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Photolytic Formation of a Uranium(V)-DMSO Complex and the Paramagnetic Shift of DMSO by Uranium(V)

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Synopsis. A U(V)-DMSO complex (DMSO=dimethyl sulfoxide) formed by photoreduction of $[UO_2(dmso)_5]^{2+}$ was stable in acid-free DMSO and a small quantum yield of U(V) was attributed to the difficulty in electron transfer from ligands to U(VI). The paramagnetic shift of DMSO by U(V) indicates that only the pseudo-contact shift is induced.

Uranium(V)[1] ions are known to be extremely unstable in aqueous solution owing to its rapid disproportionation.[2,3] Therefore, the absorption spectrum of U(V) was only roughly obtained as that of an intermediate in aqueous solution[2,4] and in rigid methanol matrix.[5] Gritzner and Selbin obtained the absorption spectrum of U(V) by electrolytic reduction of $UO_2(NO_3)_2$ in DMSO solution.[6] Miyake et al. observed the absorption and ESR spectra of U(V) in photo- and electrolytic reduction processes of $[UO_2(dmf)_5](ClO_4)_2$ in DMF (=*N,N*-dimethylformamide).[7] Recently, photoreduction of U(VI) in nonaqueous solutions was found to be a better method for U(V) preparation.[8–10] On the other hand, chemical properties of U(V) having electron configuration of $5f^1$ became a subject of great interest, but only a few of information are available about its absorption spectra in solid state,[11] in eutectic mixture,[12] and in rigid matrix,[5] and about magnetic property in solution.[9] In the present paper, we report the results of photoreduction of $[UO_2(dmso)_5](ClO_4)_2$ in DMSO and the paramagnetic shift of DMSO by the resulting U(V).

Experimental

The $[UO_2(dmso)_5](ClO_4)_2$[13] and $[U(dmso)_8](ClO_4)_4$[14] complexes were prepared by the same method as reported previously. Acetone was purified as described previously.[14] Dimethyl sulfoxide was distilled twice in vacuo and stored over 3A molecular sieves. Analytical grade benzene and acetone-d_6 (Merck 99%) were used without further purification. NMR shift reagent $Pr(fod)_3$ (Dojin, fod=6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) was dried over phosphorus pentaoxide under vacuum. Sample solutions for the measurements of UV-visible, luminescence, NMR and ESR spectra were degassed under vacuum. The UV-visible spectra were measured at 25±0.1 °C on a Shimadzu UV-210A spectrophotometer. Luminescence spectra were recorded by using a JASCO FP-550A fluorescence spectrophotometer at room temperature. NMR measurements were carried out on a JEOL JNM-FX 100 FT-NMR spectrometer. Acetone-d_6 was used as an internal lock for the measurement of paramagnetic shifts, and D_2O and benzene were used as an external lock and an internal standard, respectively, for the measurement of magnetic susceptibility. The DMSO solution of $[UO_2(dmso)_5](ClO_4)_2$ was irradiated with the light from a 500 W ultrahigh-pressure mercury lamp (Ushio USH-500D) through a filter (Corning 052) which cut off the wavelengths shorter than 365 nm. ESR spectra were recorded on a JEOL JES-FX3 spectrometer during the light irradiation.

Results and Discussion

The molar extinction coefficient of $[UO_2(dmso)_5](ClO_4)_2$ in DMSO was 34.8 $M^{-1}\,cm^{-1}$ ($M=mol\,dm^{-3}$) at 430 nm. The luminescence of the uranyl ion was not observed in DMSO at room temperature, but observed in acetone. Figure 1a shows spectral changes of 0.04 M $[UO_2(dmso)_5]^{2+}$ in DMSO during the light irradiation, where a different absorption peak at 770 nm appeared at the beginning of the irradiation, and further irradiation induced another absorption spectrum with two peaks at 558 and 657 nm. The 770 nm peak disappeared immediately with addition of a small amount of perchloric acid under nitrogen atmosphere, and the two peaks at 558 and 657 nm became more intense. *Addition of concentrated perchloric acid to the DMSO solution should be carried out with great caution to avoid a possible explosion.* The appearance of the peak at 770 nm suggests the

