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Article

Coordination of a Uranium(IV) Sulfate Monomer in an Aqueous Solution and in the Solid State

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Uranium(IV) sulfate in an aqueous solution and the solid state has been investigated with extended X-ray absorption fine structure (EXAFS) and X-ray diffraction (XRD). The coordination polyhedron comprises monodentate sulfate, bidentate sulfate, and water molecules. The coordination modes of sulfate in solution have been determined from the U−S distances with EXAFS. The U−S distance of 3.67 ± 0.02 Å indicates monodentate sulfate, and the U−S distance of 3.08 ± 0.02 Å indicates bidentate coordination. The obtained sulfur coordination numbers of a solution with a $[SO_4{}^{2-}]/[U^{4+}]$ ratio of 40 suggest species with compositions of $[U(SO_{4,bid})_2(SO_{4,mon})_2 \cdot nH_2O]^{4-}$ and $[U(SO_{4,bid})_3 (SO_{4,mon})_2 \cdot mH_2O]^{6-}$. Charge-compensating countercations or ion pairing with Na^+ and $NH_4{}^+$ could not be detected with EXAFS. One of the solution species, $[U(SO_4)_5H_2O]^{6-}$, has been conserved in a crystal. The corresponding crystal structure of $Na_{1.5}(NH_4)_{4.5}[U(SO_4)_5 \cdot H_2O] \cdot H_2O$ [space group $P\bar{1}$, $a = 9.4995(16)$ Å, $b = 9.8903(16)$ Å, $c = 12.744(2)$ Å, $\alpha = 93.669(2)°$, $\beta = 103.846(2)°$, $\gamma = 109.339(2)°$] has been determined by single-crystal XRD. Two monomeric uranium(IV) sulfate complexes and three sodium units are linked in alternating rows and form a one-dimensoinal ribbon structure parallel to the a axis.

Introduction

Coordination of hexavalent uranium sulfate in an aqueous solution has been extensively investigated by different spectroscopic techniques.[1–5] Because of small differences in the Gibbs free energy, the sulfate group is able to coordinate in monodentate as well as in bidentate fashion.[1,6] The solution species $UO_2SO_4{}^0$ shows monodentate sulfate coordination, but this species also comprises to a small extent a bidentate-coordinated sulfate isomer.[1,7] The species $UO_2(SO_4)_2{}^{2-}$ shows predominantly bidentate sulfate coordina-

tion.[1] In contrast, studies on the coordination of tetravalent uranium sulfate in an aqueous solution are scarce. The current NEA thermodynamic database reports only two sulfate species, $USO_4{}^{2+}$ and $U(SO_4)_2(aq)$.[8] Uranium(IV) sulfate species occur as monomers with monodentate and bidentate sulfate coordination.[1] The fraction of bidentate coordination increases with an increasing $[SO_4{}^{2-}]/[U^{4+}]$ ratio. However, uranium(IV) often forms polynuclear complexes and polymers.[8,9] Known crystal structures of uranium(IV) sulfate show only ternary polymers with monodentate bridging sulfate ligands.[10–12] These structures result from a rearrangement of the sulfate group during the crystallization process and do not represent the solution species. The aim of this

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paper is to investigate the monomeric uranium(IV) sulfate molecule in solution and to preserve it in a crystal structure.

Experimental Section

Sample Preparation. The samples were prepared with 0.05 M UO_2SO_4, 0.38 M H_2SO_4, 1.57 M $(NH_4)_2SO_4$, and 0.1 M NaCl. Uranium(VI) has been reduced to uranium(IV) by electrolysis at a constant potential of −370 mV vs Ag/AgCl. The electrolysis has been performed using an electrochemical cell described previously.[13] A platinum gauze was used as the working electrode. A counter electrode of the second kind was used, consisting of a silver rod and 0.1 M Cl^- ions in the solution. The presence of Cl^- ions does not disturb the sulfate coordination because the formation constant of uranium(IV) chloride is significantly lower. The electrochemical reduction of uranyl sulfate solutions at pH $\geq$ 1.5 is immediately accompanied by a precipitation. This precipitation prevents a complete reduction of uranium(VI) by passivating the electrodes. Therefore, the pH of the uranium(VI) sulfate solution was initially adjusted at pH 1.0 and subsequently increased by the addition of NaOH. Up to pH 1.5, the solution (sample **A**) remained clear at least for several months, whereas at pH 2.0, a pale-green precipitate (sample **B**) occurred immediately. After 12 months, dark-green crystals were obtained from the solution at pH 1.5 (sample **C**).

