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Synthesis and Characterization of Polynuclear Actinide(IV) Species

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The actinide chemistry is largely influenced by the formation of polynuclear species that have attracted valuable interest over the last decades. These species have been proven to play a potential role in the management of waste, fuel reprocessing and even in biological media. The polynuclear species of tetravalent actinides (i.e., actinides clusters) discussed here materialize as molecules containing multiple metal centers connected by oxo and/or hydroxo groups. This forms the core of the cluster, often described by its nuclearity, N , which represent the number of actinides in it. These entities are formed through condensation reactions (referred to as olation and oxolation reactions) in the presence of water and are surface-stabilized by organic or inorganic ligands.^[1]

In the solid state, various polynuclear species of actinides(IV) have been identified from XRD crystal structures, with various nuclearities ranging from 2 to 38. However, the hexamer consisting of 6 plutonium atoms (Pu_6) is frequently observed.^[1] This nuclearity has been studied and stabilized several times in the form of the $[\text{Pu}_6\text{O}_4(\text{OH})_4]^{12+}$ core. Takao *et al.* investigated the formation of hexanuclear clusters of neptunium, uranium, and thorium in solution, in the presence of carboxylate ligands.^[2] Our group have also studied the formation of plutonium hexameric clusters under various conditions. The results revealed similarities in UV-Vis spectra associated with this nuclearity.^{[1] [3, 4]} However, studies in aqueous solutions are still inadequate, and it remains difficult to identify these polynuclear species in solution.

Additionally, recent studies suggest that these species could play a role in the formation mechanism of PuO_2 colloidal nanoparticles.^[5] Indeed, some hexanuclear Pu(IV) clusters have been identified as reactive intermediates in this process. Colloid formation is an irreversible process that may pose challenges in the context of used nuclear fuel reprocessing. Understanding the formation of polynuclear actinide species is thus crucial for comprehending and mastering the formation of colloids in solution.

The first objective of this study is to develop reliable spectroscopic databases, in order to help the identification of polynuclear species in solution. This work begins with the synthesis of plutonium(IV) single crystals characterized by X-ray diffraction (SCXRD), which specific spectra are collected with UV-visible and vibrational spectroscopies (IR and Raman). This approach will simplify the identification of these species in solution, enhance the understanding of the mechanisms involved in the formation of polynuclear species, as well as their evolution towards the formation of colloids. Preliminary results will be presented in the poster.

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