



	Investigation of sulfato-complexes of uranium(VI) in a hydrophobic ionic liquid Speciation of 2 platinum group metals, Pt(IV) and Pd(II), extracted in ionic liquids	Experiment number: CH-4485 CH-4486
Beamline: BM20	Date of experiment: from: 7/10/2015 to: 12/10/2015	Date of report: 10/02/2016 <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): Christoph Hennig and Kristina Kvashnina	
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Report:

Two consecutive experiments were led during the 15 shifts of beamtime.

The first 3 days were dovoted to the project CH-4485, at the uranium L₃ edge. The speciation of uranium (VI) in aqueous media in presence of sulfates is complex with the coexistence of various species according to the sulfate concentration and the pH of the medium. In acidic conditions, UO₂(SO₄)_(aq), UO₂(SO₄)₂²⁻ and UO₂(SO₄)₃⁴⁻ may co-exist. At pH > 3, the speciation is even more complex as oligomeric species or ternary species may form as a consequence of the uranium hydrolysis. Therefore, it is a challenge to perform an accurate characterization of the speciation in view to determine not only the stoichiometry of the species in solution, but also their structure. Sulfate ions have the ability to bind uranium (VI) in two ways, as monodentate or as bidentate fashion, and some contradictory results were obtained, especially at low sulfate ratio. According to authors, a monodentate or a bidentate coordination is evidenced for the 1:1 complex. In this context, we would like to use the specific properties of ionic liquids (IL) to investigate the coordination of sulfate ions with uranium (VI). In this kind of solvent constituted only by ions and easy to dry, we can get rid of the uranium (VI) hydrolysis. Also, we can choose the dissolved uranyl and sulfate salts so that their counter-ions are identical to the ions constituting the IL. In that way, we avoid any interferences due to counter-ions, the studied system being composed only by uranyl, sulfate and the cation and anion of the IL.

We used this experiment at the uranium L₃ edge to identify the stoichiometry and configuration of sulfato-complexes of uranium(VI) in ionic liquids, as a function of the sulfate/uranium ratio in solution. We show in particular the formation of a solid compound which corresponds to the 1:1 complex where the sulfate group is bound to uranium in a bidentate fashion (cf. figure 1).

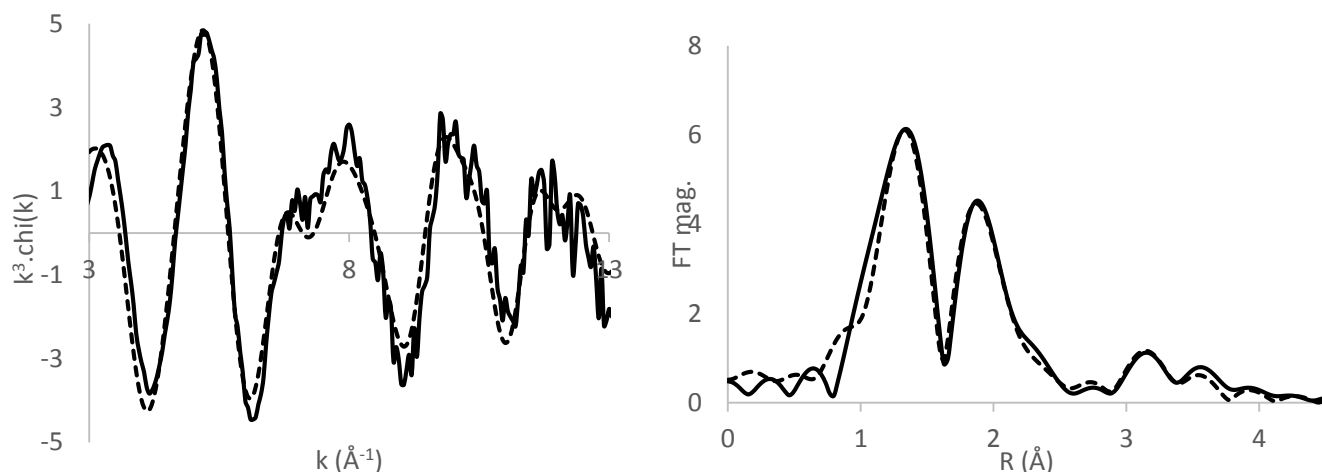


Figure 1: EXAFS spectrum of a sulfato-uranyl precipitate, formed in the ionic liquid. Fit of the data is displayed as a dotted line.

