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Comparative investigation of N donor ligand and lanthanide/actinide partitioning complexes from the metal and ligand point of view

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Abstract:

N-donor ligands such as n-Pr-BTP (2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine) [1] studied here preferentially bind trivalent actinides (An(III)) over trivalent lanthanides (Ln(III)) in liquid-liquid separation of An(III) from spent nuclear fuel [2]. However, the chemical and physical processes responsible for this selectivity are not yet well understood [3]. We present systematic comparative X-ray absorption spectroscopy (XAS) investigations at the An/Ln L3 edge and the N K edge of An/Ln(n-Pr-BTP)₃ An/Ln(n-Pr-BTP)₃ and Ln(n-Pr-BTP)₃ complexes. These studies will potentially help to differentiate bonding mechanisms between An and Ln bound to different ligands and counter ions by determining orbital energy differences and relative electronic populations.

We find that the energy position of the pre-edge in N K edge XAS spectra for all studied Ln metal complexes is inversely correlated with the distribution ratios for Ln extraction into the organic phase. The origin of the pre-edge is explained by TDDFT (ORCA, ADF, TURBOMOLE) calculations [4]. It consists of excitations to several frontier orbitals, each containing contributions from several chemically non-equivalent N atoms. Analyzing the origin of the 1s electronic transitions allows to identify the contributions of non-equivalent N atoms of the BTP molecule to the spectra. Calculations of the La(BTP)₃ complex show a different transition sequence, suggesting higher charge density in the vicinity of the bonding N atoms. The lower oscillatory strength of transitions from bonding N atoms compared to non-bonding N atoms for the complex compared to the free ligand might be interpreted as evidence for lower contributions of N p states to π^* molecular orbitals, suggesting strong admixtures of metal orbitals in the complex. We will compare calculations for La/Eu(BTP)₃ and Am(BTP)₃. High-energy resolution An/Ln L3 edge XANES (HR-XANES) shows that complexation with n-Pr-BTP influences the electronic structure in terms of higher charge density on the An/Ln cations. The pre-edge observed in Ln(n-Pr-BTP)₃ originates from 2p \rightarrow 4f electronic transitions as shown by ab initio quantum chemical calculations (FEFF9.5 code [5]).

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