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Paramagnetic Shifts of DMF and DMA by Uranium(V)

Toshie Harazono and Hiroshi Fukutomi*
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152

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Paramagnetic shifts of DMF (*N,N*-dimethylformamide) and DMA (*N,N*-dimethylacetamide) induced by U(V) were studied by the ^{1}H and ^{13}C NMR spectroscopy. It was found that the ^{1}H and ^{13}C NMR signals of bulk DMF and DMA exhibited the paramagnetic shifts to the higher field by U(V). Positive pseudocontact shift and negative contact shift for both DMF and DMA are discussed on the basis of the electronic structure of U(V) complexes. The values of magnetic susceptibilities of U(V) complexes are also presented.

Paramagnetic shifts induced by lanthanoid compounds have been extensively studied since the pioneer work of Hinckley,[1-4] while a little of information are available for actinoid compounds. Some diketonato complexes of U(IV) having the electron configuration of 5f^2 were found to induce the shift of ^{1}H and ^{13}C NMR signals of ligands,[5-8] and the ^{1}H signals of U(IV) (allyl)$_4$ were also found to shift to the higher field.[9,10] On the other hand, there are very few studies on the paramagnetic shift by U(V) which has the 5f^1 electron configuration, since U(V) is extremely unstable in aqueous solution owing to its rapid disproportionation. We found that U(V) was formed by photoreduction of [UO$_2$(dmf)$_5$]$^{2+}$,[11,12] [UO$_2$(dma)$_5$]$^{2+}$,[13] and [UO$_2$(dmso)$_5$]$^{2+}$,[14] and the resulting U(V) was stable over several hours in acid-free organic solvents in the dark. This has enabled the determination of the paramagnetic shift by U(V) in solution reported in this paper. In the previous paper,[11] we reported briefly the result of paramagnetic shift of DMF owing to the fast exchange between the first coordination sphere of U(V) and the bulk solvent. It is the purpose of this paper to investigate the paramagnetic shifts of DMF and DMA by U(V) in more detail and to elucidate the mechanism of spin localization.

Experimental

The [UO$_2$(dmf)$_5$](ClO$_4$)$_2$ and [UO$_2$(dma)$_5$](ClO$_4$)$_2$ complexes were prepared by the same methods so far reported.[15] Elemental analysis was performed by using a Shimadzu CHN-1A analyzer. Calcd for [UO$_2$(dmf)$_5$](ClO$_4$)$_2$: C, 21.59; H, 4.23; N, 8.39%. Found: C, 20.98; H, 4.10; N, 8.39%. Calcd for [UO$_2$(dma)$_5$](ClO$_4$)$_2$: C, 26.56; H, 5.01; N, 7.74%. Found: C, 26.65; H, 5.00; N, 7.65%. Reagent grade DMF and DMA were distilled twice under vacuum and stored over 3A molecular sieves. Benzene and acetone-*d*$_6$ (CD$_3$COCD$_3$, Merck 99%) were of analytical grade and used without further purification. NMR shift reagents Pr(fod)$_3$ (fod=6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) and Eu(fod)$_3$ (Dojin) were dried in a vacuum dessicator over phosphorus pentoxide. [UO$_2$(dmf)$_5$]$^+$ and [UO$_2$(dma)$_5$]$^+$ solutions were prepared by irradiation of [UO$_2$(dmf)$_5$](ClO$_4$)$_2$ in DMF and [UO$_2$(dma)$_5$](ClO$_4$)$_2$ in DMA, respectively with the light of 365 nm from a 500 W ultrahigh-pressure mercury lamp (Ushio USH 500D). The U(V) concentration was determined spectrophotometrically by using a Shimadzu UV-210A spectrophotometer, where the values of 45.5 M^{-1} cm^{-1} (M=mol dm^{-3}) at 755 nm and 45.4 M^{-1} cm^{-1} at 760 nm were used for the molar extinction coefficients of the U(V)–DMF[12] and U(V)–DMA[13] complexes,respectively. NMR spectra were recorded on a JEOL JNMFX-100 FT NMR spectrometer equipped with a disc system NM-3974. Acetone-*d*$_6$ was used as an internal lock for the measurement of paramagnetic shifts. In the measurement of magnetic susceptibility, D$_2$O and benzene were used as an external lock and internal standard, respectively.

