex that has, up to our knowledge, never been reported in the literature. Characterizations made with Vis-NIR, XAFS and Raman spectroscopies confirmed the formation of a polynuclear Pu(IV) peroxy complex which is found to be very stable but slowly transforms into stable Pu(IV) colloid suspensions composed with smaller PuO_2 particles in comparison to what observed with “classical colloids”. More generally, this study brings new knowledge about plutonium chemistry in the presence of hydrogen peroxide. Moreover, radiolytic hydrogen peroxide formation has been demonstrated in environmental conditions which force to

consider the formation of water soluble peroxo complexes in the actinide migration models. We demonstrate in this study that this polynuclear complex can be an intermediate between dissolved ionic Pu species and the formation of Pu(IV) colloids.

Experimentals

The experiments were performed in Atalante facility (Marcoule) in a glove box dedicated to Pu chemistry. The stock solution of Pu(IV) (96.9% ^{239}Pu , 2.98% ^{240}Pu , 0.04% ^{241}Pu , 0.06% ^{242}Pu) was prepared in 2 M HNO_3 by standard anion exchange resin according to previous procedures.[6] During the experiments, the solutions were characterized with UV-vis-NIR absorption spectroscopy (shimadzu UV3600) in 1 cm quartz cells. Raman spectra of the Pu complex were measured on a droplet of a centrifuged solutions previously concentrated under Ar flow and deposited onto a glass slide. XAFS experiments were performed at the Pu L_{III} -edge at the European Synchrotron (ESRF, France; BM20 ROBL beamline). HR-TEM investigations were carried out at the Joint Research Centre of the Institute for Transuranium Elements (Karlsruhe, Germany) using a TecnaiG2 (FEITM) 200 kV microscope modified for the examination of radioactive samples.

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