

Combined TRLFS, EXAFS and Theoretical Investigations on Actinide/Lanthanide Complexed with Partitioning-relevant N-Donor Ligands

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Partitioning & transmutation (P&T) aims at reducing the long-term radiotoxicity of high-level nuclear wastes through separation of long-lived actinides from spent nuclear fuels and transmuting them by irradiation with neutrons into short-lived isotopes. The separation of trivalent actinides (An(III)) from lanthanides (Ln(III)) is a key step in the partitioning & transmutation (P&T) strategy as some Ln nuclides have a high neutron absorption, which would reduce actinide transmutation efficiency. The chemical properties and the ionic radii of An(III) and Ln(III) are comparable, rendering high demands on the selectivity of the extraction ligand. Various soft N-donor ligands have been developed, which separate An(III) from Ln(III) elements in liquid-liquid extraction with high separation factor. Alkylated 2,6-di(1,2,4-triazin-3-yl)pyridines (BTP) are such highly effective extraction ligands. In liquid-liquid extractions these extractants are able to extract An(III) selectively over Ln(III) from nitric acid solutions into the organic phase. This is of technological importance, as these elements will be in a nitric acid solution following dissolution of spent nuclear fuel and subsequent separation of Pu in the PUREX process. Our research focuses on attempts to understand the underlying reason for the partitioning ligand selectivity. This information can potentially be used to optimize partitioning ligand design and, hence, extraction performance.

Comparative structural investigations using X-ray absorption spectroscopy (EXAFS) on An(III) and Ln(III) complexed with 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (BTP) are performed in order to evaluate if ligand selectivity is caused by coordination structure differences, specifically in variations in the metal cation-N bond lengths. Our EXAFS investigation on Cm(III), Am(III), Gd(III), and Eu(III) complexed with BTP in non-aqueous organic solution show the solution structure to be the 1:3 complex with a structure comparable to crystal structures of solid Ln-BTP₃. The complex is comprised of three ligands directly bond to the metal ion, with BTP acting as a tridentate ligand via binding of the central pyridine nitrogen (N_{py}) and two triazine nitrogens (N_{tz}) of the neighboring rings to the metal cation. In our EXAFS analysis we find no significant differences in the coordination numbers and bond distances of An-BTP₃ and Ln-BTP₃. We conclude that the observed selectivity of BTP for An(III) over Ln(III) is not structural in origin. Quantum

chemical calculations performed at different levels support this finding.

In contrast, trends in their TRLFS spectra are different. Depending on the ligand concentration, different Ln/An-BTP complexes are formed, namely the 1:1 and 1:3 complex for Eu(III) and the 1:1, 1:2 and 1:3 complex for Cm(III). Eu-BTP₂ has never been observed though we assume that it is formed as an intermediate product during the transformation of the 1:1 into the 1:3 complex but can not be detected as a stable species. In addition, speciation studies on Cm(III) and Eu(III) performed at elevated temperature (20-80 °C) and kinetic studies reveal significant differences in the thermodynamic constants and rate constants of the complex formation indicating a significantly higher affinity of the BTP toward Cm(III), which is in good agreement with the high selectivity for trivalent actinides over lanthanides in liquid-liquid extraction.

In order to determine the influence of the electron density of BTP ligands on the complexation properties and the extraction behavior, new BTP ligands with additional groups (Cl, OMe) are synthesized displaying a decreased/enhanced electron density in comparison to the non substituted BTP ligand. Thereby, an excellent correlation is found between the high electron density, the complexation strength and the extraction properties (separation factors, distribution coefficients).

Our results show that the observed selectivity of BTP for Cm(III) over Eu(III) is not structural in origin. Despite insignificant differences in the structure, the complexation behavior of An(III)- and Ln(III) toward BTP is significantly different: The higher affinity of BTP toward trivalent actinides (*thermodynamics*) and the faster formation of An(III)-BTP₃ (*kinetics*), in particular for ligands with bulky alkyl groups, are consistent with the extraction behaviour and the selectivity in liquid/liquid extraction. These results yield insight into the selectivity of N-donor ligands and can make a valuable contribution to a future design of highly efficient extraction ligands.