Glenn T. Seaborg Center Special Seminar

Ligands Design for Actinide Separations in Spent Fuel Reprocessing: From Fundamental Chemistry to Application

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Bldg. 70A, Rm. 3377

The separation of trivalent actinides, An(III), from Ln(III) and the separation of Cm(III) from Am(III) are two very challenging tasks in spent nuclear fuel reprocessing and in high level nuclear waste treatment. The fundamental chemistry in a promising process for the separation of An(III) from Ln(III) and for the separation the Am(III) and Cm(III) from each other has been systemically studied.

In contrast to usual ligands forming similar complexes with all trivalent lanthanide ions, Am(III), and Cm(III), bis-2,4,4-trimethylpentyldithiophosphinic acid (HA, purified commercial product Cyanex301) forms different complexes along with the lanthanide series, Am(III) and Cm(III). The bonding of the softer sulfur donor to light Ln(III) and the replacement of the sulfur donors of HA by the oxygen donors of water molecules in heavier Ln(III) complexes illustrates the significant contribution of the 4f orbitals to bonding for light lanthanides, presenting a piece of striking evidence that the 4f orbitals stretch to the valence shell in some degree for the light lanthanides through Gd. These results are contrary to popular belief that the 4f orbitals are deeply buried beneath the valence shell and they rarely play an important role in chemical change or bonding in lanthanide complexes.

In comparison with the 4f orbitals, the 5f orbitals are less shielded by the valence shell and in the complexes of Am(III) and Cm(III) they contribute more to bonding with the sulfur donors of HA. The stronger bonding of HA with Am(III) and Cm(III) results in excellent selectivity for An(III) over Ln(III), which may provide solutions to the very challenging task of An(III)-Ln(III) separation in the spent nuclear fuel reprocessing. Moreover, the HA-Ln(III)/An(III) system provides a perfect subject for computational chemists to develop suitable methods for the study on Ln/An complexation.

With another ligand, N,N,N',N'-tetramethyl-3-oxa-glutaramide (TMOGA), in aqueous phase, Am(III) might be separated from Cm(III) also by extraction with purified Cyanex301, because Cyanex301 forms a little stronger bond with Am(III) than Cm(III) while TMOGA forms stronger complexes with Cm(III) than Am(III).

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