



	Experiment title: EXAFS study of uranium(VI) complexation with dicarboxylic acids	Experiment number: 20-01-619
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Shifts: 6	Local contact(s): André ROSSBERG	<i>Received at ESRF:</i>
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Report:

A recent spectrophotometric study by Havel et al. [1] describes for the first time the formation of two binuclear uranium(VI) complexes with oxalic acid in aqueous solution. Previous studies reported polynuclear species only in solids [2] but not in solutions [3]. The aim of our study was to apply EXAFS spectroscopy to detect and possibly determine the structure of the species $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]^{2-}$ and $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]^{6-}$, which were derived from UV-vis spectroscopy, conductometry, and vapor pressure osmometry [1].

For the EXAFS measurement, nine samples with 10 mM uranium(VI) and an ionic strength of 1 M NaClO_4 were prepared at pH 3.0 under ambient conditions. The concentration of oxalic acid in the solutions varied between 0 and 60 mM. According to the equilibrium model of Havel et al. [1], $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]^{6-}$ is the dominating species in solution at an oxalic acid concentration greater than 25 mM (see Fig. 1). Multiple sweeps of the uranium L_3 -edge EXAFS spectra were recorded in transmission mode using Ar filled gas ionization chambers. The stability of the solution samples was confirmed by pH measurements and UV-vis spectroscopy (350 – 550 nm) before and after the EXAFS experiments.

The eigenanalysis of the uranium L_3 -edge k^3 -weighted EXAFS spectra showed that the sample series contained two uranium(VI) species (spectral components) of different molecular structure. Therefore, the experimental spectra shown in Fig. 2 could be reproduced using the first two factors of the eigenanalysis. The relative concentration of these two species was determined by iterative target testing as described in [4] and is shown in Fig. 3. Without oxalic acid present, the 10 mM uranium(VI) solution at pH 3.0 contains only the uranium aquo ion. Its concentration decreases and the relative amount of the second uranium species increases as the oxalic acid concentration increases (see Fig. 3). The EXAFS spectra of the two uranium species and the best theoretical fit to the data are shown in Fig. 4. The corresponding EXAFS structural parameters are summarized in Table 1. The first species, which dominates at low oxalic acid concentrations, shows the characteristic U-O bond distances of the uranium(VI) aquo ion, i.e., 1.76 ± 0.02 and 2.40 ± 0.02 Å. The second species, which dominates the speciation at higher oxalic acid concentrations, is a mononuclear uranium(VI) complex with oxalate ligands. The EXAFS spectrum of the oxalate complex did not show any evidence of an U-U interaction at approximately 3.9 Å, which would be expected if binuclear uranium species were formed. The U-O and U-C bond distances of the aqueous uranium(VI) oxalate complex agree well with recent quantum chemical calculations by Vallet et al. [5] for oxalate ligands forming five-membered chelate rings.

In summary, our uranium L_3 -edge EXAFS study did not show any indication of binuclear uranium(VI) species and, therefore, does not support the equilibrium model of Havel et al. shown in Fig. 1. Our data

support the equilibrium models of Ferri et al. [3] and the previous work of Havel [6] that include only mononuclear species, i.e., $[\text{UO}_2\text{C}_2\text{O}_4]_{(\text{aq})}$, $[\text{UO}_2(\text{C}_2\text{O}_4)_2]^{2-}$, and $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$.

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References

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Table 1 EXAFS structural parameters for the two spectral components

Species	Shell	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
Oxalate complex	Oax	2.1	1.78	0.0021	-8.7
	Oeq	5.2	2.38	0.0063	
	C	5.2*	3.26	0.0078	
	C (MS)	10.4*	3.38	0.0022	
	O (MS)	5.2*	4.44	0.0041	
Aquo ion	Oax	2.2	1.76	0.0021	-9.1
	Oeq	5.6	2.40	0.0079	

* Parameter linked to Oeq during the fit.

