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Covalency in actinide extractants

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Nuclear energy is the most viable alternative to fossil fuel combustion until large-scale renewable energy technologies can be implemented. However, use of nuclear energy is limited by the difficulties in remediation, management, and disposal of nuclear waste and the significant hazard posed by the minor actinides present in spent fuel. Efficient separation of trivalent minor actinides from lanthanide ions represents a long-standing challenge because of the similar chemical properties shared by 4f- and 5f-elements. For reasons not well understood, some soft-donor ligands (e.g., dithiophosphinic acids, R₂PS₂H) are known to selectively extract actinides from lanthanides, with Am/Eu separation factors on the order of 100,000 observed (Klaehn, J. R. et al. *Inorg. Chim. Acta* 2008, 361, 2522). It is likely that this phenomenon results from increased covalency with actinides over lanthanides; however, a clear understanding of f-element participation in covalent bonding has not been established. Recent pioneering work of Solomon, Hedman, and Hodgson significantly advanced capabilities in ligand K-edge X-ray absorption spectroscopy (XAS) to directly measure covalency in bonding (Solomon, E. I. et al. *Coord. Chem. Rev.* 2005, 249, 97). We will discuss the use of ligand K-edge XAS and time-dependent density functional theory (TDDFT) to evaluate a novel family of dithiophosphinate extractants. We investigate M–S₂PR₂ orbital mixing for a carefully selected series of dithiophosphinate complexes by comparing the solid-state and solution-phase sulfur K-edge X-ray absorption spectra, in conjunction with TDDFT. The conclusions derived from solid-state S K-edge measurements are validated through comparison with extractants in solution, providing a foundation for in situ studies of liquid-liquid extraction systems. Furthermore, we investigate the relative roles of 3d, 4d, 5d, and 6d/5f-orbitals in M–S covalent bonding and provide preliminary insight into the structure-to-function relationships that may correlate with the selective extraction of trivalent minor actinides from trivalent lanthanides.

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