ESRF	**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: 18/04/2007 to: 20/04/2007	**Date of report**: 15/12/2007
Shifts: **6**	**Local contact(s)**: Dr. Andreas SCHEINOST (e-mail: scheinost@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Michel MEYER
Institut de Chimie Moléculaire de l'Université de Bourgogne
(ICMUB - UMR 5260 du CNRS)
9, avenue A. Savary
21078 DIJON Cedex

Dr. Andreas SCHEINOST

Rossedorf Beamline at ESRF (ROBL - BM 20)

Report:

The development of separation techniques, which selectively extract metal ions from dilute wastewaters and industrial process streams, is a challenging scientific problem. A series of functionalized tetraazamacrocyclic ligands covalently bound on the surface of silica-gel beads have been developed by the Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB, UMR 5260, Dijon-France) for the selective extraction of actinides.[1] In collaboration with the Commissariat à l'Energie Atomique (CEA Center of Valduc), one of these materials has been prepared on a semi-industrial scale and used in the final decontamination step of real effluents for removing the residual α-emitters (U, Pu, Am) contained at the sub-ng/L level.[2] The next goal is to unravel the coordination scheme of the radiotoxic metal ions embedded in this material in order to shed light on the structural aspects of the extraction process.

To this aim we have performed L3-edge X–ray Absorption Spectroscopy (XAS) measurements at BM20 of the Eu^{3+} ions bound to two materials used as sequestrants of lanthanide ions (see Fig. 1). Eu^{3+} is taken as a structural model of the highly emitting Am^{3+} cation since the maximum allowed amount of ^{241}Am does not exceed 1.5 mg. For comparison purposes XAS spectra have been collected also for the same ion bound to a number of isolated metal complexes formed with the corresponding macrocycles, well known for their affinity towards transition and non-transition metallic cations (see Fig. 2).[3,4] A number of control measurements have also been performed on $EuCl_3$, $EuOH_3$, $EuNO_3$ and Eu^{3+} sorbed on silica gel samples.

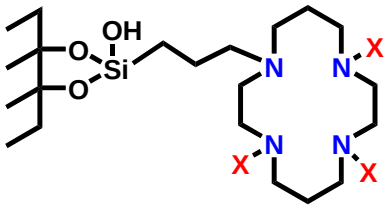

Fig. 1. The two investigated silica gel bound ligands Si2323Ac (X = $CH_2CO_2^-$) and Si2323Pr (X = $CH_2CH_2CO_2^-$).

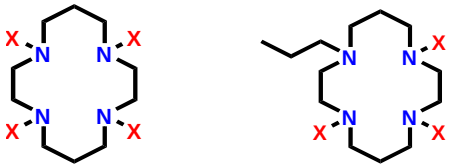

Fig. 2. ligands used to form the reference europium complexes.
Left: TETA (X = $CH_2CO_2^-$) / TETPr (X = $CH_2CH_2CO_2^-$).
Right: TE3A (X = $CH_2CO_2^-$) / TE3Pr (X = $CH_2CH_2CO_2^-$).

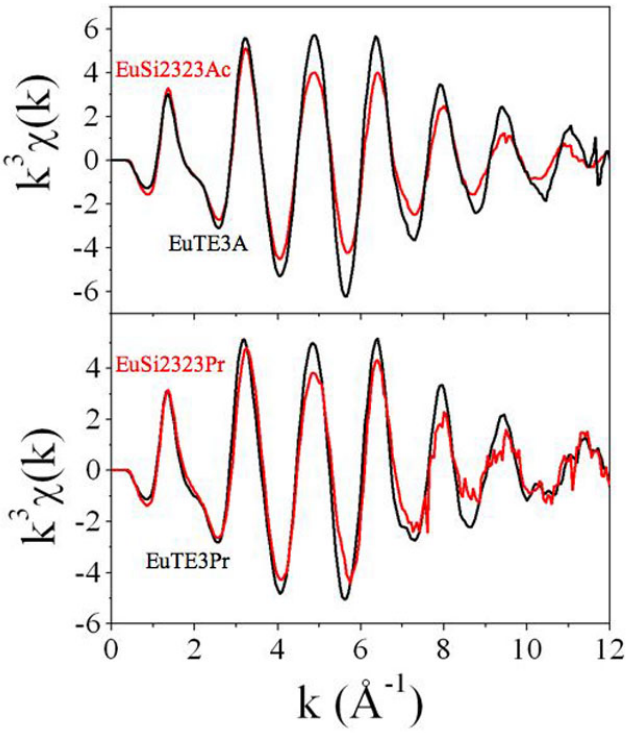

Fig. 3. Collected EXAFS functions for the materials shown in Fig. 1 (red lines) and for the two reference complexes EuTE3A and EuTE3Pr (see Fig. 2).

Data of very good quality have been collected for the reference compounds as well as for the investigated materials. As an example we report in Fig. 3 raw data collected for the investigated materials EuSi2323Ac and EuSi2323Pr (red line) compared to those collected for the two reference models EuTE3A and EuTE3Pr (black line).

The EXAFS functions of the two materials exhibit quite different spectral features as compared to those collected for the corresponding reference models, suggesting a different coordination scheme. Preliminary first shell analysis indicates an average coordination number of 8 O(/N) atoms for the investigated materials and an average distance of 2.42 Å with a Debye Waller factor of about 0.01 $Å^2$. The high value found for the disorder parameter (we recall at this respect that all the measurements have been performed at 20 K) suggests the presence of structural disorder of the first neighbors. A detailed data analysis, using both multiple-scattering and difference analysis approach, is still in progress. This analysis is expected to clarify the stereochemical arrangement of the neighboring atoms in the vicinity of Eu^{3+} for the isolated complexes versus that formed on the silica gel surface.

[1] H. Chollet, J. L. Babouhot, F. Barbette, R. Guilard, PCT application WO 01 15806, **2001**.
[2] F. Barbette, F. Rascalou, H. Chollet, J. L. Babouhot, F. Denat, R. Guilard, *Anal. Chim. Acta* **2004**, *502*, 179-187.
[3] R. M. Izatt, K. Pawlak, J. S. Bradshaw, R. L. Bruening, *Chem. Rev.* **1995**, *95*, 2529-2586.
[4] M. Meyer, V. Dahaoui-Gindrey, C. Lecomte, R. Guilard, *Coord. Chem. Rev.* **1998**, *178-180*, 1313-1405.