Extended X-ray Absorption Fine Structure (EXAFS) Measurements. EXAFS measurements were performed in transmission mode using a Si(111) double-crystal monochromator on the Rossendorf Beamline[14] at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Higher harmonics were rejected by two platinum-coated mirrors. The uranium L_{III}-edge spectra were collected using argon-filled ionization chambers at ambient temperature and pressure. Data were collected in equidistant k steps of 0.05 Å^{-1} across the EXAFS region. An yttrium metal foil (first inflection point at 17 038 eV) was used for energy calibration. The uranium L_{III} threshold energy, $E_{k=0}$, was arbitrarily defined as 17 185 eV. EXAFS data were extracted from the raw absorption spectra by standard methods including a spline approximation for the atomic background using the programs *WINXAS*[15] and *EXAFSPAK*.[16] Theoretical phase and amplitude functions were calculated with FEFF 8.2.[17] The amplitude reduction factor, S_0^2, was defined as 1.0 in the FEFF calculation and fixed to that value in the data fits.

X-ray Diffraction (XRD). The single-crystal X-ray data collection was carried out on a Bruker AXS SMART diffractometer at room temperature using Mo Kα radiation (λ = 0.710 73 Å) monochromatized by a graphite crystal. Data reduction was carried out using the Bruker AXS *SAINT* and *SADABS* packages. The

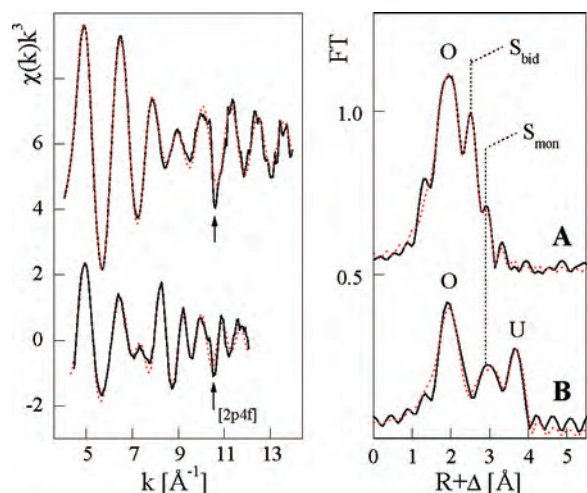**Figure 1.** Uranium L_{III}-edge k^3-weighted EXAFS data and their FTs of uranium(IV) sulfate in solution at pH 1.5 (sample **A**) and amorphous precipitate from a solution obtained at pH 2.0 (sample **B**). The steplike interruption at $k \sim 10.5$ Å^{-1} originates from 2p4f double-electron excitation.[20] The corresponding EXAFS fit parameters are given in Table 1.

Table 1. EXAFS Fit Parameters[a]

sample	shell	R [Å]	N	σ^2 [Å^2]	$\Delta E_{k=0}$	F
A	U−O	2.40	9.4	0.013	−8.1	0.10
	U−S$_{bid}$	3.08	2.4	0.0047		
	U−S$_{mon}$	3.67	2.2	0.011		
B	U−O	2.43	6.1	0.015	−7.6	0.11
	U−S$_{mon}$	3.66	2.8	0.0086		
	U−U	3.87	2.1	0.0073		
C	U−O	2.41	9.5	0.012	−7.3	0.11
	U−S$_{bid}$	3.09	3.3	0.0048		
	U−S$_{mon}$	3.68	2.1	0.011		