Results

The magnetic susceptibility of U(V) was determined by Evans' method,[16] the equation of which is given by

$$\frac{\Delta H}{H_0} = \frac{2\pi}{3}\Delta\kappa, \qquad (1)$$

where H_0 is the external magnetic field, ΔH is the difference in chemical shift of the signal of benzene between reference and sample solutions containing benzene, and $\Delta\kappa$ is the difference in volume magnetic

Table 1. Molar Magnetic Susceptibilities of U(V) Complexes at 25 °C

U(VI) complex (concentration)	$\frac{[V(V)]}{10^{-2}\,M}$	$\frac{\Delta\nu(C_6H_6)^{a)}}{Hz}$	$\frac{\Delta\nu(C_6H_6)^{b)}}{Hz}$	$\frac{\chi_M}{10^{-6}\,emu\,mol^{-1}}$
[UO$_2$(dmf)$_5$](ClO$_4$)$_2$ (0.277 M)	1.59	7.08	445	2140
[UO$_2$(dma)$_5$](ClO$_4$)$_2$ (0.307 M)	1.08	5.25	486	2330
	0.925	4.30	465	2230

a) Difference in chemical shift of benzene. b) Reduced values at [U(V)] = 1 M.

susceptibility between reference and sample solutions. The results are shown in Table 1.

For the ^1H and ^{13}C NMR spectra of bulk DMF and DMA in the absence of U(V)-DMF and U(V)-DMA complexes respectively, assignments of DMF and DMA signals were performed by using $Pr(fod)_3$. In the following descriptions, hydrogen and carbon atoms with subscripts, e.g. H_1, C_3, correspond to the atoms of positions 1, 3, in Figs. 1 and 2. Since the pseudocontact term is a principal term for Pr(III),[17]

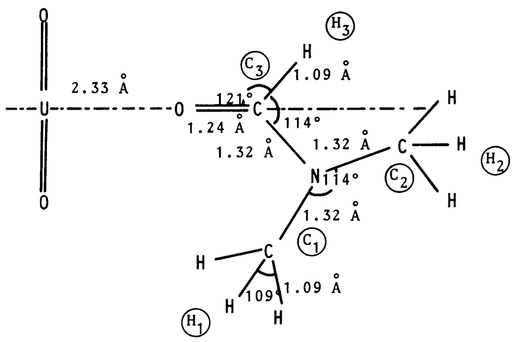

Fig. 1. Postulated structure of the U(V)-DMF complex.

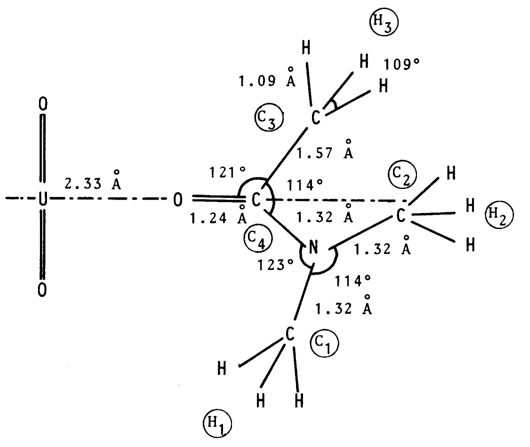

Fig. 2. Postulated structure of the U(V)-DMA complex.

Table 2. Relative Chemical Shifts of DMF Containing $Pr(fod)_3$

	Exptl	Calcd
H_1	0.47	0.43
H_2	0.26	0.35
H_3	1.00	1.00
C^1	0.40	0.30
C_2	0.20	0.23
C_3	1.00	1.00

The values indicated in Fig. 1 were used for the values of the bond lengths and angles.

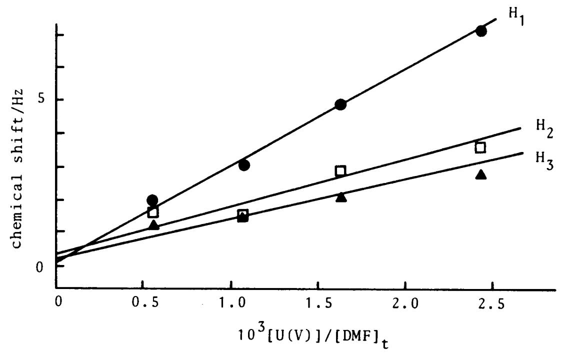

Fig. 3. Plots of ^1H chemical shifts of DMF vs. $[U(V)]/[DMF]_t$ at 25 °C. $[UO_2(dmf)_5^{2+}]$=0.40 M, $[DMF]_t$ =9.04 M.

