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Inner and outer sphere plutonium(IV) coordination with amide and carbamide ligands

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INTRODUCTION

A thorough characterization of actinide coordination chemistry in organic solution is of particular interest in the development of effective solvent extraction separations for waste remediation in advanced nuclear fuel cycles. This is all the more important for plutonium(IV) extraction that Pu(IV) exhibits a large diversity of coordination structures in organic solution.

In the present work, we have combined spectroscopic and computational methods to elucidate the structures of plutonium(IV) ions with dialkyl monoamide and tetraalkyl-carbamide ligands in the solid state and in solution. Monoamides are the most serious alternative candidates to replace tri-n-butyl phosphate (TBP) to achieve uranium(VI) and plutonium(IV) separation and they have received increasing attention.[1] It has been shown that slightly altering ligand's structure or experimental conditions induce large variations of Pu(IV) extraction properties while uranium(IV) extraction is much less impacted. In order to better understand the key contributions that govern plutonium extraction efficiency, Pu(IV) coordination structures with monoamide and carbamide ligands have been investigated by varying the extractant structures (size and branching of alkyls chains, amide versus carbamide) and experimental conditions (nitric acid or extractant concentrations).[2,3]

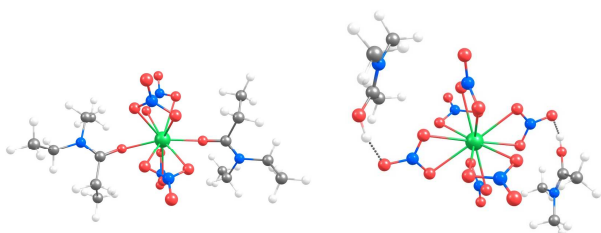


Fig. 1. Schematic representation of Pu(IV)-monoamide inner- and outer-sphere complexes $\text{Pu}(\text{NO}_3)_4\text{L}_2$ (left) $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$ (right)

RESULTS

Pu(IV) structures were first determined in the solid state from single crystal X-ray diffraction methods. The molecular structure is $\text{Pu}(\text{NO}_3)_4\text{L}_2$ with four bidentate nitrates and two monoamide or carbamide ligands

The structures of Pu(IV) complexes were further determined in organic solution upon extraction from a nitric acid aqueous solution to determine whether Pu(IV) maintains its solid state structure in the organic solution. By coupling UV-Vis and EXAFS spectroscopies with DFT calculations, it is shown that Pu(IV) in solution can adopt inner- or outer-sphere coordination structures. Inner-sphere Pu(IV) complex corresponds to the $\text{Pu}(\text{NO}_3)_4\text{L}_2$ structure while outer-sphere complex corresponds to $\text{Pu}(\text{NO}_3)_6(\text{HL})_2$ with two protonated ligands in the second coordination sphere (Figure 1.) Furthermore, the spectroscopic studies shows that the preference for outer- over inner-sphere complexation can be monitored by subtle variations of extractant's structure and experimental conditions. Steric hindrance in the metal's first coordination were quantified from DFT calculations and show that it is not only the first coordination sphere that modulates coordination structure, key contributions also come from the surrounding beyond the inner coordination sphere.

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