[a] Errors in distances R are ±0.02 Å; errors in coordination numbers N are ±15%. The overall goodness of the fits, F, is given by χ^2 weighted by the magnitude of the data. The threshold energy, $E_{k=0}$, was arbitrarily defined at 17 185 eV and varied as a global fit parameter, resulting in the energy shift $\Delta E_{k=0}$. S_0^2 was defined as 1.0.

structure was solved by direct methods and refined by full-matrix least-squares calculation using *SHELX*.[18,19]

Results and Discussion

The k^3-weighted EXAFS spectrum of sample **A** with uranium(IV) sulfate in solution and the corresponding Fourier transform (FT) are shown in Figure 1. The FT represents a pseudoradial distribution function, where the peaks are shifted to lower values $R + \Delta$ relative to the true near-neighboring distances R. The Δ shift depends on the scattering behavior of the electron wave in the atomic potentials and was considered in the shell fits.

The first high peak in the FT results from the backscattering signal of 9.4 ± 1 oxygen atoms in the first coordination sphere. These oxygen atoms belong to sulfate in monodentate (mon) and bidentate (bid) coordination, as well as oxygen from water molecules. The distances of these ligands to the uranium atom are known from the literature and vary as follows: U−O$_{H_2O}$ $\sim$ 2.41 Å; U−O$_{Smon}$ $\sim$ 2.32 Å; U−O$_{Sbid}$ $\sim$ 2.47 Å. Because of the distance resolution $\Delta R = \pi/2\Delta k$

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of 0.16 Å, resulting from the limited Δk range of 9.7 Å^{-1}, the different U−O distances cannot be separated in the fit, but the differences of the U−O distances are reflected by an increased Debye–Waller factor, σ^2, of 0.013 Å^2. As a consequence, the U−O distances are not appropriate to gain insight into the sulfate coordination in solution. The difference in the U−S distances of sulfate in bidentate and monodentate coordination is around 0.6 Å, which is above the EXAFS distance resolution. The FT of sample **A** shows two peaks at $R + \Delta \sim 2.5$ and 2.9 Å. These peaks could be fit with sulfur atoms at distances of 3.08 and 3.67 Å, indicating bidentate and monodentate sulfate coordination. If one takes into account that bidentate sulfate binds with two oxygen atoms and monodentate sulfate binds with one oxygen atom, their coordination numbers reveal that two or three water molecules may participate in the coordination. However, one has to consider that this spectrum is an average over the present species and isomers in the solution.

In a previous attempt to isolate solution species, we provoked the precipitation of uranium(IV) sulfate species by increasing the pH $\geq$ 1.5.[1] At pH $\geq$ 1.8, only amorphous precipitates could be obtained. As an example, the EXAFS spectrum of such a precipitate (sample **B**) is shown in Figure 1. The broadening of the peaks results at least partly from the shorter k range used for sample **B**. The data fit reveals a reduced number of oxygen atoms in the first coordination sphere, related with a large σ^2. This coordination number may result from a partly destructive superposition of different scattering contributions in the first coordination shell. The data analysis indicates a rearrangement of the SO$_4^{2-}$ groups from mixed bidentate/monodentate in solution to exclusive monodentate coordination in the solid state. The rearrangement of the sulfate groups during crystallization is a typical behavior of sulfate, frequently forming monodentate bridging sequences in solid structures. The FT of sample **B** shows, furthermore, a U−U backscattering signal at 3.87 Å, which has not been observed in the solution. Besides, the reduced coordination number of sulfate indicates that in the precipitate one or two sulfate groups are replaced by OH groups. This is in line with the broadening of the oxygen peak at 2.43 Å. From this observation, the precipitate can be assigned as a uranium(IV) hydroxyl sulfate complex, or a mixture of such complexes, which has been investigated with IR measurements.[21] Hydroxyl sulfate complexes form usual sequences of μ_2-OH-bridged uranium(IV) dimers with U−U distances between 3.84 and 3.90 Å.[11,12] In the absence of OH groups, only sulfate itself can act as a bridging ligand, resulting in U−U distances of 5.69 Å.[10]

