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Preparation and Structural Characterization of an Original Peroxide Complex of Pu(IV)

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Forecasting the behavior of radionuclides within the geosphere or deep underground storage facilities necessitates a comprehensive grasp of the species that may arise when actinide (An) related materials interact with groundwater. A critical facet of An chemistry involves the radiolytic generation of hydrogen peroxide (H₂O₂), which can exert notable influence on the environmental dispersal of An by modifying the initial structure of the compounds and/or generate highly stable nanoscale species.[1] While peroxo-based hexavalent actinides (An) have been extensively investigated through the synthesis of uranyl cage clusters and mineral compounds, the literature description of tetravalent An peroxides is surprisingly lacking and limited to only a few Pu and Th compounds.[2-4] The interactions between H₂O₂ and Pu have been already described during the Manhattan project for several purposes (ex: oxidation state adjustment, purification, precipitation).[5] The stoichiometric addition of H₂O₂ to acidic Pu(IV) solutions was reported to generate the so-called “brown peroxo complex” which transitions to the “red peroxo complex” when increasing the concentration of H₂O₂. [Pu₂(O₂)(OH)]⁵⁺ and [Pu₂(O₂)₂]⁴⁺ have been respectively proposed as structures.[6] For higher amounts of H₂O₂, the precipitation of a green solid that may vary in composition and structure was described.[7] Until now, the precise structures for these complexes and solid precipitates have remained elusive and only postulated.

This presentation will discuss the recent preparation and structural characterization of an original water-soluble peroxo complex of Pu(IV). The latter was prepared by dilution of an acidic Pu(IV) solution aliquot into a large volume of an aqueous solution of concentrated H₂O₂ at pH= 1-2. Such a procedure resulted in the formation of a stable green solution devoid of any precipitate. Laboratory and synchrotron characterizations allowed acquiring structural information about this compound. Both the solution and solid precipitated from a saturated solution evidenced structural similarities that allowed us to propose a relevant structure for which the simulated EXAFS spectra perfectly matched with the experimental one.

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