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X-ray Absorption Fine Structures of Uranyl(V) Complexes in a Nonaqueous Solution

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The structures of three different U^V complexes, $[U^VO_2(\text{salophen})\text{DMSO}]^-$, $[U^VO_2(\text{dbm})_2\text{DMSO}]^-$, and $[U^VO_2(\text{saldien})]^-$, in a dimethyl sulfoxide (DMSO) solution were determined by X-ray absorption fine structure for the first time.

Actinide elements at oxidation states 5+ and 6+ form actinyl ions (AnO_2^{n+}, An = U, Np, Pu, Am, n = 1 and 2) with typical *trans*-dioxo arrangement. Among them, U^V is quite unstable in solutions because of disproportionation. Recently, the chemistry of U^V is attracting special interest because this field of actinides had so far been poorly explored.[1] Uranyl(V) carbonate, $U^VO_2(CO_3)_3^{5-}$, is currently the only known stable U^V species in an aqueous solution.[2] Other stable U^V species were reported only in molten chloride salts at 600−750 °C.[3] We have previously found two stable U^V complexes in nonaqueous systems, $[U^VO_2(\text{salophen})\text{DMSO}]^-$ (**1**^{V}) and $[U^VO_2(\text{dbm})_2\text{DMSO}]^-$ (**2**^{V}), in dimethyl sulfoxide (DMSO; Scheme 1).[4a−d] Several U^V complexes have also been reported by other groups.[4e−n] Most recently, we found a new stable U^V complex in a nonaqueous solution, $[U^VO_2(\text{saldien})]^-$ (**3**^{V}, in DMSO, Scheme 1).[5]

The molecular structure of the U^V species represents an essential chemical aspect. For solid U^V compounds, the structure determination is easily doable by single-crystal X-ray diffraction (XRD). This technique provides precise structural data, and, in fact, most of the structural characterizations of crystalline U^V species have been done this way.[4e−m] A structure in the solid state is, however, not necessarily representative for that in solution, while single-crystal XRD is not applicable to solution species. IR[4b,c] and NMR[4h−m] spectroscopic methods were used in the previous studies on U^V solution species. However, these methods provide only qualitative evidence (e.g., vibration, ligand coordination, molecular symmetry, and molecular weight estimated from diffusion coefficients) but do not provide quantitative structures such as bond distances. Furthermore, any information on solvent coordination (e.g., DMSO of **1**^{V} and **2**^{V}) cannot be obtained because of strong absorption and/or rapid chemical exchange of the solvent. The most promising technique to overcome this problem is X-ray absorption fine structure (XAFS) spectroscopy. The absorption edge is a good indicator of the oxidation state, and extended XAFS (EXAFS) can be transformed to a one-dimensional radial distribution function providing coordination numbers (N) and interatomic distances (R) of atoms around

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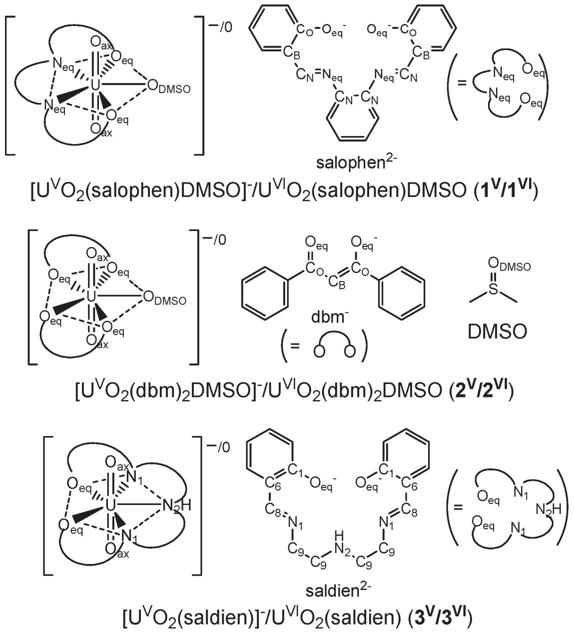
Scheme 1



