 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: 23/11/2007 to: 26/11/2007	Date of report: February 18, 2009
Shifts: 12	Local contact(s): Dr. Andreas SCHEINOST (scheinost@esrf.fr)	<i>Received at ROBL:</i> February 19, 2009
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 Rossendorf Beamline at ESRF (ROBL - BM 20)		

Report:

The development of separation processes aimed at the selective uptake of radiotoxic metal ions from dilute wastewaters and industrial process streams is of paramount importance for preventing environmental contamination, but still remains a challenging scientific task. From that point of view, solid-liquid extraction using chelating agents covalently grafted on hydrophilic supports is appealing, mainly because the affinity and selectivity of the scavenging material towards the targeted species can be fine-tuned by molecular design. Hybrid organic-inorganic materials consisting of *N*-functionalized tetraazamacrocycles bearing either three acetate ($n = 0$) or propionate ($n = 1$) dangling arms, which are covalently grafted on the surface of mesoporous silica-gel beads (Figure 1), proved to be efficient extracting agents for various actinides (U, Pu, Am) contained at sub-ng/L concentration levels in real aqueous effluents.¹

In order to probe the coordination scheme of metal cations at the surface of the modified silica gels, and thus gain further insight into the extraction mechanism at the molecular level, we have recorded the low temperature (20 K) XAFS spectra at the L_{III} edge of both hybrid materials loaded with uranium(VI) and plutonium(IV). In addition, uranyl nitrate adsorbed on amorphous Kieselgel 60, used as solid support for these materials, was also studied for comparison purposes as well as a series of solid compounds that precipitated out upon reacting the four model ligands $H_3TEPr3A$, $H_3TEPr3P$, H_4TETA , and H_4TETP (Figure 1) with uranium(VI) and plutonium(IV) nitrate in acidic media. To the best of our knowledge, this study represents the first structural investigation of plutonium(IV) complexes formed with polyazamacrocyclic ligands.

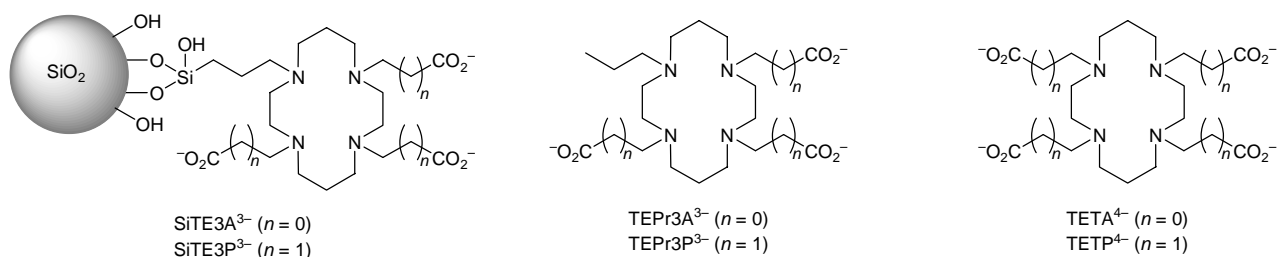


Figure 1. Structural formula and nomenclature of the modified silica gels and model ligands considered in this work.

Analysis of the EXAFS spectra at the U L_{III} edge pertaining to both hybrid gel samples provided evidence of two well-separated oxygen coordination shells in the equatorial plane at 2.3 and 2.5 Å, suggesting the formation of uranyl surface complexes. Taking into account multiple scattering contributions, the spectral morphology could be best reproduced by a binding model that involves a pentacoordinate uranium center interacting with oxygen atoms belonging both to the silica support and the organic ligand. Similarly to bare Kieselgel (Figure 2a), each uranyl ion is bound to a surface silanolate group in a bidentate fashion, thus forming an inner sphere complex. In the presence of macrocyclic chelators, carboxylate groups provide two oxygen atoms belonging either to a pair of monodentate or, more probably, to a single bidentate $-\text{CO}_2^-$ binding unit (Figure 2b). Preliminary results were disclosed at the *Actinide XAS 2008* meeting held in Saint-Aubin (France) in July 2008, while a brief account of the work has been accepted for publication in the proceedings of this conference.²

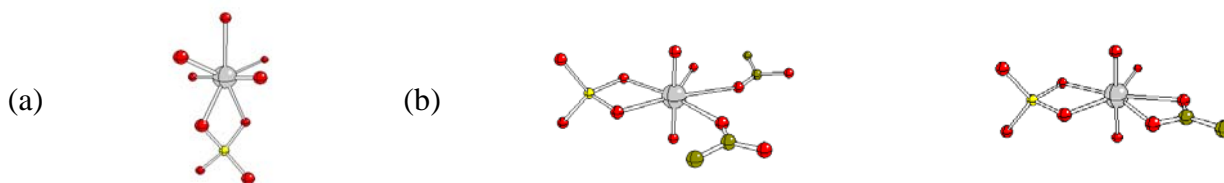


Figure 2. Suggested binding schemes of UO_2^{2+} at the surface of (a) Kieselgel 60 and (b) the modified silica gels SiTE3A and SiTE3P.

As far as the Pu L_{III} edge spectra are concerned, analysis of the XANES region enabled to safely conclude that plutonium did not undergo significant reduction and thus remained in the +IV oxidation state during the preparation of all six samples. The EXAFS spectra recorded for the isolated complexes involving the free macrocycles are almost superimposable and show great similarities with those pertaining to both silica gels. The first peak appearing in the 1–2.1 Å region was assigned to the backscattering signal from 8 to 9 oxygen atoms comprising the first coordination sphere around the absorbing plutonium(IV) centers. Together with a relatively intense peak in the FT near 3.8 Å, which was assigned to 3 or 4 Pu–Pu contributions, these features point to the presence in all samples of small plutonium clusters whose structures are reminiscent of PuO_2 . However, the 2–2.8 Å range exhibits subtle differences that enabled to discriminate free from immobilized complexes. The corresponding spectral morphology was explained either by Pu–C back scattering paths involving two mono- (3.46 Å) and two bidentate (2.88 Å) carboxylate groups for the complexes, or by Pu–C (3.88 and 3.45 Å) and Pu–Si (3.11 Å) interactions in the case of the silica-based materials.

- 1 F. Barbette, F. Rascalou, H. Chollet, J. L. Babouhot, F. Denat, R. Guillard, *Anal. Chim. Acta* **2004**, 502, 179-187. H. Chollet, J. L. Babouhot, F. Barbette, R. Guillard, WO 01 15806, **2001**.
- 2 L. Giachini, S. Faure, M. Meyer, L. V. Nguyen, B. Batifol, H. Chollet, R. Guillard, A. C. Scheinost, C. Hennig, *Proceedings of the 5th Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources (Actinide XAS 2008)*, Saint-Aubin, France, in press.