In further experiments, where the pH value has been restricted to 1.5, single crystals have been obtained (sample **C**). The EXAFS spectrum of sample **C** is shown in Figure 2 together with the spectrum of solution sample **A**. These spectra have a clear similarity, indicating that a solution species is preserved in the crystal structure. The first coordination sphere shows a U−O distance of 2.41 Å and a
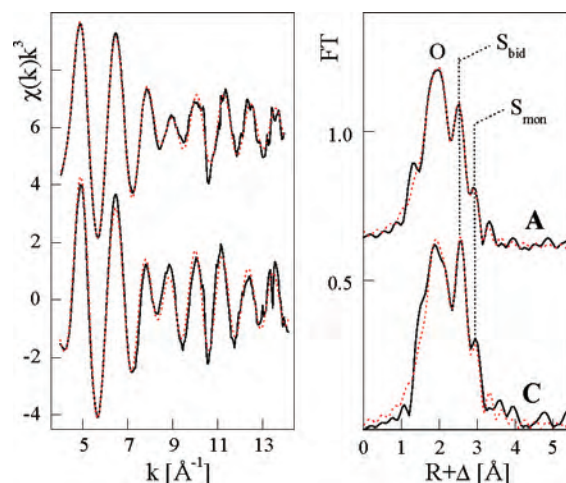

Figure 2. Uranium L$_{III}$-edge k^3-weighted EXAFS data (left) and the corresponding FTs (right) of uranium(IV) sulfate in solution at pH 1.5 (sample **A**) and the crystalline precipitate obtained at pH 1.5 (sample **C**). The corresponding fit parameters are given in Table 1.

coordination number of 9.5 ± 1. In contrast to sample **A**, where this peak shows a Gaussian-like shape, sample **C** shows a weak fine structure, which has not been considered in the data fit.

The coordination number of the sulfur atom, representing the monodentate sulfate, remains nearly unchanged among the solution and solid state, whereas the coordination number of the sulfur in bidentate sulfate increases from 2.4 to 3.3. The similarity of the Debye–Waller factors rules out the possibility that this is an effect of different ordering in the solution and solid state. It is rather a hint that the solution comprises at least two species with similar coordination, e.g., [U(SO$_{4,bid}$)$_2$(SO$_{4,mon}$)$_2 \cdot n$H$_2$O]$^{4-}$ and [U(SO$_{4,bid}$)$_3$(SO$_{4,mon}$)$_2 \cdot$ mH$_2$O]$^{6-}$. The latter species is preserved in the crystal structure. The solution species have high negative charge that requires compensation. However, there is no indication of countercations or ion pairing from EXAFS spectroscopy, because EXAFS is not sensitive to light counterions like Na$^+$ and NH$_4^+$ in distances >4 Å. In contrast, heavier counterions like Ca^{2+} have been observed with EXAFS in the environment of the [Th(OH)$_8$]$^{4-}$ complex with a Th−Ca distance of 3.98 Å.[22]

To obtain detailed information on the uranium coordination, a single crystal of sample **C** has been investigated by XRD. The compound Na$_{1.5}$(NH$_4$)$_{4.5}$[U(SO$_4$)$_5 \cdot$H$_2$O]$\cdot$H$_2$O crystallizes in the triclinic space group $P\bar{1}$ with two [U(SO$_4$)$_5 \cdot$ H$_2$O]$^{6-}$ units in the unit cell. The structure was solved by direct methods and expanded using FT techniques. Most of the hydrogen atoms were found in the difference Fourier analysis and refined with restraints in bond lengths and angles. The final cycle of full-matrix least-squares refinement converged with an R value of R1 = 0.0505. Details of the measurement and the structural analysis are given in the Supporting Information. The coordination polyhedron of uranium is shown in Figure 3, and some selected bond lengths are listed in Table 2.