$[U^VO_2(salophen)DMSO]^-/U^{VI}O_2(salophen)DMSO$ (**$1^V/1^{VI}$**)

$[U^VO_2(dbm)_2DMSO]^-/U^{VI}O_2(dbm)_2DMSO$ (**$2^V/2^{VI}$**)

$[U^VO_2(saldien)]^-/U^{VI}O_2(saldien)$ (**$3^V/3^{VI}$**)

U regardless of sample forms (e.g., crystalline, amorphous, and solution). In practice, the structures of $U^VO_2(CO_3)_3^{5-}$ and $U^{VI}O_2(CO_3)_3^{4-}$ in an aqueous solution have been investigated by using XAFS.[2f,g] In this Communication, we report the XAFS spectra and the structures of U^V complexes (**1^V**, **2^V**, and **3^V**) in DMSO for the first time. The corresponding U^{VI} species (**1^{VI}**, **2^{VI}**, and **3^{VI}**) were also studied, and the difference between U^V and U^{VI} is discussed.

Sample solutions of **1^V** (3.6×10^{-2} M), **2^V** (3.3×10^{-2} M), and **3^V** (3.1×10^{-2} M) in DMSO containing 0.30 M tetrabutylammonium perchlorate were prepared by galvanostatic electrolysis. The color of the U^V solutions was green or dark green. All operations were performed under a dry N_2 atmosphere in a dedicated glovebox. The corresponding U^{VI} samples in DMSO ([**1^{VI}**] = 5.3×10^{-2} M, [**2^{VI}**] = 4.0×10^{-2} M, and [**3^{VI}**] = 3.1×10^{-2} M) were also prepared.[4a,c,5,6] U L_{III}-edge X-ray absorption spectra of the U^V and U^{VI} samples were recorded at the Rossendorf Beamline at the European Synchrotron Radiation Facility (6 GeV; 70−90 mA).[7] Single-scattering paths from coordinating O and N atoms and surrounding C and S atoms (if necessary) and multiple-scattering paths from the linear uranyl ion were included in the EXAFS curve fit. Further experimental details are described in the Supporting Information.

U L_{III}-edge XANES spectra of **1^V**/**1^{VI}**, **2^V**/**2^{VI}**, and **3^V**/**3^{VI}** in DMSO are shown in Figure 1. The absorption edges of the U^{VI} complexes are 17 172.5 eV for **1^{VI}**, 17 172.9 eV for **2^{VI}**, and 17 172.6 eV for **3^{VI}**, whereas those of **1^V**, **2^V**, and **3^V** are 17 171.3, 17 171.1, and 17 170.5 eV, respectively. These U L_{III} edges of the U^V and U^{VI} species are comparable with those of $U^VO_2(CO_3)_3^{5-}$ (17 171.1 eV) and $U^{VI}O_2(CO_3)_3^{4-}$ (17 173.3 eV).[2g] The shift of the absorption edge by ca. 1−2 eV toward lower energy arises from the lower effective charge of U in U^V than in U^{VI}. After the white line, the characteristic XANES oscillation due to multiple scattering along the linear uranyl unit was observed in both U^V and U^{VI} of each pair, indicating the presence of UO_2^{n+}.[2g,8]

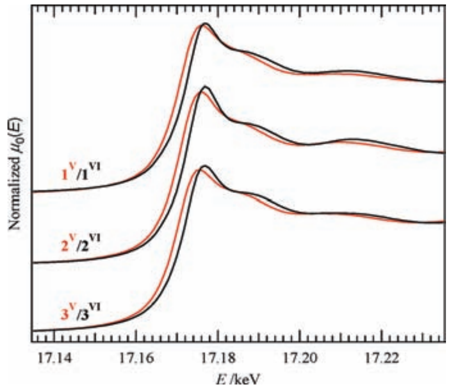


Figure 1. U L_{III}-edge XANES spectra of U^V (red) and U^{VI} (black) complexes in DMSO.

