Inorganica Chimica Acta, 33 (1979) 235–239
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A Proton Magnetic Resonance Study of Ligand Exchange on Pentakis(N,N-dimethylformamide)dioxouranium(VI) Ion

RICHARD P. BOWEN, GEOFFREY J. HONAN, STEPHEN F. LINCOLN, THOMAS M. SPOTSWOOD and EVAN H. WILLIAMS
Department of Physical and Inorganic Chemistry, University of Adelaide, S.A. 5001, Australia

Received September 7, 1978

Proton magnetic resonance studies show that $UO_2(DMF)_5^{2+}$, pentakis(N,N-dimethylformamide)-dioxouranium(VI) ion, is the greatly predominant dioxouranium(VI) species in mixed solutions of DMF and d_2-methylene chloride. The virtual independence of the rate of intermolecular exchange of DMF of free DMF concentration over a 20.3 fold concentration range is interpreted in terms of a dissociative exchange mechanism. A typical set of kinetic data for this process is $k_{ex}(220K) = 199 \pm 11$ s^{-1}, $\Delta H^{\#} = 31.9 \pm 0.3$ kJ mol^{-1} and $\Delta S^{\#} = -53.4 \pm 1.5$ J K^{-1} mol^{-1}, where the observed exchange rate $= 5 k_{ex}[UO_2(DMF)_5^{2+}]$, and the concentrations of $UO_2(DMF)_5^{2+}$, DMF and d_2-methylenechloride are respectively 0.008648, 0.04323 and 15.05 mol dm^{-3}. The observed magnetic equivalence of the methyl groups in bound DMF over the experimental temperature range 170–300 K is shown to arise as a consequence of the cis *and* trans *DMF methyl groups experiencing significantly different magnetic shielding modifications upon coordination to the dioxouranium(VI) ion probably in part as a consequence of the magnetic anisotropy of that ion.*

Introduction

The dioxouranium(VI) ion, as a consequence of the kinetically inert nature of the two axial oxo ligands [1, 2], offers the unusual opportunity to study the dynamics of ligand exchange processes in the equatorial plane of the uranium(VI) atom. Such an opportunity is rare in ligand substitution studies on metal ions, but surprisingly it has only been very recently that the number of uni-dentate ligands occupying this equatorial plane, and their lifetimes therein, have been investigated. The stoichiometry $UO_2L_5^{2+}$ is often consistent with the most stable ground state species when L is an oxygen donor ligand of medium donor strength as exemplified when L = trimethylphosphate [3] (23.0), triethylphosphate [3], dimethylsulphoxide [4] (29.8), N,N-dimethylacetamide [5] (32.2), dimethylphosphonate [6], and tetramethylurea [7] (29.6), but when L is a particularly strong donor, as in the case of hexamethylphosphoramide (38.8) the stoichiometry $UO_2L_4^{2+}$ may prevail in the ground state (the numbers in parentheses are Gutmann donor numbers [8]). It further appears that a fine balance between the donor strength and the size of L may exist in determining ground state stoichiometry [9]. The consequences of variation in ground state stoichiometry may have a profound effect upon the mechanism of the exchange of L on the uranium(VI) centre as exemplified when L is hexamethylphosphoramide [9] when two exchange paths, one dissociative and the other probably associative, are observed whereas when L is any of the other previously discussed ligands a dissociative path appears to provide the dominant exchange mechanism [3–6].

In this study the solution dynamics of a further $UO_2L_5^{2+}$ species, $UO_2(DMF)_5^{2+}$, (where DMF is N,N-dimethylformamide (26.6)) are investigated. This species is somewhat unusual in that the chemically non-equivalent methyl groups of bound DMF are magnetically equivalent.

Experimental

Preparation of the Dioxouranium(VI) Complex

Hydrated dioxouranium(VI) perchlorate (G. Frederick Smith) (2.5 g) was stirred with triethylorthoformate [10, 11] (10 g) at 320 K for one hour. Dry N,N-dimethylformamide (2.2 g) was added at room temperature and the resultant yellow crystals of $[UO_2(DMF)_5](ClO_4)_2$ were filtered off, washed with dry ether and pumped down on a vacuum line for several hours. All preparative and handling operations were carried out under dry nitrogen and exposure of $[UO_2(DMF)_5](ClO_4)_2$ to light was kept to a minimum to avoid the possibility of photochemically induced redox processes. The product yield was 92%. *Anal.* Calcd. for $[UO_2(DMF)_5](ClO_4)_2$: UO_2^{2+}, 32.36; C, 21.59; N, 8.39; H, 4.23%. Found: UO_2^{2+}, 32.07; C, 21.60; N, 8.21; H, 4.13%. The UO_2^{2+} analysis was carried out using an ion exchange method [12] and the C, N and H analyses

TABLE. Exchange of DMF on $UO_2(DMF)_5^{2+}$. Solution Compositions and Kinetic Parameters.