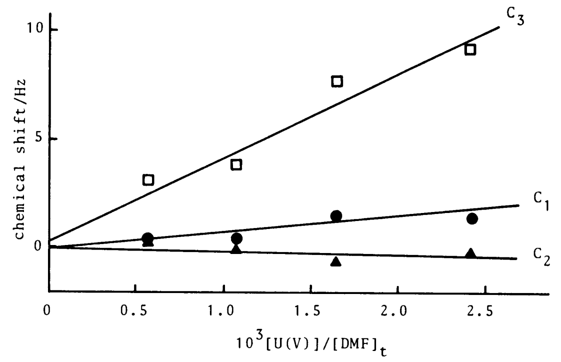

Fig. 4. Plots of ^{13}C chemical shifts of DMF vs. $[U(V)]/[DMF]_t$ at 25 °C. $[UO_2(dmf)_5^{2+}]$=0.40 M, $[DMF]_t$ =9.04 M.

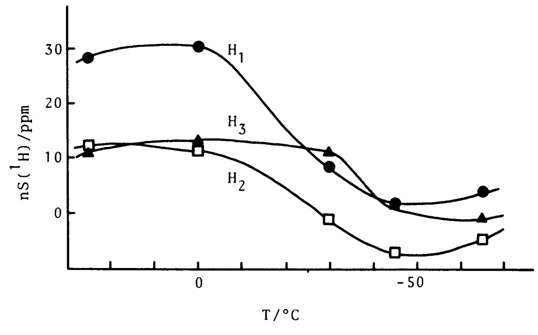

Fig. 5. Plots of $nS(^1H)$ of the U(V)-DMF complex as a function of temperature.

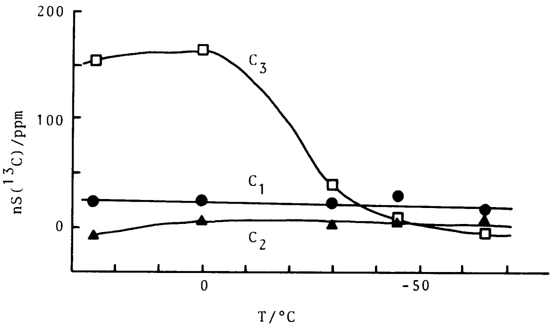

Fig. 6. Plots of $nS(^{13}C)$ of the U(V)-DMF complex as a function of temperature.

the chemical shifts of each atom, which are induced to the higher field by Pr(III), can be calculated by using the McConnell and Robertson equation[18] on the assumption that a principal axis passes through Pr···O=C. Experimental results of chemical shift of DMF are given in Table 2 and shows close agreement with the theoretical values. It was found that the NMR signals of bulk DMF exhibited the paramagnetic shift to the higher field by U(V), especially in signals of H_1 and C_3. Figures 3 and 4 show the plots of ^1H and ^{13}C chemical shifts of DMF vs. $[U(V)]/[DMF]_t$ at 25 °C, where $[DMF]_t$ denotes the total DMF concentration, and each plot gives a straight line. The value of the slope is expressed as n*S*, where n is the number of ligands coordinated to U(V). The number of coordinated dmf in the U(V)-DMF complex has not yet been determined, but 5 is most likely. In Figs. 5 and 6, the n*S* values of ^1H and ^{13}C signals are plotted as a function of temperature, respectively. With respect to the chemical shift of DMA, similar plots are given in Figs. 7 and 8, which also show the paramagnetic shift to the higher field by U(V), especially in the C_4 signal. The n*S* values were nearly constant at a temperature range from 25 to 0 °C.

