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PARAMAGNETIC SHIFT AND LIGAND EXCHANGE IN URANIUM(V)-DMF COMPLEX

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The rate of ligand exchange in a U(V)-DMF complex was determined for the first time in N,N-dimethylformamide(DMF) at temperatures below -40°C by using the ^1H NMR method. The paramagnetic shift by U(V) was also observed in the ^1H and ^{13}C NMR signals of bulk DMF owing to the fast exchange between the first coordination sphere of U(V) and the bulk solvent at 25°C.

Pentavalent U(V) ions are known to be extremely unstable in aqueous solution because of rapid disproportionation.1,2) On the other hand, Cauzzo et al. reported that U(V) was relatively stable in nonaqueous solvents such as triethylphosphate.3) In our recent study on the photoreduction of a U(VI)-DMF complex,4) it was found that U(V) was stable over several hours in acid-free organic solvents in the dark. This paper presents the results of the kinetics of ligand exchange in U(V)-DMF complex and the paramagnetic shift by U(V) having electron configuration of $5f^1$ in the ^1H and ^{13}C NMR spectra of DMF.

The preparation of pentakis(N,N-dimethylformamide)dioxouranium(VI) perchlorate, $UO_2(dmf)_5(ClO_4)_2$, was performed by the same method reported by Lincoln et al.5) Crystalline $UO_2(dmf)_5(ClO_4)_2$ was dissolved in DMF and irradiated with a 500-W ultra-high pressure mercury lamp for reducing U(VI) to U(V). A SHIMADZU UV-210A spectrophotometer was used for spectrophotometric measurements. The NMR spectra were recorded on a JEOL JNM-FX-100 NMR spectrometer equipped with a disc system NM-3974 using acetone-d_6 as an internal lock.

The irradiation of $UO_2(dmf)_5(ClO_4)_2$ in DMF(1×10^{-3} - 4×10^{-1} M, M = mol dm^{-3}) with 365 nm light yielded a different absorption peak at 755 nm indicating the formation of a new complex(A). After further irradiation, the solution was becoming green and showed two absorption peaks at 558 nm and 657 nm, which are consistent with those of the U(IV)-DMF complex prepared by dissolving $U(dmso)_8(ClO_4)_4$ into DMF.4) The addition of perchloric acid to the solution containing (A) caused the rapid formation of U(VI) and U(IV) complexes.1,2) Therefore, the complex (A) was identified as a U(V)-DMF complex. The absorption spectrum of the U(V)-DMF complex was shown in Fig. 1. The concentration of U(V) was determined spectrophotometrically as follows. An appropriate quantity of perchloric acid was added to the U(V) solution and the concentration of the resulting U^{4+} ($\varepsilon_{U^{4+}} = 155.7 \pm 1.5$ $M^{-1}cm^{-1}$ at 657 nm) was used for the determination of the U(V) concentration using the relation, $[U(V)] = 2[U^{4+}]$, which was derived from the disproportionation stoichiometry, $2UO_2^+ + 4H^+ \longrightarrow UO_2^{2+} + U^{4+} + 2H_2O$.

The ^1H and ^{13}C NMR measurements were carried out for bulk DMF in the presence of the U(V)-DMF complex obtained by the above-mentioned photoreduction. The irradiation of $UO_2(dmf)_5(ClO_4)_2$ in DMF was stopped before the U(IV) complex appeared in the solution. The temperature dependence of line widths $(1/T_2 - 1/T_{2a})$, where T_2 and T_{2a} are the transverse relaxation times for the ^1H NMR signal (H_3 in Fig.2) in the presence and the absence of the U(V) complex respectively, is shown in Fig. 3. In this plot, the slow exchange region$^{6)}$ appears at temperatures below -40 °C. The rate constant, k_{ex}, for the exchange between the first coordination sphere of U(V) and bulk DMF is calculated by the following equation.$^{6)}$

$$1/T_2 - 1/T_{2a} = p_m k_{ex} \quad , \qquad (1)$$

where p_m can be approximated by Eq. 2 in dilute solutions.

$$p_m = n[U(V)]/[\text{total DMF}] \quad , \qquad (2)$$

where n is the number of ligands coordinated to U(V). Since the coordination number of U(V) has not been known, n is assumed to be five, which is the same in $UO_2(dmf)_5(ClO_4)_2$, for the calculation of k_{ex}. The values of k_{ex} and activation parameters were as follows:

$$k_{ex}(25°C) = 2.1 \times 10^6\ s^{-1},\ \Delta H^{\ddagger} = 56\ kJ\ mol^{-1}\ \text{and}\ \Delta S^{\ddagger} = 63\ J\ mol^{-1}\ K^{-1}.$$

