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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:** Speciation of aqueous uranyl(VI) polymeric species using EXAFS spectroscopy	**Experiment number**: 20_01_665
Beamline: BM 20	**Date of experiment**: from: 30.06.2007 to: 01.07.2007	**Date of report**: 31.3.2008
Shifts: 3	**Local contact(s)**: Dr. Andreas C. Scheinost	*Received at ROBL:*

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Report:

In this work, we used EXAFS spectroscopy to solve the structures of uranyl(VI) hydroxo dimer and trimer complexes in aqueous solution. One of the main challenges for EXAFS is to prepare solutions in which the target polymeric species are dominant, while in the uranium concentration range suitable for EXAFS measurements, there is always a mixing of several species. Therefore, uranium(VI) concentration and pH was optimized as far as possible based on thermodynamic calculations to reduce the number of coexisting species, while vibrational spectroscopy (FTIR) and UV-vis absorption spectroscopy was used to support the discrimination of coexisting species, in case they could not be avoided experimentally.

Experimental

The EXAFS measurements were recorded at the Rossendorf Beamline at BM20. The Uranium L$_{III}$-edge spectrum of samples were recorded either in fluorescence mode or in transmission mode at room temperature. The energy scale was calibrated using the maximum of the first derivative of the K-edge spectrum of yttrium (17038 eV), which was simultaneously measured with each spectrum. The threshold energy, E$_0$, of the uranium L$_{III}$-edge was defined as 17185 eV. The EXAFS spectra were analyzed according to standard procedures using EXAFSPAK including statistical weighting of the 13 fluorescence channels and dead-time correction. Theoretical scattering phases and amplitude functions were calculated with the *ab initio* calculation program FEFF8 by using the structure of the most stable form of the trimer complex obtained by DFT calculations.

RESULTS

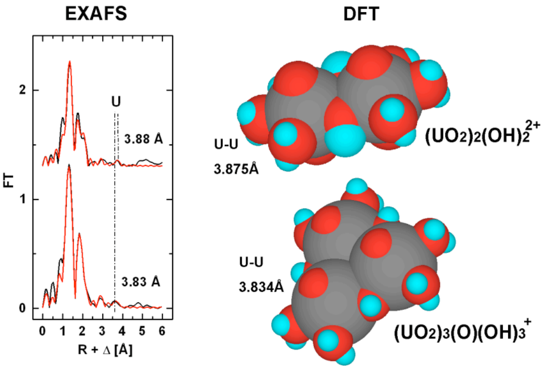

Figure 1: Both the EXAFS spectroscopy and DFT calculations show that the trimer complex $(UO_2)_3(O)(OH)_3^+$ has the U-U distance which is significantly shorter than that of the dimer complex $(UO_2)_2(OH)_2^{2+}$, thereby the presence of oxo bridging in the trimer complex has been confirmed.

The k^3-weighted EXAFS spectra of the uranyl (VI) dimer and trimer samples and corresponding Fourier transforms are shown in Figure 1. According to the FTIR and UV-vis measurements, the samples contain mixtures of UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$. The formation of polynuclear complexes is confirmed by EXAFS for both samples which show U-U backscattering. By shell fitting we obtained a U-U radial distance of 3.82-3.83 Å, which is in line with the trimer complex $(UO_2)_3(OH)_5^+$. For dimer sample, a weak FT peak at 3.71 Å could be fitted by 0.5 U atoms at a radial distance of 3.88 Å. The U-U distances found here show good agreement with crystal structure data and the DFT calculations. The averaged U-U distances are 3.875Å (DFT) versus 3.88 Å (EXAFS) for $(UO_2)_2(OH)_2^{2+}$, and 3.834 Å (DFT) versus 3.81 - 3.82 Å (EXAFS) for $(UO_2)_3(\mu_3\text{-}O)(OH)_3^+$. A shorter U-U distance of 3.81 – 3.82 Å in the trimeric complex suggests the presence of the central oxo bridging instead of the OH bridging. The U-U coordination numbers is less than 1 and hence too small for the dimer and the trimer. This is related to the fact that the sample was a mixture of monomeric and polymeric species. In addition, the CN obtained from EXAFS always have an error of 10 ~ 20%. Clearly, the coordination numbers obtained from EXAFS do not help to identify the polymer structures, while the U-U distances give reliable results.

To summarize, the EXAFS spectra of two uranyl(VI) samples show two distinct U-U distances of 3.88 Å and 3.81~3.82 Å which correspond to $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(\mu_3\text{-}O)(OH)_3^+$, respectively. These distances agree well with the results of the DFT calculations. Our combined DFT and EXFAS results confirm that $(UO_2)_3(OH)_5^+$ in aqueous solution exists as $(UO_2)_3(\mu_3\text{-}O)(OH)_3^+$ with an oxo central bridging.

Reference

[1] S.Tsushima, A.Rossberg, A.Ikeda, K.Müller, A.C.Scheinost, *Inorg. Chem.* 2007, 46, 10819-10826.