

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

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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 PuO₂ 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 H₂O₂ 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/O₂ atmosphere (203 kHz, 250 mL, 20°C, 0.13 W mL⁻¹). 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 PuO₂ particles covered by hydrolyzed Pu(IV) moieties of approximately 2.4 nm.

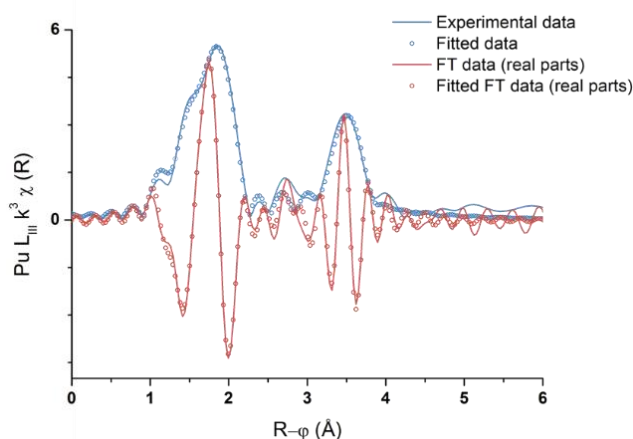


Fig. 1: Fourier transform of the k₃-weighted EXAFS spectrum exhibiting two coordination spheres for the green peroxo complex.

[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.