It was found that the NMR signals of bulk DMF exhibited the paramagnetic shift to the higher field by U(V). Signals of DMF were assigned on the basis of the chemical shift of DMF containing $Pr(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate). Since the pseudocontact term is of major importance for Pr(III), the chemical shifts of each atom, which are induced by Pr(III), can be calculated from the McConnell and Robertson equation$^{7)}$ on the assumption

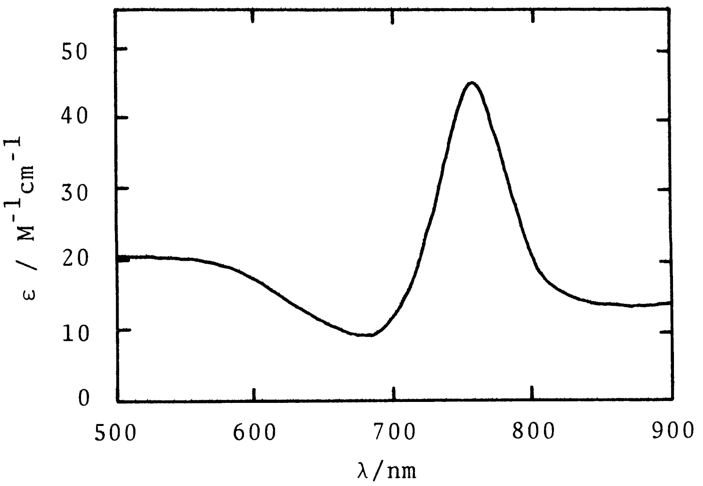

Fig. 1. Absorption spectrum of U(V) formed by the irradiation of $UO_2(dmf)_5(ClO_4)_2$ in DMF with light(365 nm) at 25°C.

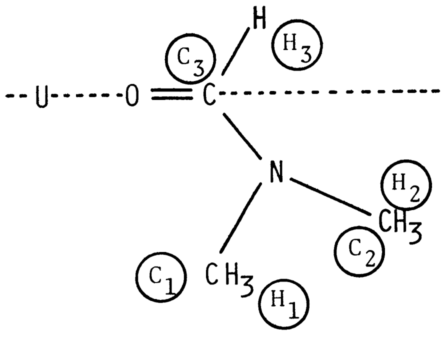

Fig. 2. Structure of U(V)-DMF complex.

that a principal axis passes through Pr--O = C. Experimental results of chemical shifts were in good agreement with the theoretical values.

The paramagnetic shifts depend on the U(V) concentration, and as Fig. 4 shows the plots of the ^{13}C chemical shifts of DMF vs. [U(V)]/[DMF] give straight lines. In Fig. 5, the S values, $S_n(^{13}C)$, which are the values of slopes in Fig. 4, are plotted as a function of temperature. In temperature region above 0°C, the $S_n(^{13}C)$ values change only slightly with temperature. This fact suggests that the ligand exchange is very fast in this temperature region and the chemical shift in bulk DMF is no longer affected by the rate of the ligand exchange. These results are well correlated with those of the line broadening measurements, where the slow exchange took place at temperatures below -40°C(Fig. 3).
It should be noted that the change in the chemical shifts with temperature is particularly large in C_3 signal as seen in Fig. 4. This indicates evidently that the oxygen atom of DMF coordinates to U(V). Therefore, in analogy with the Pr(III) complex, the structure in which a principal axis passes through U--O = C is to be expected for the U(V)-DMF complex. Assuming that the above structure is correct and the spin density(ρ_n) is the same in both methyl groups of DMF, the paramagnetic shift by U(V) can be divided into two terms, i.e. the contact(CS_n) and pseudocontact(PCS_n) terms. The results are listed in Table 1, where a_n represents a hyperfine coupling constant. The fact that the pseudocontact term has positive value and the contact term has negative one in the paramagnetic shift by U(V) bring