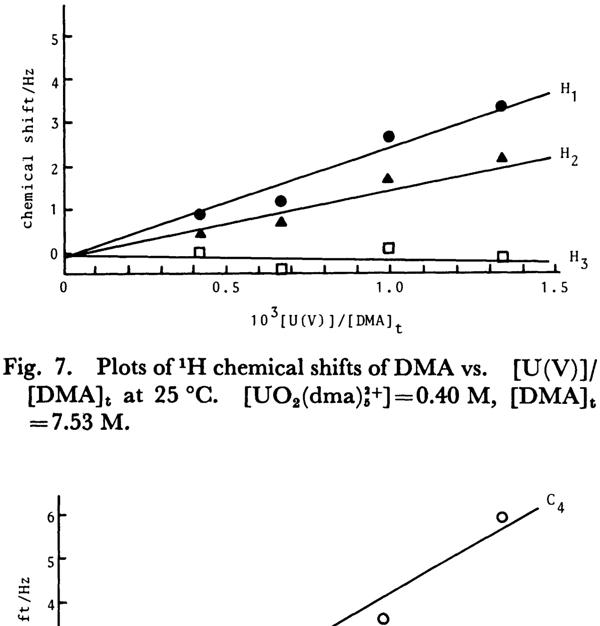

Fig. 7. Plots of ^1H chemical shifts of DMA vs. $[U(V)]/[DMA]_t$ at 25 °C. $[UO_2(dma)_5^{2+}]=0.40$ M, $[DMA]_t=7.53$ M.

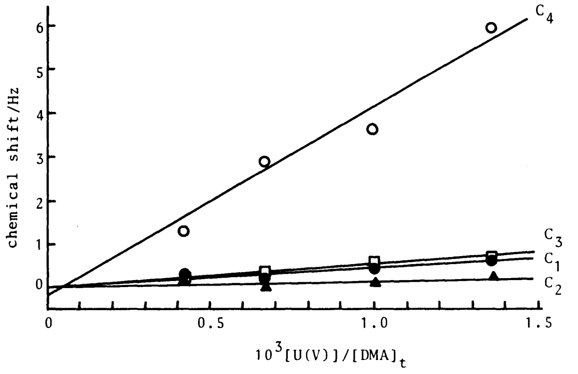

Fig. 8. Plots of ^{13}C chemical shifts of DMA vs. $[U(V)]/[DMA]_t$ at 25 °C. $[UO_2(dma)_5^{2+}]=0.40$ M, $[DMA]_t=7.53$ M.

Discussion

The values of magnetic susceptibilities of the U(V)-DMF and U(V)-DMA complexes are fairly large and are well consistent with that of the U(V)-TEP complex (2014×10^{-6}, TEP=triethyl phosphate).[19] The chemical shift induced by U(V) is expected to involve three terms, i. e. contact shift (CS), pseudocontact shift (PCS), and complex formation shift (CFS).[17] The CFS corrections for the U(V)-DMF and U(V)-DMA complexes were estimated by using $[UO_2(dmf)_5]^{2+}$ and $[UO_2(dma)_5]^{2+}$, respectively, which are diamagnetic complex ions having the $5f^0$ electron configuration. In the DMF complex, the CFS correction is negligibly small for H_1 and H_2 signals, and a small correction is required for H_3 signal (0.95 ppm for $[U(V)]/[DMF]_t=1$).[20] However, the information of CFS for ^{13}C is not available, and the CFS correction was neglected for ^{13}C on the basis of the fact that CFS is very small for aliphatic compounds.[17] As seen in Figs. 5 and 6, a fast ligand exchange region[21] appears at temperatures above 0 °C, and the ligand exchange comes gradually down below 0 °C. This was also confirmed by the temperature dependence of linewidths ($1/T_2-1/T_{2a}$), where T_2 and T_{2a} are the transverse relaxation times for the ^1H NMR signal (H_3 in Fig. 1) in the presence and the absence of U(V), respectively. The fact that the change in chemical shift with temperature is particularly large in C_3 signal as seen in Fig. 4 definitely indicates that the oxygen atom of DMF coordinates to U(V). Therefore, the structure of the U(V)-DMF complex shown in Fig. 1 seems to be most likely from the analogy to the Pr(III) complex.[22] On the assumption that the above structure is correct and the spin density (ρ) is the same in both methyl groups of DMF, the paramagnetic shift by U(V) is divided into CS and PCS terms. The results are listed in Table 3, where *A* represents a hyperfine coupling constant. The values of PCS are positive, and the nagative values of CS result in the positive

Table 3. Values of *S*, PCS, CS, *A*, and ρ for the U(V)-DMF Complex at 25° C

	n·*S* / ppm	n·PCS / ppm	n·CS / ppm	n·*A* / gauss	n·ρ
H_1	28.5	95.0	−66.5	0.896	
H_2	10.9	77.7	−66.5	0.896	
H_3	12.9	220	−207 (−206)	2.79 (2.78)	
C_1	26.7	140	−113	0.030	−0.039
C_2	−7.5	105	−113	0.030	−0.039
C_3	153	462	−309	0.081	−0.124 (−0.123)

$A=\rho Q$. $Q=-22.5$ gauss. ( ): corrected value.

