ROBL-CRG	**Experiment title:** Free and silica-gel-bound tetraazamacrocycles as complexing agents of actinide cations: investigation of the solid-state coordination scheme.	**Experiment number:** CH-2423
Beamline: BM 20	**Date of experiment:** from: 14/02/2009 to: 17/02/2009	**Date of report:** October 12, 2009
Shifts: 9	**Local contact(s):** Dr. Andreas SCHEINOST (scheinost@esrf.fr)	*Received at ROBL:*

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Report: Speciation of actinides in the presence of organic ligands is a topic that is extremely significant to the safe disposal of nuclear wastes resulting from the use of fission technologies, to assess the contamination risks in case of accidental release of radionuclides in the environment, to design new separation processes and remediation technologies, or to predict the behavior of radionuclides in biological systems. Most importantly, the migration and bioavailability of actinides in the biosphere are highly dependent upon the presence of both artificial and natural chelators. Currently, the systematic studies on complex formation of actinides with organic ligands are far beyond those of inorganic ligands. This is clearly reflected by the Nuclear Energy Agency (NEA) monograph series entitled *Chemical Thermodynamics*. Only one among the eleven volumes of this series reports data for actinide complexes with organic ligands, albeit in a limited number (only data for EDTA, oxalic, citric, and isosaccharinic acids are compiled). The same is valid for the overviews about studies on X-ray absorption spectroscopy of the actinides. The goal of our ongoing **chelation studies of uranium(VI) and plutonium(IV)** is to collect reliable **structural** and **thermodynamic solution data** (i.e. binding constants) by combining XAFS, potentiometric, and spectrophotometric measurements performed under strictly controlled experimental conditions with technologically and/or environmentally relevant ligands. Among them, two classes of compounds were targeted in this experiment, namely **polyaminocarboxylic acids** on the one hand and **siderochelates** like hydroxamic acids on the other.

1. Polyaminocarboxylic acids

Although known for more than 50 years and in spite of their technological, environmental and medicinal significance (the storage tanks on the US Hanford site are reputed to contain ca. 80 t of EDTA among the 350 000 m^3 of wastes, while DTPA is currently the only FDA-approved *in-vivo* decorporating agent for plutonium), solution equilibrium studies of ligands such as EDTA, CDTA, or DTPA with respect to 5f-elements are extremely scarce and most often unreliable as pointed out by the IUPAC and NEA-sponsored reviews. In that context, the applicants unraveled the complexation thermodynamics of Pu^{4+} with $EDTA^{4–}$, $CDTA^{4–}$, and $DTPA^{5–}$ in nitric media by means of potentiometry and visible spectrophotometry.[1] The purpose of this experiment was to complete these speciation studies of Pu^{4+} by XAFS measurements in order to gain insight into the structure of the various solution species. Hence, 9 samples of predefined pH were analyzed at room temperature. Moreover, these studies performed at the 0.05 M concentration level should also enable to validate the pH-dependent Pu speciation and thus ascertain the accuracy of the equilibrium constants measured at the millimolar concentration range.

2. Natural and biomimetic siderochelates

Until recently, siderophores have been perceived mainly as selective iron chelators that are excreted by most bacteria to solubilize ferric hydroxide and supply them with iron(III) as an essential nutrient. Indeed, ferric siderophore complexes are recognized by specific membrane proteins and transported inside the bacterial cell. However, such ligands may engage in a diverse chemistry with a variety of important metal ions, including actinides. It turns out that a more complex paradigm is required to describe their participation in bio- and geochemical processes. The general aim of our studies in that area is to investigate in-depth the complex formation of actinides with natural or synthetic siderophores.

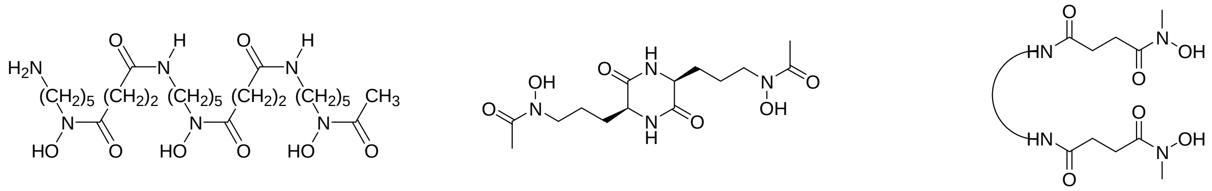

Figure 1. Chemical structure of desferrioxamine B (left), rhodotorulic acid (middle), and of the dihydroxamic analog studied herein (right, the curved line represents a propyl chain).

In the present experiment, we focused our attention on the UO_2^{2+} complexes formed in aqueous solution with two linear hydroxamic acids, the ubiquitous siderophore desferrioxamine B and a dihydroxamic analog of rhodotorulic acid (Figure 1). Preliminary equilibrium studies pointed towards the formation of various protonated species of $[UO_2(LH_x)]^{x+}$ general formula. Based on the stability constants, distribution diagrams were computed that enabled to define pH ranges where each species predominates. Accordingly, 3 room-temperature U L_{III}-edge spectra were collected for each ligand at such predefined pH values (Figure 2) in order to confirm the speciation of U(VI) and to assess the geometrical features related to the coordination sphere of uranium. Numerical modeling of the experimental spectra is under progress.

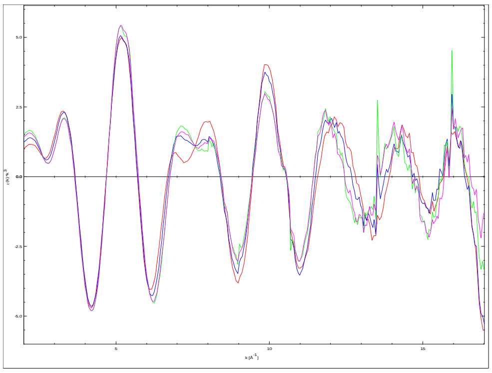

Figure 2. Overlay of the U L_{III}-edge EXAFS spectra of uranium(VI)-desferrioxamine B solutions recorded at three different pH values with that corresponding to an acidic $UO_2(NO_3)_2$ solution (red).

[1] M. Meyer, R. Burgat, S. Faure, B. Batifol, J.-C. Hubinois, H. Chollet, R. Guilard, *C. R. Chimie* **2007**, *10*, 929-947.