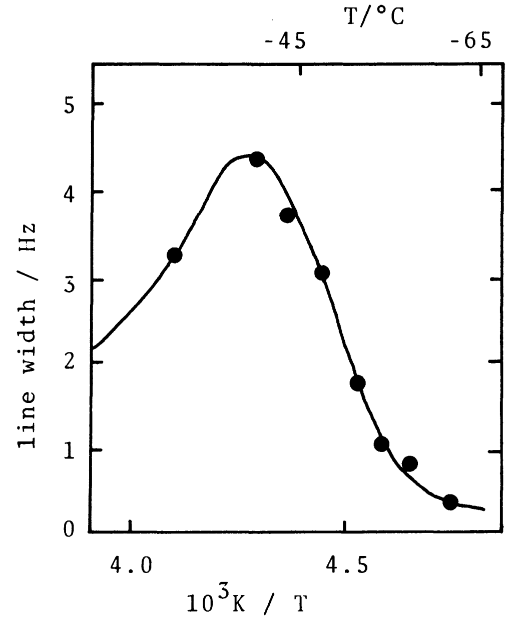

Fig. 3. Temperature dependence of the line width of ^1H NMR signal (H_3) of bulk DMF.
$[UO_2(dmf)_5(ClO_4)_2]$ = 0.304 M, [DMF] = 9.04 M, [U(V)] = 1.57 x 10^{-2} M.

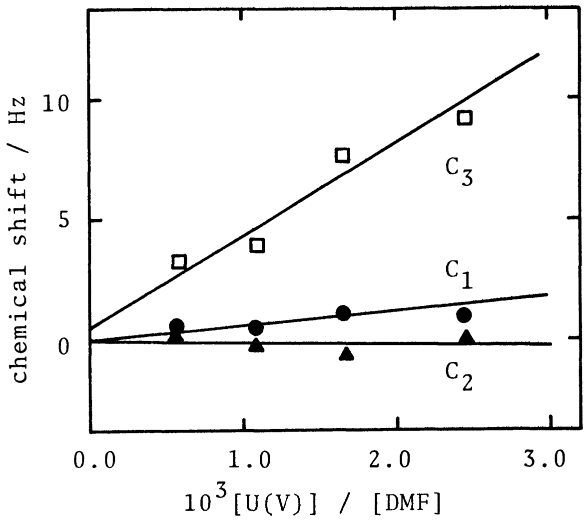

Fig. 4. Plots of the chemical shifts of DMF(^{13}C) vs. [U(V)] / [DMF]. $[UO_2(dmf)_5(ClO_4)_2]$ = 0.400 M, [DMF] = 9.04 M, T = 25°C.

about the results that the hyperfine coupling constant is positive and the negative spin density is induced on the C atoms of DMF. It might be interesting that the contact term had the largest absolute value at C_3 which is the nearest C atom to U(V).

More detailed experiments are in progress with respect to the kinetics of ligand exchange reactions and to the magnetic properties of U(V).

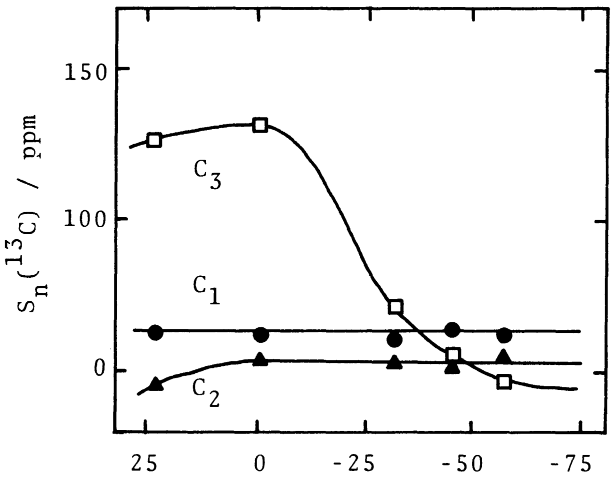

Fig. 5. $S_n(^{13}C)$ values of the U(V)-DMF complex. $[UO_2(dmf)_5(ClO_4)_2]$ = 0.400 M, [U(V)] = (0.506 - 2.19) x 10^{-2} M, [DMF] = 9.04 M.

Table 1. Values of S_n, PCS_n, a_n, and ρ_n of the U(V)-DMF complex at 25°C

	S_n / ppm	PCS_n / ppm	CS_n / ppm	a_n / G	ρ_n
H_1	29	80	-52	0.70	
H_2	11	63	-52	0.70	
H_3	13	180	-160	2.2	
C_1	27	130	-100	1.4	-0.031
C_2	-7.5	95	-100	1.4	-0.031
C_3	150	400	-250	3.3	-0.10

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