

A comparative NMR study of complexes of trivalent actinides and lanthanides with partitioning relevant N-donor ligands

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ABSTRACT. 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 and fissioning them 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, as every observable effect on the electron density of the ligand may be attributed to a change in the central metal ion of the complex. NMR spectroscopy, as a tool to study such effects on the electron density around the observed nuclei, is ideally suited to address this question. By separating different contributions to the overall chemical shift, especially separating and monitoring the dipolar and Fermi-contact part of the paramagnetic chemical shift on selected ligand nuclei, it is possible to elucidate the ratio and nature of interactions between the ligands and the chelated trivalent actinide or lanthanide. A comparison of complexes with different *f*-element metal ions is revealing different degrees of covalency in the interaction between metal ions and BTP.

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