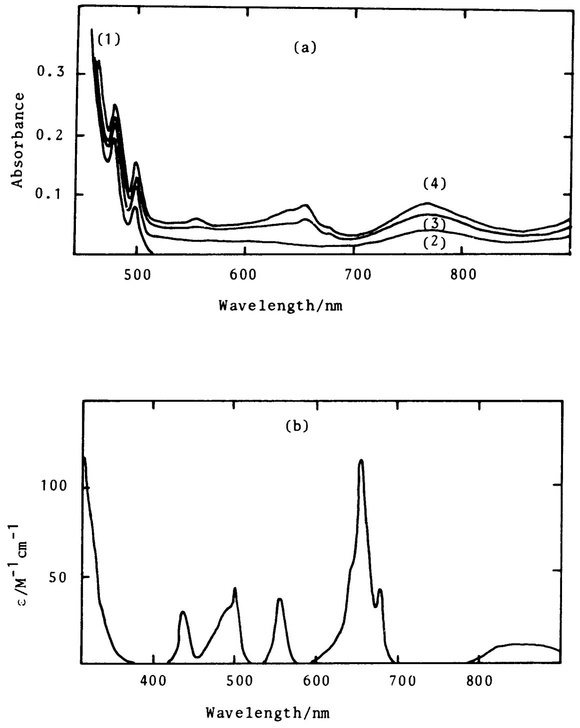

Fig. 1. (a): Spectral changes of 0.04 M $[UO_2(dmso)_5]^{2+}$ in DMSO irradiated with the light (>365 nm) at 25 °C. (1), 0 h; (2), 3 h; (3), 4.5 h; (4), 6 h. (b): Absorption spectrum of $[U(dmso)_8]^{4+}$ in DMSO.

formation of a new cmplex(I), and the absorption spectrum with the two peaks after further irradiation implies the formation of another complex(II). The latter two peaks are well consistent with those of $[U(dmso)_8](ClO_4)_4$ in DMSO (ε=115.2±2.0 $M^{-1}\,cm^{-1}$ at 657 nm) as shown in Fig. 1b. Therefore, complex II was assigned to the U(IV)-DMSO complex. On the other hand, complex I was identified as the U(V)-DMSO complex which rapidly disproportionated with addition of perchloric acid as follows:

$$2UO_2^+ + 4H^+ \longrightarrow UO_2^{2+} + U^{4+} + 2H_2O$$

The concentration of U(V) was determined from the resulting U(IV) by using a relation, [U(V)]=2[U(IV)], after adding an appropriate amount of perchloric acid to the solution containing U(V). The absorption spectrum of the U(V)-DMSO complex is shown in Fig. 2, and the value of the molar extinction coefficient at 770 nm was determined to be 59.0±3.2 $M^{-1}\,cm^{-1}$. This spectrum is almost the same as that of the U(V)-DMSO complex prepared by electrolytic reduction of $UO_2(NO_3)_2$ in DMSO, which has the absorption maximum at 773 nm,[8] and very similar to those of U(V)-DMF[9] and U(V)-DMA (DMA=*N*,*N*-dimethylacetamide) complexes,[10] both of which were obtained by photoreduction of U(VI).

The quantum yield of the U(V)-DMSO complex was estimated to be 1.5×10^{-3}, which is very small compared with the values (0.3—0.4) for U(V)-DMF and U(V)-DMA complexes. This might be due to the difference in structure of ligands. The light irradiation of $[UO_2(dmf)_5]^{2+}$[14] and $[UO_2(dma)_5]^{2+}$[10] at −170 °C yielded the radicals $HCON(CH_3)CH_2\cdot$ and $CH_3CON(CH_3)CH_2\cdot$ respectively, while $[UO_2(dmso)_5]^{2+}$ gave no radical formation. As was reported in an earlier paper,[15] electron transfer from ligands to the excited uranyl ion leads to the formation of radicals and U(V) as follows:

$$UO_2L_5^{2+} \xrightarrow{h\nu} (UO_2L_5^{2+})^* \longrightarrow$$

$$(\overset{e^-\,\curvearrowleft}{UO_2L}L_4^{2+})^* \longrightarrow UO_2L_4^{+} + L\cdot + H^+,$$

where L represents a ligand. In DMF and DMA, all the atoms of $O{=}C{-}N{<}^{C}_{C}$ lie on the same plane, and π orbitals of C=O and $-N<$ overlap pseudo π orbitals of two methyl groups. This favors transfer of electrons from ligands to the uranyl ion on excitation by light irradiation. On the other hand, DMSO has a trigonal pyramidal structure and no overlap of the π orbital of S=O with the pseudo π orbitals of two methyl groups. This structure of DMSO seems to be unfavorable to electron transfer from ligand dmso to the excited uranly ion, which results in no release of radicals and a rather small quantum yield of U(V).

