

EXAFS study of uranium(VI) complexation with oxalic acid

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In a recent publication, Havel et al. reported the formation of binuclear uranium(VI) complexes with oxalic acid in aqueous solution for the first time [1]. The existence of the binuclear aqueous species $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]^{2-}$ and $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]^{6-}$ was derived from UV-vis spectroscopy, conductometry, and vapor pressure osmometry. Similar binuclear species have been observed in solids [2] but never in solution [3]. The aim of our study was to obtain direct spectroscopic evidence of the formation of binuclear species in solution and to determine their structure.

We prepared nine samples with 10 mM uranium(VI) at an ionic strength of 1.0 M NaClO_4 at pH 3. The concentration of the oxalic acid varied between 0 and 60 mM. According to the stability constants of Havel et al. [1], $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]^{6-}$ is the dominating species in solutions when the concentration of oxalic acid is greater than 25 mM (see Fig. 1). The uranium $\text{L}_{3\text{-edge}}$ EXAFS spectra were measured in transmission mode at the Rossendorf Beamline ROBL at the European Synchrotron Radiation Facility ESRF in Grenoble, France. The stability of the samples was checked before and after the EXAFS experiments by pH measurements and UV-vis spectroscopy in the range of 350 to 550 nm.

The factor analysis of the U $\text{L}_{3\text{-edge}}$ k^3 -weighted EXAFS spectra showed that these spectra contain only two species with different structures. The EXAFS spectra of these two spectral components were determined using the iterative target test [4]. One spectral component (red curve in Fig. 2) corresponds to the aquo ion of uranium(VI). The two axial oxygen atoms have a U- O_{ax} distance of 1.76 Å. The oxygen atoms of water were detected at a distance of 2.40 Å in the equatorial plane of the UO_2^{2+} moiety (Tab. 1). The second spectral component (blue curve Fig. 2) is a monomeric uranium(VI) complex with oxalic acid. None of EXAFS spectra showed any U-U interaction at a distance of approximately 3.9 Å. Therefore, the existence of dimeric species such as $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]^{2-}$ or $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]^{6-}$ is not consistent with our EXAFS results. The EXAFS structural parameters of the monomeric species agree well with recent quantum chemical calculations [5].

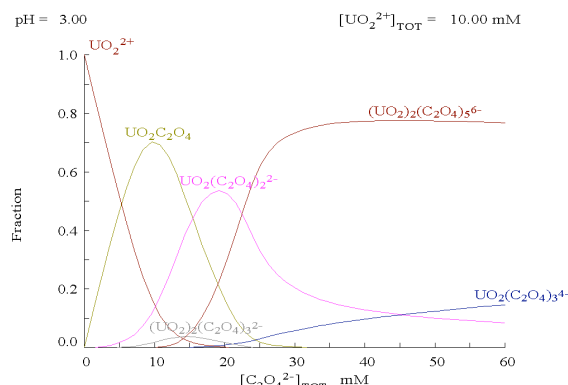


Fig. 1. Speciation diagram according to Havel et al. [1]; $I = 1.0 \text{ M NaClO}_4$.

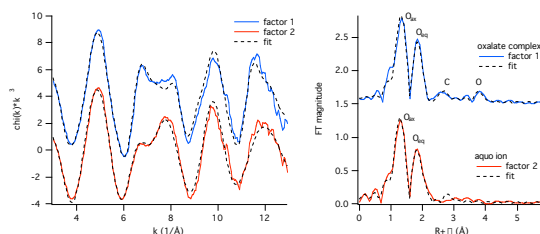


Fig. 2. Uranium $\text{L}_{3\text{-edge}}$ k^3 -weighted EXAFS spectra and corresponding Fourier transforms of spectral components 1 and 2.

Table 1. EXAFS structural parameters of spectral components 1 and 2.

Factor	Shell	N	R(Å)	$\sigma^2(\text{Å}^2)$	$E_0(\text{eV})$
1	O_{ax}	2.1(1)	1.78	0.002	-8.7(2)
	O_{eq}	5.2(3)	2.38	0.006	
	C	5.2	3.26	0.008	
	C(MS)	10.4*	3.38	0.002	
	O(MS)	5.2*	4.44	0.004	
2	O_{ax}	2.2(1)	1.76	0.002	-9.1(3)
	O_{eq}	5.6(3)	2.40	0.008	

* Linked to O_{eq} during the fit. MS – multiple scattering.

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