

Comparative NMR study of partitioning-relevant complexes with trivalent actinides and lanthanides to elucidate the origin of their selectivity

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Partitioning and transmutation (P&T) is a strategy of reducing the long term radiotoxicity of spent nuclear fuel, thereby minimizing the required storage time. P&T involves separating actinides, possibly recycling them as nuclear fuel, and fissioning the long-lived actinides into shorter-lived fission products. In this context the separation of trivalent actinides from the chemically similar lanthanides is a key step. This separation can be performed by liquid-liquid extraction using selective N-donor extracting agents, e.g., alkylated bis-triazinyl-pyridines (BTP). These have high separation factors (>100) for trivalent americium over europium. However, little is known of the origin of their selectivity.

Previous studies have shown that actinide and lanthanide complexes of BTP are isostructural. Therefore a comparative study of the different binding modes of actinides and lanthanides is possible: NMR spectroscopy, as a tool to study the effect of changes of the electron density around the observed nuclei, is ideally suited to address this question. By separating different contributions to the overall chemical shift, especially monitoring the paramagnetic chemical shift on selected ligand nuclei, it is possible to elucidate the ratio of dipolar and covalent interactions between ligand and the chelated trivalent actinide or lanthanide. A comparison of the different metal ions is given.

An additional contribution to the overall chemical shift is the interaction of the electron poor aromatic system with the charge compensating anion. To elucidate the mode of interaction, a number of complexes were investigated and the resulting shifts referenced to a complex with non coordinating anions as charge compensation. The differences in the interaction mode of chloride and nitrate anions in these complexes will be presented.

Acknowledgement: This work is supported by the German Federal Ministry of Education and Research (BMBF) under contract numbers 02NUK012A and 02NUK012D.