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Synthesis and characterization of a hexanuclear plutonium(IV) in acetate solution from EXAFS and DFT

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Texte: Polynuclear actinide complexes (or clusters) are molecular entities composed of several metallic centers. Beyond the different types of clusters, we are interested in molecules in which actinide atoms are connected through aquo, hydroxo or oxo ligands. Those structures require further complexation by organic or inorganic ligands (Cl^- , SO_4^{2-} , NO_3^- or RCOO^-) to be stabilized.¹ This project focuses on tetravalent actinide, especially Pu(IV) in acetate solutions. In order to obtain plutonium cluster, pH and ligand concentration was set to allow both condensation and complexation. First, the Vis-NIR absorption spectroscopy at $[\text{AcOH}]_{\text{tot}}=1$ M and $\text{pH}=4.5$ suggested the Pu(IV) complexation with acetate, without colloid formation. Secondly, the EXAFS spectrum evidenced the formation of a polynuclear plutonium cluster in solution. In order to confirm this observation, the *ab initio* EXAFS spectrum of the expected $\text{Pu}_6\text{O}_4(\text{OH})_4(\text{AcO})_{12}(\text{H}_2\text{O})_6$ complex was calculated using DFT method. The k^3 -weighted simulated signals were compared to the experimental one and confirmed its synthesis in solution. Finally, in order to observe if this signal was specific to hexanuclear system, plutonium clusters EXAFS spectra from trimer to hexamer were simulated by DFT (figure 1). The cluster geometry and nuclearity have an impact on the EXAFS simulated signal and confirmed the $\text{Pu}_6\text{O}_4(\text{OH})_4(\text{AcO})_{12}(\text{H}_2\text{O})_6$ stoichiometry. This result highlights the importance of polynuclear species for plutonium speciation in hydrolytic conditions and the necessity to study them to reevaluate distribution diagrams which, up to now, do not take into account such species.

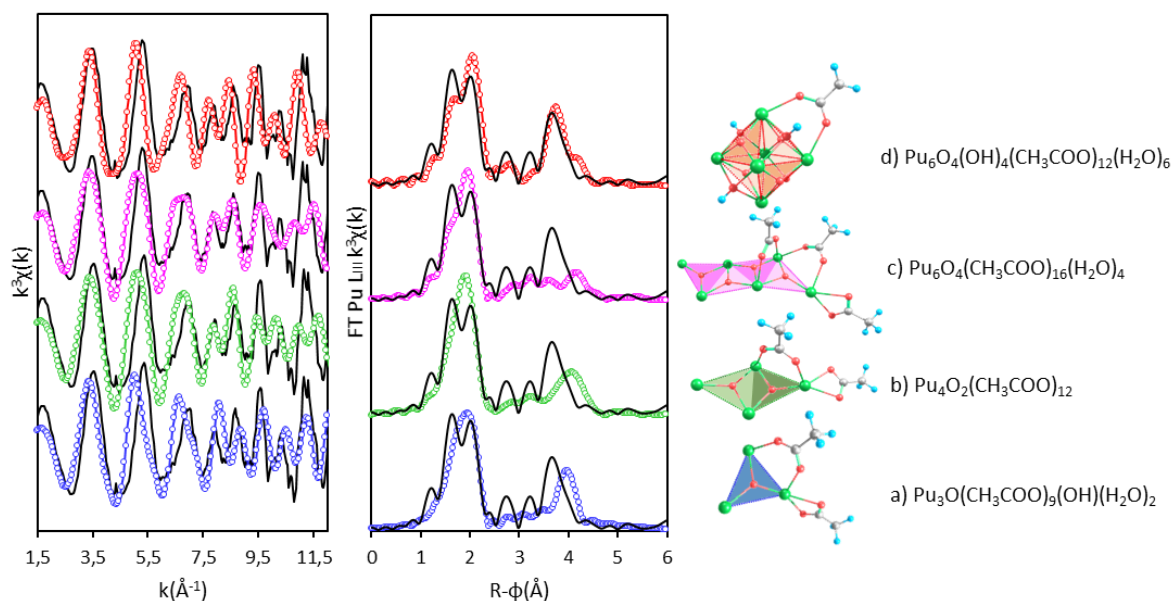


Fig. 1 Calculated k^3 -weighted EXAFS oscillation and corresponding FT between 1.5 \AA^{-1} and 12 \AA^{-1} for trimer $\text{Pu}_3\text{O}(\text{CH}_3\text{COO})_9(\text{OH})(\text{H}_2\text{O})_2$ (blue open circles), tetramer $\text{Pu}_4\text{O}_2(\text{CH}_3\text{COO})_{12}$ (green open circles), flat hexamer $\text{Pu}_6\text{O}_4(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4$ (pink open circle) and octahedral hexamer $\text{Pu}_6\text{O}_4(\text{OH})_4(\text{CH}_3\text{COO})_{12}(\text{H}_2\text{O})_6$ (red open circles). DFT calculations at the B3LYP/RECP82/6-31G(d,p)/PCM level. Experimental data are given in black line.