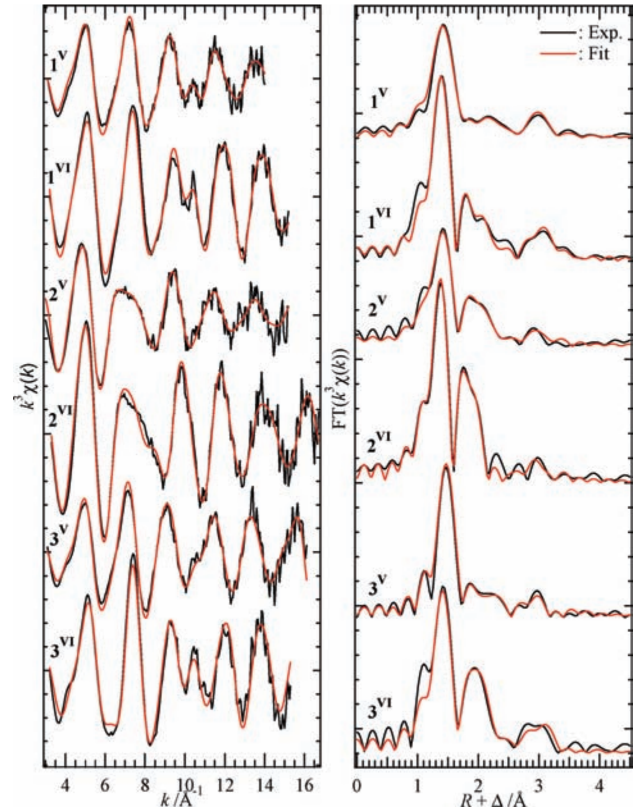


Figure 2. k^3-weighted U L_{III}-edge EXAFS spectra (left) and their FTs (right) of U^V and U^{VI} complexes in DMSO together with the best-fit lines from EXAFS curve fits.

The k^3-weighted EXAFS spectra of **1^V**, **1^{VI}**, **2^V**, **2^{VI}**, **3^V**, and **3^{VI}** in DMSO and their Fourier transforms (FTs) are shown in Figure 2. After the reduction from U^{VI} to U^V, spectral changes were observed in both the amplitude and frequency of the EXAFS oscillation, indicating structural modification around U. Several EXAFS spectra (**1^V**, **1^{VI}**, **3^V**, and **3^{VI}**) show the characteristic peak at ca. 10.5 Å^{-1} attributable to 2p4f double-electron excitation.[9] If a U^V cation−cation complex

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Table 1. Structural Parameters from EXAFS Curve Fits for U^{V} and U^{VI} Complexes in DMSO[a]

