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## Structure and Stability of plutonium hexanuclear cluster in the gas phase and in solution

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The chemistry of Plutonium(IV) is largely influenced by hydrolysis and condensation reactions leading to the formation of oxo/hydroxo oligomeric species. Such plutonium clusters are known as being an essential part of plutonium speciation in solution but their formation, stability and reactivity is yet largely unknown. For Pu(IV) and all tetravalent actinides, the hexamer is the most common unit that has been observed in solid state and in solution. Its core corresponds to  $[An_6O_4(OH)_4]^{12+}$  and is stabilized with additional organic or inorganic ligands on its surface. With Pu(IV), two hexameric structures have been characterized by Single Crystal X-Ray Diffraction X with glycine [1] and with a polyaminocarboxylate acid (DOTA) [2]. For such polynuclear species, the main difficulty is to establish their presence and stability in solution. In the present work, we have combined DFT calculations with Vis-NIR, EXAFS spectroscopies and ESI-MS Mass Spectrometry in order to investigate plutonium cluster formation with acetate ligand. By coupling spectroscopic and theoretical methods it was possible to establish the presence of the hexameric core in the solution [3]. ESI-MS was applied to the acetate solution, a series of Pu(IV) hexameric clusters were detected indicating the strong stability of such clusters. The structure and thermodynamic stability of the clusters were further analyzed by using DFT calculations.

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[1] Knope, K. E, Soderholm, L. (2013) *Inorg. Chem.* 52, 6770-6772.

[2] Tamain, C., Dumas, T., Guillaumont, D., Hennig, C., Guilbaud P. (2016) *Eur. J. Inorg. Chem.* 22, 3536-3540.

[3] Chupin, C., Tamain, C., Dumas, T., Solari, P., Moisy P., Guillaumont D. (2022) *Inorg. Chem.* 61, 4806-4817.