Anionic effects observed in complexes of trivalent lanthanides with partitioning relevant N-donor ligands

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ABSTRACT. World-wide efforts are being made to optimize separation technologies for removing trivalent actinides (An) from their chemically similar lanthanides (Ln) from nuclear waste streams. This is a key step in the partitioning and transmutation (P&T) strategy for reducing the long term radiotoxicity of spent nuclear fuel. Separation of An from Ln in nitric acid solution can be performed by liquid-liquid extraction using selective N-donor agents, e.g., alkylated bis-triazinyl-pyridines (BTP) in organic solvents. In efforts to optimize such separations, comparative investigations of An and Ln interaction with different extracting agents, solvents and solution components are performed.

Previous studies show that An- and Ln-BTP complex interaction with different charge compensating anions varies. To elucidate the nature of the interaction of (application relevant) nitrate anions, a number of BTP complexes with different anions are studied using NMR techniques. From the beginning of the '90s, anions are known to interact with electron poor aromatic systems. Associated changes in electron density on the aromatic ring are expected to affect changes in the chemical shift of nuclei in direct proximity. By separating the anionic effect from other parameters influencing chemical shifts of selected ligand nuclei using comparative NMR data on "reference complexes" with a non-coordinating anions, we are able to differentiate modes of interaction; chloride anions coordinate directly and nitrate anions insert between ligands in the complexes.

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