

The Structure of Uranyl Sulfate in Aqueous Solution - Monodentate Versus Bidentate Coordination

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Abstract. The structure of U(VI) aquo sulfato complexes has been investigated by L_{III}-edge EXAFS spectroscopy. A monodentate coordination with a U-S_{mon} distance of 3.57±0.02 Å prevails in equimolar [SO₄²⁻]_{total}/U(VI) solutions. With increasing [SO₄²⁻]_{total}/U(VI) ratio, bidentate coordination with a U-S_{bid} distance of 3.11±0.02 Å becomes dominant.

Keywords: EXAFS, U L_{III} edge, uranyl sulfate, aqueous solution

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INTRODUCTION

The uranyl ion, UO₂²⁺, forms binary sulfato complexes in acidic aqueous solution. Thermodynamic speciation reveals three sulfato species, UO₂SO₄(aq), UO₂(SO₄)₂²⁻ and UO₂(SO₄)₃⁴⁻, summarized in the NEA thermodynamic database [1]. At pH > 5 different ternary sulfato complexes with bridging hydroxide and oxide occur.

The coordination structure of the binary sulfate species is still under debate. Monodentate coordination has been suggested with high-energy X-ray scattering (HES) in equimolar [SO₄²⁻]_{total}/U(VI) solutions [2]. This result was also observed with infrared and Raman spectroscopy [3,4]. In contrast, U L_{III}-edge EXAFS measurements revealed a bidentate coordination in excess of sulfate [5].

In order to clarify the relationship between monodentate and bidentate coordination we performed the U L_{III}-edge EXAFS measurements, using the preparation as given in the literature.

EXPERIMENTAL

The formation of ternary UO₂²⁺-SO₄²⁻-OH⁻ complexes was avoided by using a pH < 3. A stock solution of 0.1 M uranyl sulfate was prepared by dissolving UO₃ in 0.1 M H₂SO₄. The total sulfate concentration and the pH was adjusted with (NH₄)₂SO₄ and H₂SO₄. Samples **B** and **C** were prepared according to [2] in equimolar [SO₄²⁻]_{total}/U(VI) solutions, sample **A** was prepared according to [5] in excess of sulfate. The samples contain 50 mM U(VI) and 3 M [SO₄²⁻]_{total} at pH 0.99 (sample **A**); 0.5 M U(VI) and 0.5 M H₂SO₄

at pH 1.96 (sample **B**); 0.05 M U(VI) and 0.05 M H₂SO₄ at pH 2.53 (sample **C**). The mineral zippeite, K(UO₂)₂SO₄(OH)₃·H₂O, was chosen as reference (sample **D**, courtesy R. Vochten, Univ. of Antwerp).

EXAFS measurements were carried out on the Rossendorf Beamline (ROBL) at the ESRF. The monochromator, equipped with Si(111) double-crystals, was used in channel-cut mode. Higher harmonics were rejected by two Pt coated mirrors. All experiments were performed at room temperature. The spectra were collected in transmission mode using argon-filled ionization chambers. The monochromator energy scale was calibrated to the K-edge of a Y metal foil (first inflection point at 17038 eV). The EXAFS data were treated with the EXAFSPAK software package by using theoretical phase and amplitude functions obtained by the FEFF 8.2 code.

RESULTS AND DISCUSSION

Structure data derived from single crystal diffraction are often used as model for the ligand arrangement in solution. This approach is valid only as long as the molecular structure units are isolated in the solid structure. The published crystal structures of uranyl sulfate show sulfate bridged between adjacent uranyl units. Most of the sulfate units are monodentate-bridging. Bidentate sulfate coordination is rare in solid structures, and only one bidentate together with three monodentate coordinated sulfate units is described in the literature so far, i.e., in Na₁₀[(UO₂)(SO₄)₄](SO₄)₂·3H₂O [6]. The coordination in solution presented here is different from that observed in solides.