	U^{V}			U^{VI}			
shell[b]	N	R/Å	σ^2/Å^2	N	R/Å	σ^2/Å^2	R_{cryst}/Å
$\mathbf{1^{V}/1^{VI}}$		ΔE_0 = 7.1 eV			ΔE_0 = 6.1 eV		
O_{ax}	2[c]	1.84	0.0040	2[c]	1.80	0.0017	1.78
O_{eq}	2.2	2.29	0.0079	2.1	2.25	0.0025	2.27
O_{DMSO}	1.1	2.91	0.0048	1.1	2.38	0.0020	2.41
N_{eq}	2.0	2.62	0.0098	2.1	2.56	0.0029	2.55
C_O	2.4	3.22	0.0100	2.0	3.23	0.0054	3.27
C_N	3.9	3.52	0.0094	4.0	3.44	0.0054	3.44
S	1.1	3.71	0.0067	1.1	3.64	0.0019	3.61
C_B	2.4	3.80	0.0044	2.0	3.71	0.0044	3.74
O_{ax}(MS)	2[c]	3.69	0.0047	2[c]	3.60	0.0033	
$\mathbf{2^{V}/2^{VI}}$		ΔE_0 = 9.8 eV			ΔE_0 = 5.4 eV		
O_{ax}	2[c]	1.85	0.0043	2[c]	1.78	0.0017	1.77
O_{eq}	3.9	2.49	0.0107	4.2	2.35	0.0043	2.33
O_{DMSO}	1.0	2.89	0.0057	1.1	2.48	0.0033	2.46
C_O	4.2	3.54	0.0100	4.5	3.50	0.0145	3.38
S	1.0	3.67	0.0040	1.1	3.57	0.0070	-[d]
C_B	2.0	3.73	0.0040	2.8	3.69	0.0087	3.79
O_{ax}(MS)	2[c]	3.70	0.0120	2[c]	3.57	0.0030	
$\mathbf{3^{V}/3^{VI}}$		ΔE_0 = −4.5 eV			ΔE_0 = −2.0 eV		
O_{ax}	1.7	1.86	0.0015	2[c]	1.81	0.0025	1.79
O_{eq}	1.7	2.27	0.0032	2.1	2.26	0.0018	2.23
N_2	1.0	2.41	0.0008	3.0[e]	2.59[e]	0.0055[e]	2.59[e]
N_1	1.7	2.60	0.0042				
C_1	2.0	3.22	0.0163	2.0	3.12	0.0130	3.32
C_9	4.0	3.49	0.0032	6.0[f]	3.54[f]	0.0065[f]	3.48[f]
C_8	2.2	3.62	0.0011				
O_{ax}(MS)	1.7	3.73	0.0024	2[c]	3.62	0.0069	
C_6	2.1	3.76	0.0046				3.84

[a] σ^2 = Debye−Waller factor; ΔE_0 = threshold energy shift. [b] Atomic notation follows Scheme 1. [c] Fixed parameter. [d] Not available because the model structure is $U^{VI}O_2(dbm)_2$(ethanol) in ref 10. [e] Total of N_2 and N_1. [f] Total of C_9 and C_8.

is formed, a peak due to the U···U interaction (ca. 3.5 and 4.3 Å) would be observable in the FT. In Figure 2, all of the three different U^{V} complexes do not show remarkable peaks correlated to such a U···U interaction. This suggests that the U^{V} complexes are present as mononuclear species. From the viewpoint of the molecular weight calculated by the diffusion coefficient, Nocton et al. already proposed that $\mathbf{2^{V}}$ keeps its monomeric structure in DMSO.[4i] Their proposition was corroborated by our EXAFS study.

To determine the structures of the U^{V} and U^{VI} complexes in the DMSO solutions, EXAFS curve fits were performed. The estimated structural parameters of all complexes are summarized in Table 1 together with the mean interatomic distances in the crystalline U^{VI} complexes (R_{cryst}).[5,6,10] The calculated quantities, N and R, in this table well reproduce the experimental EXAFS spectra and FTs as shown in Figure 2 and are in line with those of the corresponding U^{VI} species in the solid state.

