Investigation of metal-ligand bonding in lanthanide partitioning complexes by high-resolution XANES

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One of the major steps in the partitioning and transmutation (P&T) strategy for reduction of the long-term radiotoxicity and heat load of spent nuclear fuel is the separation of 5f elements (actinides, An) from the chemically similar 4f counterparts (lanthanides, Ln) and subsequent fission of long-lived 5f elements to shorter lived nuclides (transmutation). This separation is necessary as some of the lanthanides (Ln(III)) have large neutron cross sections and thereby compromise transmutation efficiency in the nuclear fission process. Separation of An(III) from Ln(III) by selective liquid-liquid extraction has been demonstrated using soft donor extracting agents such as heterocyclic N-donor ligands. The hydrophobic bistriazinylpyridines (BTP) [1] (Fig. 1(a)) and bistriazinylbipyridines (BTBP) [2] (Fig. 1(b)) show excellent extraction efficiency, e.g., their separation factors (SF) for Am(III) over Eu(III) are greater than 100 (SF = distribution ratio $D_{Am}/D_{Eu}$; $D_M = [M]_{org}/[M]_{aq}$) upon extraction. Optimization of partitioning ligands for selectivity and radiolytic stability is a topic of global interest, as the present ligands do not yet fulfill all criteria for application in an industrial process.

![Figure 1: (a) 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (BTP); (b) 6,6’-bis(5,6-dialkyl-[1,2,4]triazin-3-yl)-[2,2’] bipyridine (BTBP)](image)

Our aim is to characterize the role of Ln 4f and 5d states in Ln-ligand bonding in Ln(III)-complexes (Ln = Sm, Eu, Gd) studying their high-energy resolution (HR-) X-ray absorption near edge structure (XANES) spectra by varying the metal ligands (BTP, BTBP) and counter-ions ((ClO$_4^-$), (NO$_3^-$)). and correlating changes in spectral features with changes in the Ln coordination environment. The applied HR-XANES overcomes instrumental and core-hole lifetime broadening effects and thereby provides detailed spectral features. Only the results for Gd are described in detail here.

Experiment:
Incident X-rays were tuned to energies from 40 eV below to 70 eV above the Gd L3 edge. The X-rays emitted from the sample were energy analyzed by a Johann spectrometer in dispersive geometry [3]. A spherically bent crystal with a 1 m radius of curvature at Bragg angle $\theta = 78.3^\circ$ (Gd L\,\alpha\, emission line, 6053.4 eV) was employed as analyzer. XANES spectra were extracted by partial integration over all emission lines.

Results:
The influence of different counter-ions on the Gd-BTP complex and Gd(ClO$_4$)$_3$ and Gd(NO$_3$)$_3$ spectra lies mainly in differences in the area above the most intense absorption resonance (white...
line, WL) at \(\sim 7.255\) keV (Figure 2(a)). As expected, the counter-ions have less influence on this part of the complex spectra than on those for the perchlorate and nitrate species. However, the counter-ions do influence the electronic structure of the cation, as indicated by the shift of the Gd(BTP)\(_3\)(ClO\(_4\))\(_3\) spectrum to lower energies and by the decreased area of its WL, which indicates less cation-to-ligand charge donation and a higher relative population of 5d states in Gd(BTP)\(_3\)(ClO\(_4\))\(_3\) than in Gd(BTP)\(_3\)(NO\(_3\))\(_3\). The charge density on gadolinium in Gd(BTP)\(_3\)(NO\(_3\))\(_3\) is less than in Gd(NO\(_3\))\(_3\), as the Gd(BTP)\(_3\)(NO\(_3\))\(_3\) spectrum is shifted to lower energies compared to the Gd(NO\(_3\))\(_3\) spectrum. In Figure 2(b) the effects of metal complexation with different ligands are shown. While the Gd(BTBP)\(_3\)(NO\(_3\))\(_3\) spectrum hardly varies compared to the Gd(NO\(_3\))\(_3\) spectrum, the Gd(BTP)\(_3\)(NO\(_3\))\(_3\) spectrum shows pronounced differences, suggesting larger relative differences in geometric and electronic structure. The additional intensity below the white line, especially noticeable for Gd(BTP)\(_3\)(NO\(_3\))\(_3\), points to the presence of a pre-edge associated with photoelectron transitions to partially allowed 4f final states. Future work will focus on experiments using a spectrometer with enhanced energy resolution, in order to resolve the pre-edge feature. From analysis of this pre-edge and the white line, we expect to obtain information about the energy position and electronic population of the Ln 4f and 5d states, which will help us to understand their role in the metal-ligand bonding. By comparing the obtained results with analog investigations of An(III) partitioning complexes we hope to be able to explain the origin of these ligands’ selectivity for An(III) over Ln(III).

![Graphs showing absorption spectra](image)

**Figure 2:** Comparison of compounds with (a) different counter-ions; (b) different ligands

**References**