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Full paper / Mémoire

A comparative spectroscopic study of U(III)/Am(III) and Ln(III) complexed with N-donor ligands

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Abstract

Selected soft N-donor ligands are highly effective extractants for the separation of trivalent actinides (An(III)) from lanthanides (Ln(III)) in the partitioning and transmutation (P&T) strategy. Comparative structural investigations using X-ray absorption spectroscopy (EXAFS) on An(III) and Ln(III) complexed with tris[(2-pyrazinyl)methyl]amine (TPZA) and 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (BTP) are performed in order to evaluate if ligand extraction performance is reflected in coordination structure differences, specifically in variations in the metal cation—N bond lengths. We observe U(III) to generally exhibit a decrease in the bond distance over that expected for pure ionic binding for the ligand complexes investigated and interpret this as higher covalent character of the U(III)—N binding. In contrast, no measurable differences for Am(III), Cm(III), and the Ln(III) elements in the middle of the 4f series are observed. Time-resolved laser fluorescence spectroscopy (TRLFS) investigations on solution BTP complexed with Cm(III) and Eu(III) reveal that the selective extraction behavior of this ligand can be explained by the large difference in conditional stability constants of their 1:3 complexes (K_{13}). The K_{13} value for Cm—BTP$_3$ is a number of orders of magnitude larger than that for Eu—BTP$_3$. ***To cite this article: Melissa A. Denecke et al., C. R. Chimie 10 (2007).***

Résumé

Certains ligands comportant des atomes d'azote donneurs mous sont des extractants très efficaces pour séparer les actinides trivalents (An(III)) des lanthanides (Ln(III)), dans le cadre de la stratégie séparation/transmutation. Des études structurales comparatives utilisant la spectroscopie d'absorption X (EXAFS) sur des An(III) et des Ln(III) complexés par la tris[(2-pyrazinyl)méthyl]-amine (TPZA) et la 2,6-di(5,6-dipropyl-1,2,4-triazine-3-yl)pyridine (BTP) ont été menées afin de déterminer si les performances en extraction liquide/liquide de ces ligands sont corrélées à des différences structurales, en particulier à des variations dans les distances de liaison cation métallique—azote. Nous observons que les complexes d'U(III) étudiés se caractérisent par un raccourcissement général des distances de liaison par rapport à celles attendues pour une liaison purement ionique, pouvant être expliqué par un caractère plus covalent de la liaison U—N. En revanche, aucune différence mesurable n'est observée jusqu'ici entre les An(III) mineurs étudiés et les Ln(III) du milieu de la série des éléments 4f. Des études de spectroscopie de fluorescence laser résolue dans le temps (TRLFS) sur des solutions de Cm(III) et d'Eu(III) complexés par la BTP indiquent que la sélectivité de ce ligand

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en extraction peut être expliquée par une grande différence dans les constantes de stabilité conditionnelle de leurs complexes 1:3 (K_{13}). La valeur de K_{13} du complexe Cm(BTP)$_3$ est supérieure de plusieurs ordres de grandeur à celle du complexe Eu(BTP)$_3$. ***Pour citer cet article : Melissa A. Denecke et al., C. R. Chimie 10 (2007).***

Keywords: EXAFS; TRLFS; Partitioning; Trivalent actinides

Mots-clés : EXAFS ; TRLFS ; Séparation ; Actinides trivalents

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1. Introduction

The separation of trivalent actinides (An(III)), namely Am(III) and Cm(III), from lanthanides (Ln(III)) is a key step in the partitioning and transmutation (P&T) strategy. 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. An(III)/Ln(III) separation is the decisive step in the partitioning process as some Ln nuclides have a high neutron absorption, which if not removed would reduce actinide transmutation efficiency [1]. 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. As already shown some 20 years ago [2], ligands containing soft donor atoms (such as S or N) exhibit this selectivity. The use of organic N-donor ligands has an application advantage that they can be incinerated to gaseous products, thereby reducing the volume of active waste to be disposed of [3].

Ligands containing aromatic N atoms as donor atoms are reported to complex An(III) more strongly than Ln(III), due to a greater covalent character of the An(III)−N bond [4,5]. A number of such aromatic N-donor ligands as candidates for partitioning have been reported (see, e.g., Refs. [6–8], Fig. 1). Tripodal oligoamines such as tris[(2-pyrazinyl)methyl]amine (TPZA) exhibit high selectivity for Am(III) in An(III)/Ln(III) extraction [4,9] Alkylated 2,6-di(1,2,4-triazin-3-yl)pyridines (BTP) are among the most effective extractants for the separation of Am(III) and Cm(III) from Ln(III) [10]. In liquid−liquid extractions these extractants are able to extract An(III) selectively in preference of Ln(III) from nitric acid solutions into the organic phase. This is of technological importance, as these elements are present in a nitric acid solution following dissolution of spent nuclear fuel and subsequent partitioning in the PUREX and DIAMEX processes [1,6].

Recently there has been a surge of activity in attempts to understand the underlying reason for the partitioning ligand selectivity. This understanding can potentially be used to optimize partitioning ligand design and, hence, extraction performance. The selectivity may be due to an enhanced covalence in An(III)−N bonds compared to those of their Ln(III) counterparts. This enhanced bond covalence can be expressed by a contraction in bond length and/or a higher thermodynamic stability. Our previous investigation [11] on Cm(III) and Eu(III) complexed with BTP in non-aqueous organic solution by extended X-ray absorption spectroscopy (EXAFS) and quantum chemical calculations shows the solution structure to be the 1:3 complex with a structure comparable to crystal structures of solid Ln−BTP$_3$ [12]. The complex is comprised of three ligands directly bonded 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 Cm−BTP$_3$ and Eu−BTP$_3$ [11]. We conclude, the observed selectivity of BTP for Cm(III) over Eu(III) is not structural in origin. This result is apparent contrast to the observation that in crystalline U(III) and Ce(III) BTP complexes have U(III)−N bonds

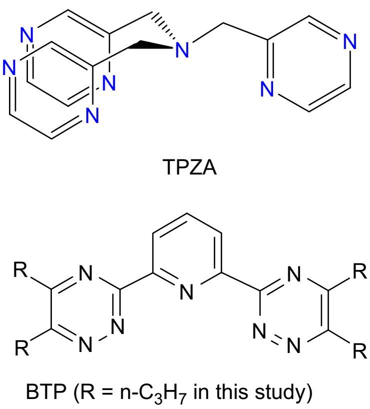

Fig. 1. Chemical structure of tris[(2-pyrazinyl)methyl]amine (TPZA) and 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridines (BTP).