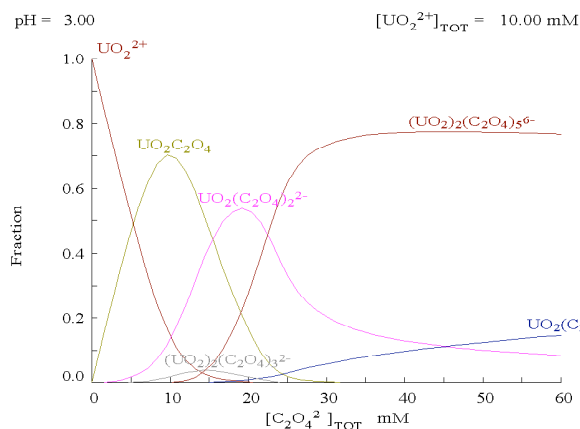


Fig. 1 Distribution diagram for solutions of $[\text{UO}_2^{2+}]_{\text{total}}=10$ mM, pH 3, $I=3$ M NaClO_4 , and $[\text{C}_2\text{O}_4^{2-}]_{\text{total}}$ varying from 0 to 60 mM at 25 °C. According to ref. [1].

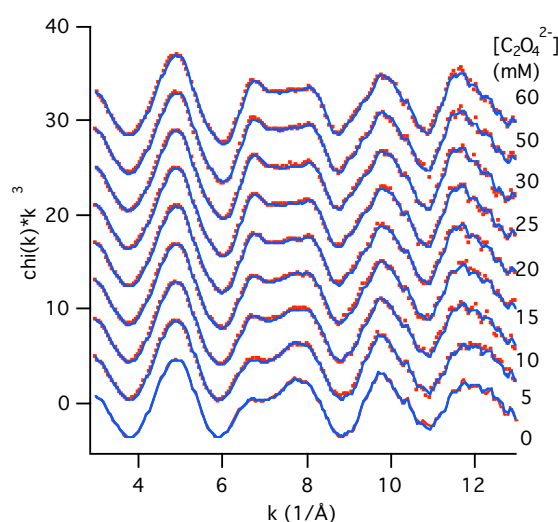


Fig. 2 Raw U L_3 -edge k^3 -weighted EXAFS spectra (dots) and their abstract reproductions (solid line).

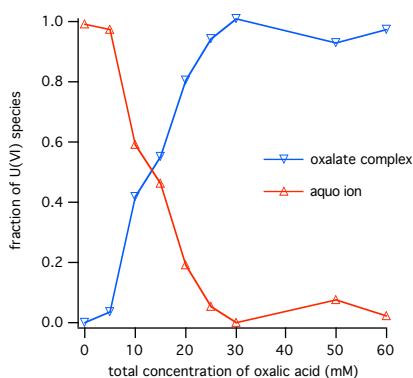


Fig. 3 The real concentration distribution of the U(VI) species as a function of pH.

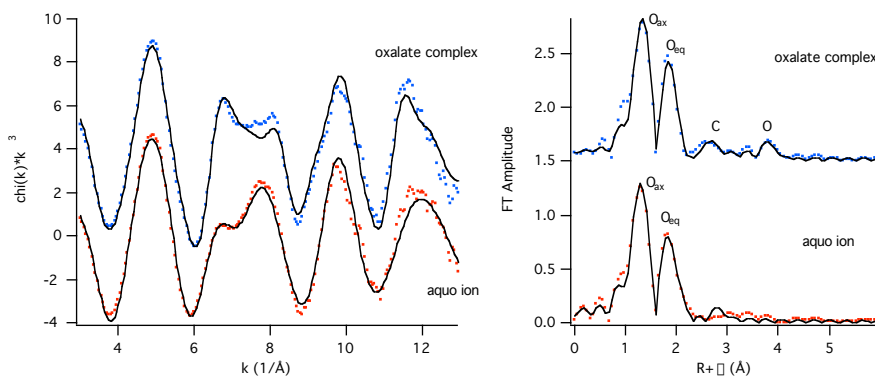


Fig. 4 Uranium L_3 -edge k^3 -weighted EXAFS spectra of the two spectral components (left) and their corresponding Fourier transforms (right). Solid line – best theoretical fit to the data (dots).