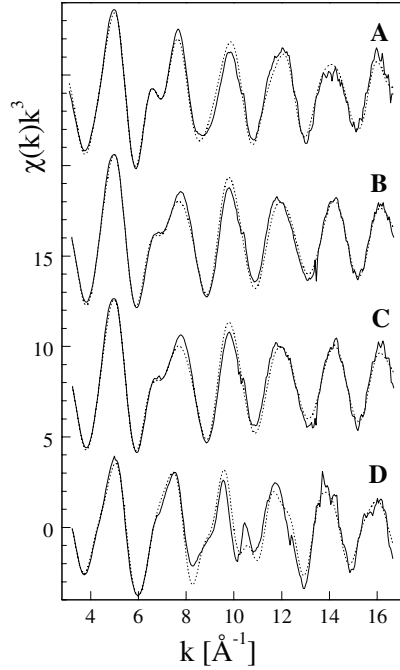


FIGURE 1. U L_{III}-edge k^3 -weighted EXAFS of U(VI) aquo sulfato species (A-C) and zippeite (D); experimental data (line); theoretical curve fit (dots).

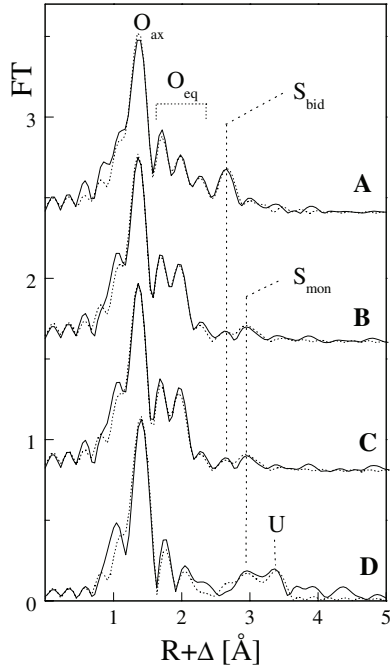


FIGURE 2. Fourier transform of the EXAFS spectra shown in Figure 1.

Figures 1 and 2 show the U L_{III}-edge k^3 -weighted EXAFS and the corresponding Fourier transforms (FT). The fit results are given in Table 1. The FTs are dominated by the peak from the 2 axial oxygen atoms (O_{ax}) that belong to the trans-dioxo uranyl cation, UO_2^{2+} . Its $U-O_{ax}$ distance is 1.77 ± 0.02 Å. The coordination of ligands is restricted to the equatorial plane. Due to the presence of several species in the solution, the equatorial shell is divided into different peaks (O_{eq}). This O_{eq} shell is not appropriate to gain details on the sulfate coordination. The stoichiometry between uranium and sulfate can be derived, however, from the coordination number of sulfur backscattering signals, because these peaks are not affected from other scattering contributions. Furthermore, the U-S distance reveals the sulfate coordination mode (see Figure 3).

TABLE 1. Structural parameters.

	path	R [Å]	N	σ^2 [Å ²]	ΔE	F
A	U- O_{ax}	1.77	2.0	0.0014	4.2	0.16
	U- O_{eq1}	2.35	2.5	0.0055*		
	U- O_{eq2}	2.49	2.4	0.0055*		
	U- S_{bid}	3.12	2.0	0.0060*		
B	U- O_{ax}	1.77	1.9	0.0014	4.9	0.11
	U- O_{eq1}	2.39	4.4	0.0073		
	U- O_{eq2}	2.51	1.4	0.0073		
	U- S_{bid}	3.11	0.3	0.006*		
	U- S_{mon}	3.57	0.6	0.009*		
C	U- O_{ax}	1.77	1.9	0.0014	4.3	0.14
	U- O_{eq1}	2.39	4.2	0.0076		
	U- O_{eq2}	2.50	0.8	0.0076		
	U- S_{bid}	3.07	0.3	0.006*		
	U- S_{mon}	3.56	0.5	0.009*		
D	U- O_{ax}	1.81	2*	0.0016	4.5	0.32
	U- O_{eq1}	2.27	2*	0.0075		
	U- O_{eq2}	2.48	3*	0.0056		
	U- S_{mon}	3.58	2*	0.0072		
	U-U	3.73	2*	0.011		

* value fixed during the fit procedure. Errors in distances R are ± 0.02 Å, errors in coordination numbers N are ± 15 %.