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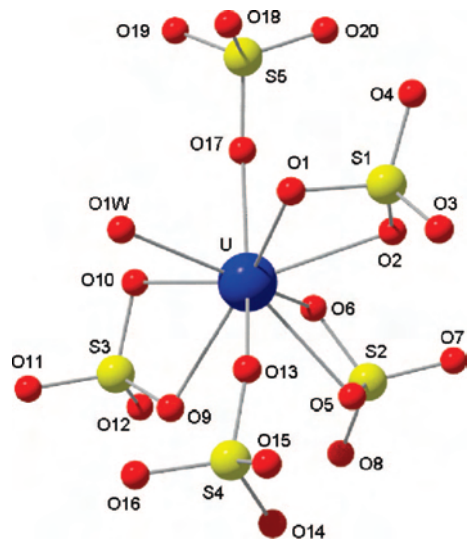
Figure 3. Coordination environment of the uranium atom in the unit $[U(SO_4)_5H_2O]^{6-}$. The countercations are omitted for clarity.

Table 2. Selected Bond Lengths (in Å) of the Crystal Structure $Na_{1.5}(NH_4)_{4.5}[U(SO_4)_5 \cdot H_2O] \cdot H_2O$

U1−O1$_{bid}$	2.491(5)	U1−S1$_{bid}$	3.1027(16)
U1−O2$_{bid}$	2.428(5)	U1−S2$_{bid}$	3.1043(15)
U1−O5$_{bid}$	2.474(5)	U1−S3$_{bid}$	3.1084(15)
U1−O6$_{bid}$	2.424(5)	U1−S4$_{mon}$	3.683(5)
U1−O9$_{bid}$	2.429(5)	U1−S5$_{mon}$	3.692(4)
U1−O10$_{bid}$	2.481(4)	U1−Na1	4.086(4)
U1−O13$_{mon}$	2.325(5)	U1−Na2	5.505(6)
U1−O17$_{mon}$	2.295(5)		
U1−O1W	2.425(5)		

There are one U^{4+} and five unique S^{6+} cations in the structure. Each S^{6+} is tetrahedrally coordinated by four oxygen atoms, with S−O bond lengths in the range of 1.444–1.511 Å. The uranium coordination polyhedron approximates closely to a monocapped square antiprism. Uranium is nine-coordinated by three sulfate groups (S1, S2, and S3) in bidentate coordination (U−S$_{bid}$ ∼ 3.10 Å) and two sulfate groups (S4 and S5) in monodentate arrangement (U−S$_{mon}$ ∼ 3.68 Å). One single water molecule completes the uranium(IV) coordination sphere with a U−O distance of ∼2.425 Å. The U−O distances of the monodentate sulfate groups are shorter (2.29 and 2.32 Å) than the bidentate-coordinated sulfate groups. The U−O distances of the three bidentate-coordinated sulfate groups are uneven; each of them splits into a slightly shorter and a longer distance of ∼2.43 and 2.48 Å. The average U−O distance over all oxygen atoms in the first coordination sphere is 2.41 Å, which is in good agreement with the value obtained by EXAFS. The negative charge of the $[U(SO_4)_5 \cdot H_2O]^{6-}$ unit is compensated for by 1.5 Na^+ and 4.5 NH_4^+ ions. The broken values are a result of two atoms (Na2 and N5) being located on special positions (Wyckoff 1e and 1b).