The $U-O_{ax}$ distances of $\mathbf{1^{V}}$ and $\mathbf{1^{VI}}$ are 1.84 and 1.80 Å, respectively. The difference between the two distances [$\Delta R(U-O_{ax})$] is 0.04 Å, which is consistent with our previous estimation from IR spectroscopy.[4c] In the equatorial plane, the distances between U and the coordinating atoms of salophen^{2-} in $\mathbf{1^{V}}$ are slightly longer than those in $\mathbf{1^{VI}}$ by 0.04−0.06 Å. It must be emphasized that the $U-O_{DMSO}$ distance in $\mathbf{1^{V}}$ is unexpectedly long (2.91 Å), while that in $\mathbf{1^{VI}}$ (2.38 Å) is almost the same as that in the solid state. Because such a long distance between U and O_{DMSO} seems to be unusual for the uranyl complex, validities of the $R(U-O_{DMSO})$ estimation and the EXAFS curve fit need to be examined. The second system, $\mathbf{2^{V}/2^{VI}}$, also involves DMSO coordination. Therefore, the comparison between $\mathbf{1^{V}}$ and $\mathbf{2^{V}}$ is suitable for this subject. The structural parameters of both $\mathbf{2^{V}}$ and $\mathbf{2^{VI}}$ show the similar trends as the $\mathbf{1^{V}/1^{VI}}$ system; i.e., $R(U-O_{ax})$ = 1.85 Å for $\mathbf{2^{V}}$ and 1.78 Å for $\mathbf{2^{VI}}$, $\Delta R(U-O_{ax})$ = 0.07 Å, in agreement with the IR result,[4c] and lengthening of $R(U-O_{eq})$ by the reduction. The quantity of interest here, $R(U-O_{DMSO})$ in $\mathbf{2^{V}}$, is estimated as 2.89 Å, which is similar to that in $\mathbf{1^{V}}$. Thus, it is highly probable that the long $R(U-O_{DMSO})$ of around 2.9 Å is present in both $\mathbf{1^{V}}$ and $\mathbf{2^{V}}$. $R(U-O_{DMSO})$ in the U^{V} complexes is still shorter than the sum of the van der Waals radii of U and O (1.86 + 1.52 = 3.38 Å),[11] indicating that such a long bond formation is feasible. R(U···S) of U^{V} is not very different from that of U^{VI} in both couples. This arises from the flexibility of the U−O−S bond angle (Figure S2 in the Supporting Information).

In the system of $\mathbf{3^{V}/3^{VI}}$, where the unidentate ligand is no longer included, a stronger equatorial coordination due to the pentadentate saldien^{2-} is expected. The structural data concerning the $U-O_{ax}$ bond are similar to those of the former two systems: $R(U-O_{ax})$ = 1.86 Å for $\mathbf{3^{V}}$ and 1.81 Å for $\mathbf{3^{VI}}$, and $\Delta R(U-O_{ax})$ = 0.05 Å.[4c] In contrast, very slight differences (within 0.01 Å) in the equatorial coordination were found between $\mathbf{3^{V}}$ and $\mathbf{3^{VI}}$, except for a significant shortening of $R(U-N_2)$ by 0.17 Å in going from U^{VI} to U^{V}. This peculiar behavior of the $\mathbf{3^{V}/3^{VI}}$ system is due to the fact that the ethylene moieties between N_1 and N_2 are rather flexible, while the moieties consisting of O_{eq}, C_1, C_6, C_8, and N_1 in the six-membered chelating rings are predicted to be rigid because of the conjugated π-electron system.

In a bare UO_2^{+}, U 5fδ and 5fϕ orbitals do not participate in any bond formation but stay as degenerated nonbonding orbitals.[12] When an equatorial coordination forms, 5fϕ with six lobes localized on the xy plane is involved in the interaction with ligands, having an antibonding character. In contrast, 5fδ is still nonbonding because its lobes are not present directly along any bonds. As a result, the unpaired electron in U^{5+} will occupy the nonbonding 5fδ in the actual U^{V} complexes. This configuration is energetically favorable from the viewpoint of electric repulsion, which is minimized at the ground state. Consequently, the unpaired U 5f electron in U^{V} does not participate in any chemical bond, while the decrease in the effective charge of U slightly lengthens both the axial and equatorial bonds in U^{V} compared to those in U^{VI}. The expansion of the equatorial coordination sphere of U^{V} is suppressed in $\mathbf{3^{V}}$ because of the stronger complexation ability of saldien^{2-}. The unique flexibility of the coordination at the fifth equatorial site in the U^{V} complexes $U-O_{DMSO}$ and $U-N_2$ is still an open question.

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Supporting Information Available: Experimental details, visible−near-IR absorption spectra of $\mathbf{1^{V}}$, $\mathbf{2^{V}}$, and $\mathbf{3^{V}}$ in DMSO, and schematic views of $O_{ax}-U-O_{DMSO}-S$. This material is available free of charge via the Internet at http://pubs.acs.org.

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