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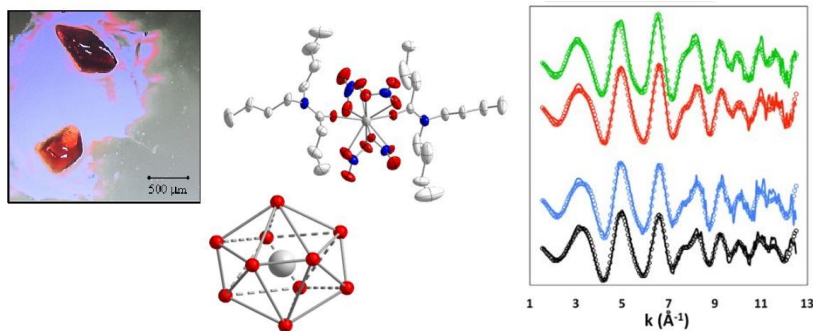
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Structure and radiolytic stability of monoamide-actinide complexes

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In the field of nuclear fuel reprocessing, N,N-dialkyl monoamides are alternative organic ligands to achieve the separation of uranium(VI) and plutonium(IV) from highly concentrated nitric acid solution. One of the very interesting features of these ligands is the strong influence of their alkyl groups on their extraction properties. It gives the possibility to tune their extracting strength and selectivity toward uranium (VI) and plutonium (IV) by altering the length and branching of monoamide alkyl chains. Despite their strong industrial interest, few basic studies have been reported on this effect and the understanding of this strong influence on monoamides extracting properties is yet to be achieved. Among the properties that are important for a comprehensive understanding of selective extraction processes, the stoichiometries and coordination structures of the actinide complexes in the organic solution can provide crucial information regarding extraction mechanisms. The study presented here combines experiments (EXAFS, XRD, ESI-MS) and theoretical calculations (DFT) aiming to describe the structures of the complexes formed between Pu(IV) and different N,N-dialkyl monoamides, and the impact of radiolysis on these complexes.

It is shown that the coordination structure of U(VI) is analogous in the solution and in the solid state and is independent of the alkyl chain: two monoamide ligands and four bidentate nitrate ions coordinate the uranyl ion. With linear alkyl chains monoamides, Pu(IV) also adopt identical structures in the solid state and in solution with two monoamides and four bidentate nitrate ions. With branched alkyl chain monoamides, the coordination structure of Pu(IV) was more difficult to establish unambiguously in solution. However, using a combination of EXAFS spectroscopy experiments with DFT calculations, it was possible to show that the branched alkyl chains amide form partly outer-sphere complexes with protonated ligands hydrogen bonded to nitrate ions, that could explain the different extraction properties of these ligands.

In the actinide solvent extraction processes, the organic solutions are subjected to radiolysis that can lead to an alteration of the ligands properties, and especially to their extraction efficiency and selectivity. Therefore, the effects of radiolysis on the speciation of the complexes in solution have been studied using ESI-MS spectrometry. Both gamma source irradiated solutions and direct in-situ alpha irradiated solutions have been studied in order to compare the nature of irradiation.