In case of sulfate in excess (sample **A**), a dominant peak appears at $R+\Delta = 2.6$ Å, fitted by sulfur at a distance of 3.12 Å. The distance is in agreement with that of bidentate sulfate coordination in crystal structures with a $U-S_{bid}$ distance of 3.09 Å [6]. The S_{bid} peak appears also in the equimolar solutions **B** and **C**, but with less intensity. These samples show a strong peak from sulfate in monodentate coordination with a $U-S_{mon}$ distance of 3.57 Å. The 4-legged multiple-scattering path $U-O_{ax1}-U-O_{ax2}$ was included by constraining its Debye-Waller factor and effective path-length to twice the values of the corresponding, freely-fitted $U-O_{ax}$ single-scattering path. The $U-S_{mon}$ distance is in good agreement with the U-S distance

observed in zippeite (sample **D**). Zippeite contains monodentate coordinated sulfate with an average U-S distance of 3.58 Å. The U-S peak is partly superposed by the U-U peak at 3.73 Å.

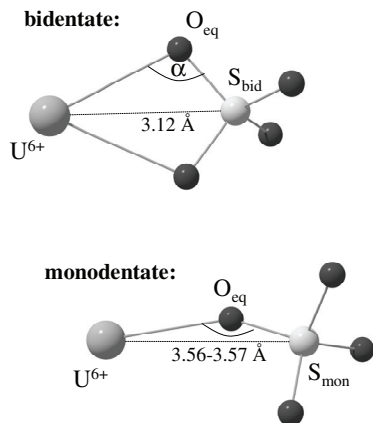


FIGURE 3. Structural features of monodentate and bidentate sulfate coordination. Distances are from EXAFS measurements.

These structural results by EXAFS spectroscopy are now compared with the thermodynamic speciation. In excess of sulfate (sample **A**), the speciation is dominated by $UO_2(SO_4)_2^{2-}$ (26 % $UO_2SO_4(aq)$, 73% $UO_2(SO_4)_2^{2-}$ at pH 0.99). The EXAFS spectrum of sample **A** shows 2 sulfur atoms at 3.12 Å, i.e., in a bidentate coordination. This is in agreement with the thermodynamic estimation that suggests the dominance of the 1:2 species.

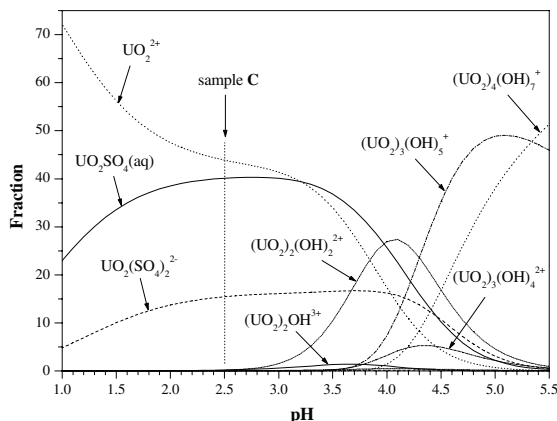


FIGURE 4. Thermodynamic speciation for sample **C** (0.05 M U(VI) and 0.05 M H_2SO_4).

In equimolar $[SO_4^{2-}]_{total}/U(VI)$ solution (samples **B** and **C**) the dominant thermodynamic species at pH 2.53 is $UO_2SO_4(aq)$, and $UO_2(SO_4)_2^{2-}$ is a minor

component only (Figure 4). It is interesting to note, that in the EXAFS spectra of these samples the dominant U-S interaction points to a monodentate coordination, but a minor bidentate coordination is also visible. Therefore we assume, that the $UO_2SO_4(aq)$ species is related to the monodentate coordination and the $UO_2(SO_4)_2^{2-}$ species to the bidentate coordination.

The U- S_{mon} distance revealed by EXAFS (3.57 Å) differs from that observed with high-energy X-ray scattering (3.67 Å) [2]. Furthermore, HES is supposed to be very sensitive to long interatomic distances, but the minor bidentate coordinated sulfate was not observed with this method. The difficulty might be, that the signal is generated by all scattering pairs in the solution. To reveal the ion pairing in the uranyl sulfate solution, a correction of the total structure factors was required, that excludes secondary scattering processes like water-water interactions. This correction, made with non-coordinating uranyl perchlorate solution, may have affected the detection of shorter distances. In contrast, EXAFS reveals only the scattering pairs in direct relation to the absorbing atom. Otherwise, the EXAFS amplitude decreases with $1/R^2$. Therefore, the peak intensity decreases dramatically with increasing absorber-backscatterer distance. This increases the error of the corresponding metrical parameters.

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