The last 2 days of beamtime were devoted to the project CH-4486. We have investigated the speciation of Pt(IV) with chloride and bromide ligands in ionic liquids. Because ionic liquids are based solely on organic cations such as ammonium or phosphonium and anions such as weakly coordinating bis(trifluoromethanesulfonyl)imide or simple chloride or bromide, Pt is expected to form specific complexes that are not yet well identified. In particular, we are interested in the complexes formed to extract those metals into specific ionic liquids from acidic aqueous phase.

We have analysed samples containing various Pt/Cl/Br ratio, from 1/6/1 to 1/6/50, and compared these data with the ones obtained for the reference samples $[\text{PtCl}_6]^{2-}$ and $[\text{PtBr}_6]^{2-}$ (cf. figure 2). As the bromine concentration increases, we evidenced the formation of mixed species in solution: $[\text{PtCl}_4\text{Br}_2]^{2-}$ for a 1/6/2 and 1/6/6 ratio, $[\text{PtClBr}_5]^{2-}$ for the 1/6/8 ratio, and $[\text{PtBr}_6]^{2-}$ for the 1/6/50 ratio. We thus evidence that the bromine incorporation in the Pt coordination sphere does not follow a linear trend according to the Br concentration. We also show that it implies a change in the Pt-Cl bond length, from 2.32 Å to 2.39 Å. These results were assessed by NMR measurements made on the same samples, and will be the subject of an article.

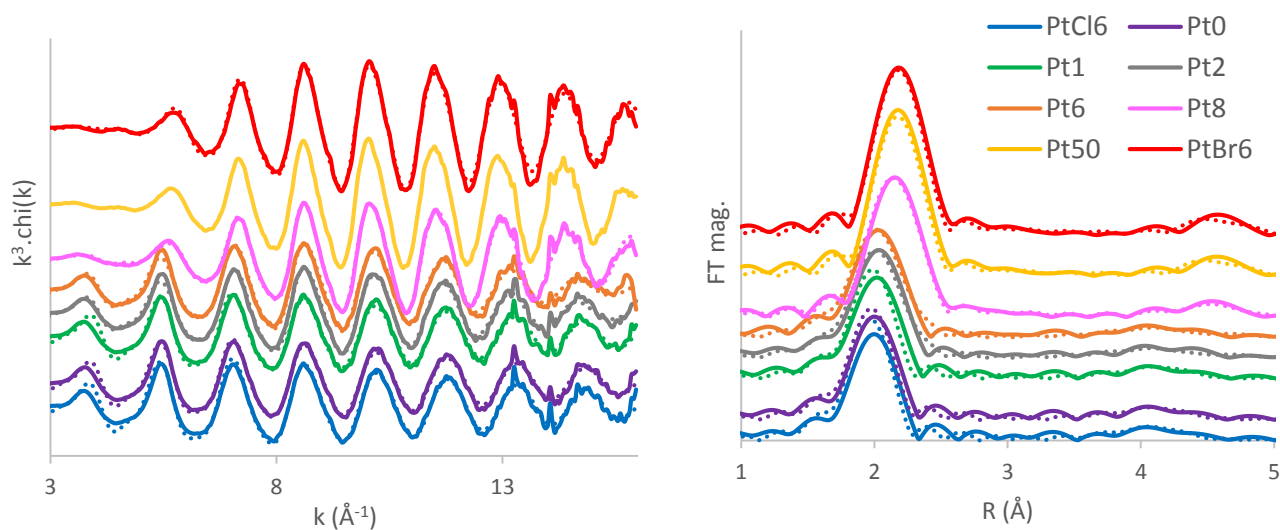


Figure 2: EXAFS spectra of the main samples analysed at the Pt L_3 edge, displaying the evolution of the Pt environment from $[\text{PtCl}_6]^{2-}$ (bottom) to $[\text{PtBr}_6]^{2-}$ (top). Fits are displayed as dotted lines.