The Rossendorf Beamline at ESRF

Forschungszentrum Dresden Rossendorf

Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the FZD. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the reference number of the proposal / experiment to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

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ROBL-CRG	**Experiment title:** complexation of uranium(VI) in room temperature ionic liquids	**Experiment number**: 20-01-654
Beamline: BM 20	**Date of experiment**: from: 27/06/2007 to: 30/06/08	**Date of report**: 04/2008
Shifts: 6	**Local contact(s)**: Dr. Christoph Hennig	*Received at ROBL:*

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Report:

The aim of this experiment is to characterize the stoechiometry and structure of uranyl-nitrato complexes in a room temperature ionic liquid, C_4mimTf_2N (1-methyl-3-butylimidazolium$^+$, Tf_2N^- = $(CF_3SO_2)_2N^-$), as a function of the nitrate/uranyl ratio (from 0 to 4) and as a function of the nature of the uranyl salt. Nitrate ligands were chosen because they are of interest in the frame of the nuclear cycle reprocessing and a previous study has shown unexpected uranyl-nitrates interaction in RTIL [1]. EXAFS was coupled to UV-visible spectroscopy, the samples being measured by both techniques. Two uranyl salts used were uranyl triflate ($UO_2(CF_3SO_3)_2$) and $UO_2(Tf_2N)_2$, in order to check a possible influence of the uranyl counteranion on complexation [2]. Nitrates were introduced as tetrabutylammonium-NO_3. Figure 1 displays the EXAFS for $UO_2(Tf_2N)_2$ solutions, as a function of the nitrate concentration. Addition of nitrates entails notable changes on spectra, as a sign of the uranyl complexation to nitrates. Fit results (table1) show that in every case the complexation is total, leading to the formation of respectively $UO_2(NO_3)^+$, $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$ species. The same

results are obtained for solutions in which uranyl was introduced as the triflate salt. These experiments show that in ionic liquids, and contrary to what happens in water, nitrates are strong ligands to uranyl, which is confirmed by the fact that the same results are obtained using uranyl triflate and uranyl-Tf_2N salts. The same behaviour was observed in organic solvents (acetonitrile), the structure of the formed species being identical [3].

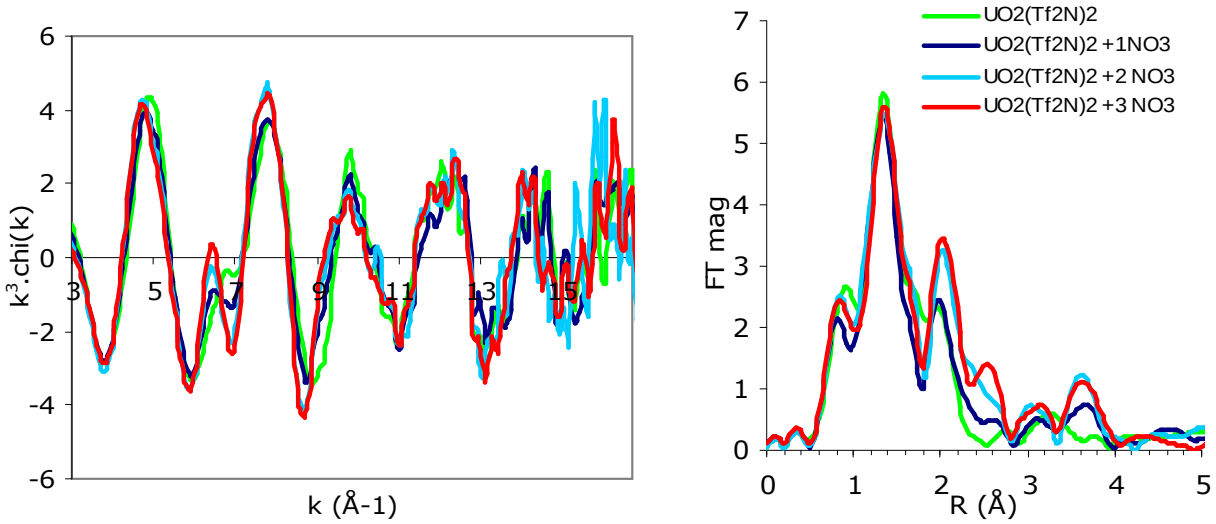

Figure 1: EXAFS spectra and their corresponding Fourier transforms of $UO_2(Tf_2N)_2$ solutions in C_4mimTf_2N for different $[NO_3^-]/[UO_2^{2+}]$ ratio: 0, 1, 2, 3.

$[NO_3^-]/[UO_2^{2+}]$	shell	N	R (Å)	σ^2 (Å²)	Rfactor
1	O_{axial}	2	1.75	0.002	0.02
	$O_{equatorial}$	4.7	2.45	0.008	
	N	0.9	2.92	0.003	
	O_{distal}	0.9	4.16	0.003	
2	O_{axial}	2	1.76	0.002	0.02
	$O_{equatorial}$	5.9	2.47	0.008	
	N	2.3	2.92	0.003	
	O_{distal}	2.3	4.16	0.006	
3	O_{axial}	2	1.76	0.002	0.01
	$O_{equatorial}$	5.9	2.47	0.007	
	N	2.8	2.92	0.003	
	O_{distal}	2.8	4.15	0.006	

Table 1: Fit results for $UO_2(Tf_2N)_2$ solutions in C_4mimTf_2N, as a function of the nitrates concentration.

[1] I. Billard, C. Gaillard, C. Hennig, Dalton Trans., 2007, 4214.
[2] C. Gaillard, A. Chaumont, I. Billard, C. Hennig, A. Ouadi, G. Wipff, Inor. Chem., 2007, 46, 4815.
[3] A. Ikeda, C. Hennig, A. Rossberg, S. Tsushima, A. Scheinost, G. Bernhard, Anal. Chem., 2008, 80, 1102.