The paramagnetic susceptibility of U(V) was determined by Evans' method[16] which was employed in a previous study.[17] It has been known that benzene, which was used as the internal standard, forms an excited complex with the uranyl ion, but does not contribute to chemical reactions except deactivation of the excited uranyl ion.[18,19] The results are shown in Table 1. The value of molar magnetic susceptibility ($10^6\chi_M$ emu mol^{-1}) of the U(V)-DMSO complex is well consistent with values of so far reported U(V)-TEP complex (2014, TEP=triethyl phosphate),[8] U(V)-DMF complex (2140)[17] and U(V)-DMA complex (2230—2330).[17]

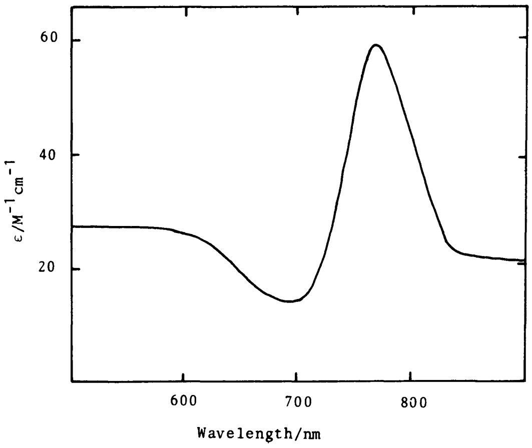

Fig. 2. Absorption spectrum of the U(V)-DMSO complex formed by photoreduction of $[UO_2(dmso)_5]^{2+}$ in DMSO at 25 °C.

Table 1. Molar Magnetic Susceptibility of the U(V)-DMSO Complex at 25 °C

$[U(V)]$[a] 10^{-2} M	$\Delta\nu(C_6H_6)$[b] Hz	$\Delta\nu(C_6H_6)$[c] Hz	χ_M 10^{-6} emu mol^{-1}
0.73	3.17	435	2080
0.68	3.66	540	2580

a) $[UO_2(dmso)_5](ClO_4)_2$ concentration=0.302 M. b) Shift values of benzene in Hz. c) Reduced values at [U(V)]=1 M.

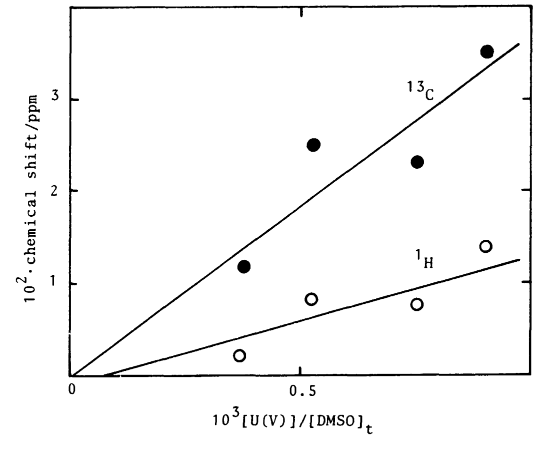

Fig. 3. Plots of ^1H and ^{13}C chemical shifts of DMSO vs. $[U(V)]/[DMSO]_t$ at 25 °C. $[UO_2(dmso)^{2+}]$= 0.40 M, $[DMSO]_t$=10.52 M.

The ^1H and ^{13}C NMR measurements for the paramagnetic shifts were carried out for bulk DMSO in the presence and absence of the U(V) complex. The

NMR spectra of the bulk DMSO gave each single signal for ^{1}H and ^{13}C, and exhibited the paramagnetic shift to the higher field by U(V). The paramagnetic shift depends on the U(V) concentration, and the plots of the ^{1}H and ^{13}C chemical shifts of DMSO against $[\mathrm{U(V)}]/[\mathrm{DMSO}]_t$ at 25 °C, where t denotes total, give straight lines as seen in Fig. 3. The value of the slope is expressed as nS, where n is the number of ligands coordinated to U(V). The ratio of nS for ^{1}H and ^{13}C of DMSO was obtained as 0.42, where the complex formation shift (CFS) was neglected from the following reason. The CFS correction was estimated by using diamagnetic $[\mathrm{UO_2(dmso)_5}]^{2+}$ in the mixture of DMSO and acetone-d_6. The value of correction was 0.84 ppm which was negligibly small compared with 14 ppm of the paramagnetic shift observed at $[\mathrm{U(V)}]/[\mathrm{DMSO}]_t=1$.

The value of S(^{1}H)/S(^{13}C) by Pr(fod)$_3$ was 0.48. A satisfactory agreement between these two values indicates that the pseudocontact shift (PCS) is mainly responsible for the paramagnetic shifts of DMSO induced by U(V) and the contribution of contact shift is negligible, because the PCS is of major importance for Pr(III). This conclusion is compatible with the fact that the quantum yield of U(V) is very small on account of a lack of orbital overlap in the DMSO complex.

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