Along the *c* direction, the monomeric $[U(SO_4)_5 \cdot H_2O]^{6-}$ units are arranged as zigzag chains, as illustrated in Figure 4a. The U−U distances between two units amount to 6.720 and 7.683 Å with an inclined angle of 131.68°. Along the chain direction, the $[U(SO_4)_5 \cdot H_2O]^{6-}$ units are interconnected only via hydrogen bonds to the ammonium ions. Within the structure, oxygen atoms of the coordinating water molecule
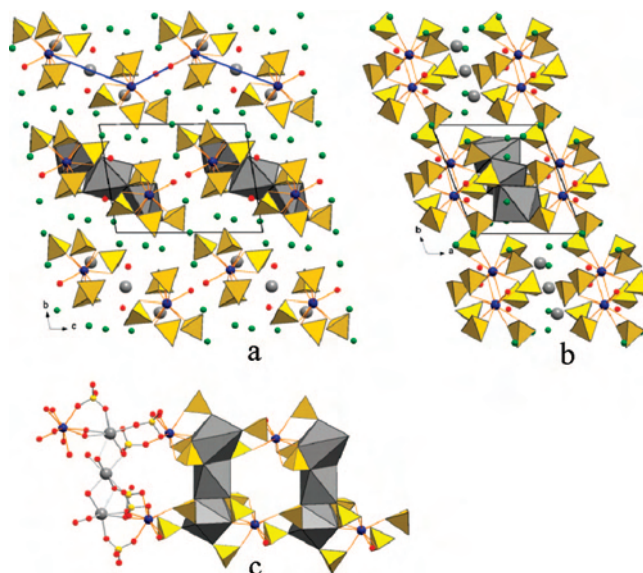

Figure 4. Crystal structure of $Na_{1.5}(NH_4)_{4.5}[U(SO_4)_5 \cdot H_2O] \cdot H_2O$ drawn along the *a* axis (a) and along the *c* axis (b). Ribbon structure of two anionic complexes of uranium and three sodium units parallel to the *a* axis (c). The SO_4^{2-} anions are represented as yellow tetrahedra; the sodium coordination environment is partly presented as gray polyhedra. Individual atoms are shown as spheres: U, blue; Na, gray; N, green; S, yellow; O, red. Blue lines denote the U−U distances discussed in the text. All hydrogen atoms are omitted for clarity.

and the ammonium atoms act as donors, whereas the sulfate oxygen atoms act as acceptors. The sulfate groups are linked through bonds to interstitial Na^+ cations. The structure contains two symmetrically independent Na^+ atoms. Na1 is coordinated by seven sulfate oxygen atoms with Na−O bond lengths ranging from 2.37 to 2.72 Å. Na2 is located at the inversion center in (½, ½, 0) and is coordinated by six sulfate oxygen atoms with Na−O bond lengths of 2.31−2.70 Å. Two anionic complexes of uranium and three sodium units are linked in alternating rows and form a one-dimensional ribbon structure parallel to the *a* axis (Figure 4c). As depicted in Figure 4a, these ribbons are separated by ammonium cations. The charge compensation of the $[U(SO_4)_5H_2O]^{6-}$ unit by Na^+ described here has some similarities with the uranium(VI)-containing $[(UO_2)(SO_4)_4]^{6-}$ complex, where three sulfate groups are monodentate-coordinated and one sulfate is bidentate-coordinated.[23−25]

This is the first time that bidentate-coordinated sulfate has been observed in a crystal structure of uranium(IV). Although bidentate coordination is common in solution,[1] uranium(IV) crystal structures investigated up to now showed only monodentate sulfate coordination. The sulfate complexes of other actinides with the same oxidation state like thorium(IV), neptunium(IV), and plutonium(IV) comprise a variety of dimers,[26] chains,[27] layers,[28] and networks.[29] Most

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of the bridging sulfates are pure monodentate, but it can be also coordinated with bidentate to one and monodentate to the next neighbor. Such coordination has been observed in plutonium(IV)[26] and thorium(IV)[30] sulfate structures. To obtain uranium(IV) as a monomer, the formation of polymers that have been observed in sample **B** needs to be suppressed by keeping the pH ≤ 1.5. The high charge of the uranium(IV) sulfate units requires a sufficient compensation by appropriate counterions. The reason that the uranium(IV) monomers do not undergo a rearrangement to polymers in the crystal structure is probably that the complex is already sterically and electrostatically saturated in the solution.

Supporting Information Available: CIF file for the crystal structure and additional details of the preparation, crystal structure, and structural analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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