Table 4. Values of *S*, PCS, and CS for the $Eu(fod)_3$-DMF Complex at 25 °C

	S ppm	PCS ppm	CS ppm
H_1	−8.7	−23.1	14.4
H_2	−4.4	−18.8	14.4
H_3	−11.9	−53.8	41.9
C_1	−8.3	−24.0	15.7
C_2	−2.7	−18.4	15.7
C_3	0.20	−80.0	80.2

Table 5. Values of *S*, PCS, CS, *A*, and *ρ* for the U(V)-DMA Complex at 25 °C

	n·*S* ppm	n·PCS ppm	n·CS ppm	n·*A* gauss	n·*ρ*
H_1	26.5	47.6	−21.1	0.206	
H_2	17.6	38.7	−21.1	0.206	
H_3	−1.9	66.4	−68.3	0.668	
C_1	19.6	55.1	−35.5	0.0093	−0.0092
C_2	6.1	41.6	−35.5	0.0093	−0.0092
C_3	22.1	75.7	−53.6	0.0140	−0.030
C_4	172	182	−10.4	0.0027	
	(180)		(−2.8)	(0.0007)	

$A=\rho Q$. $Q=-22.5$ gauss. ( ): corrected value.

hyperfine coupling constant and the negative spin density on the C atoms of DMF. It should be noted that the contact term has the largest absolute value at C_3 which is the nearest C atom to U(V). A DMF molecule is regarded as a conjugated system in which π orbitals of C=O and -N and pseudo π orbitals by hyperconjugation of two methyl groups are conjugated, and the unpaired electron of U(V) might be transferred to ^1H and ^{13}C of DMF through π electrons. Paramagnetic shifts of DMF by $Eu(fod)_3$ were also studied and divided into two terms as well as the U(V)-DMF complex. The results are listed in Table 4. Negative values of PCS and positive values of CS are just the opposite of the U(V)-DMF complex. This means that the anisotropy of manetic susceptibility or *g* tensor of U(V) $(\chi/\!/>\chi\perp,\ g/\!/>g\perp)$ is the opposite of that of Eu(III).

Almost the same discussion can be applied to the U(V)-DMA complex. The CFS corrections are negligible for all the ^1H signals and are small for C_1, C_2, and C_3 signals. The C_4 signal requires the correction of 7.6 ppm for $[U[V)]/[DMA]_t=1$.[23] As seen in Fig. 8, the change in chemical shift is most large in the C_4 signal, and this indicates that the oxygen atom of C=O coordinates to U(V). The proposed structure of the U(V)-DMA complex is illustrated in Fig. 2. The paramagnetic shift by U(V) consists of two terms, CS and PCS. The results are listed in Table 5. The signs of CS and PCS are the same as those of the U(V)-DMF complex. The absolute value of CS of C_4 is smaller than those of C_1, C_2, and C_3. If the bond length between U and O in U····O=C is slightly shorter than 2.33 Å which is the U····O bond length of U····O=C in $[UO_2(CF_3CO)_2CH]_2THF$ (THF= tetrahydrofuran),[24] the absolute value of CS of C_4 will become larger than those of CS of other carbon atoms as well as the case of U(V)-DMF. The results of the paramagnetic shifts of DMA by $Eu(fod)_3$ are given in Table 6.

Table 6. Values of *S*, PCS, and CS for the $Eu(fod)_3$-DMA Complex at 25 °C

	S ppm	PCS ppm	CS ppm
H_1	−11.0	−29.2	18.2
H_2	−5.4	−23.6	18.2
H_3	−11.8	−41.2	29.4
C_1	−11.9	−40.8	28.9
C_2	−1.9	−30.8	28.9
C_3	−20.5	−56.1	35.6
C_4	49.6	−135	185

It may be noted that the separation of paramagnetic shifts by U(V) into the CS and PCS terms was performed for the first time in this paper.

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