Solution	$[UO_2(DMF)_5^{2+}]^a$ mol dm^{-3}	$[DMF]^b$ mol dm^{-3}	$[CD_2Cl_2]$ mol dm^{-3}	C.N.^{c,d}	k(220 K)^d s^{-1}	$\Delta H^{\#e}$ kJ mol^{-1}	$\Delta S^{\#e}$ J K^{-1} mol^{-1}
i	0.008648	0.04323	15.05	4.9 ± 0.1	199 ± 11	31.9 ± 0.3	−53.4 ± 1.5
ii	0.004306	0.02152	15.10	4.9 ± 0.1	179 ± 19	33.1 ± 1.2	−48.8 ± 5.4
iii	0.002199	0.01099	15.13	5.0 ± 0.1	188 ± 8	30.9 ± 0.4	−58.7 ± 1.5
iv	0.001102	0.00551	15.17	5.0 ± 0.1	162 ± 22	33.5 ± 1.0	−47.8 ± 4.5
v	0.000737	0.00213	15.20	5.0 ± 0.1	160 ± 14	30.9 ±1.2	−59.9 ± 5.6
vi	0.009520	0.02654	15.06	4.9 ± 0.1	187 ± 17	33.6 ± 0.9	−46.0 ± 4.4

[a] Added as $[UO_2(DMF)_5](ClO_4)_2$. [b] Added as DMF. [c] CN = number of DMF molecules in the first co-ordination sphere of UO_2^{2+} as determined from the integration of the bound and free DMF resonances in the temperature range 170–185 K. [d] Errors represent one standard deviation. [e] Errors represent one standard error.

were carried out by the Australian Microanalytical Service, Melbourne.

Preparation of Solutions

DMF (BDH) and d_2-methylenechloride (CEA, France 99.4%) were distilled and stored over Linde 4A molecular sieves. Solutions of $[UO_2(DMF)_5](ClO_4)_2$ and DMF in d_2-methylenechloride were prepared in 5 cm^3 volumetric flasks in a dry nitrogen atmosphere. Approximately 0.4 cm^3 of each solution was degassed prior to sealing under vacuum in a 5 mm o.d. NMR tube.

Spectroscopic Measurements

^{1}H NMR spectra were run at 90 MHz on a Bruker HX90E spectrometer using a deuterium lock. Depending upon the concentration of the sample up to fifteen spectra were computer averaged (Nicolet BNC 12) at each temperature prior to digitising onto paper tape (from 500 to 800 data points per spectrum respectively ranging from fast to slow exchange conditions). The spectrometer temperature control was better than ±0.3 K. The data stored on the paper tapes was subjected to a complete line shape analysis using a CDC 6400 computer. The 270 MHz spectra were run at the National NMR Centre, Canberra.

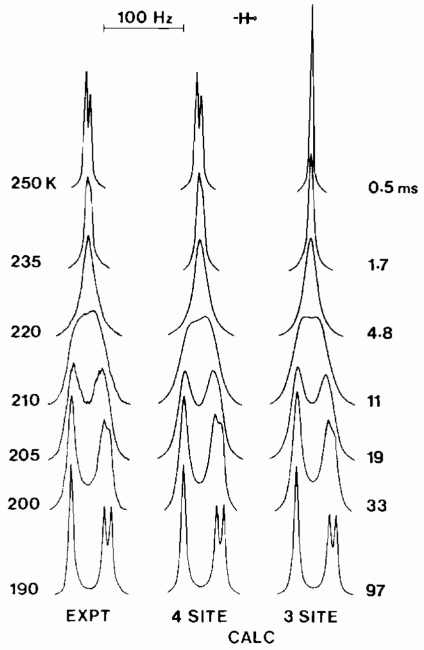
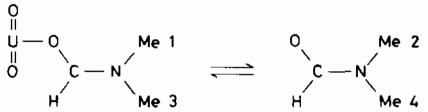


Figure 1. The experimental ^{1}H NMR spectral coalescence phenomenen for solution (i) in which $[UO_2(DMF)_5^{2+}]$, [DMF] and [d_2-methylenechloride] were respectively 0.008648, 0.04323 and 15.05 mol dm^{-3} and the experimental temperatures are shown at the left of the figure. The bound DMF methyl resonance appears as the downfield singlet. The free DMF methyl resonances appear as the upfield doublet at 190 K. The best fit computer calculated lineshapes for the four site exchange scheme (2) appear in the centre of the figure and the corresponding best fit τ_B values appear at the right of the figure. Lineshapes for the three site exchange scheme (2) for these τ_B values appear at the right of the figure.

Results and Discussion

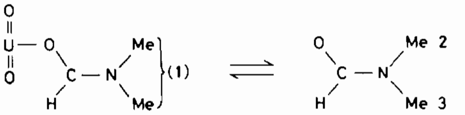
At low temperature in d_2-methylenechloride solution the bound DMF methyl ^{1}H NMR resonance appears as a singlet downfield from the doublet methyl resonance of free DMF (Figure 1). A comparison of the integrated singlet and doublet areas at 170, 180 and 185 K indicates that $UO_2(DMF)_5^{2+}$ is the greatly predominant dioxouranium(VI) species in solutions (i)–(vi) (Table). Integration of the formyl proton resonances which appear further downfield is also consistent with this finding [13]. In a d_2-methylenechloride solution of $[UO_2(DMF)_5](ClO_4)_2$ alone the bound DMF methyl singlet persists as such over the temperature range 170–300 K both at 90 and 270 MHz. As the temperature is increased the singlet and doublet resonances of the bound and free DMF methyl groups coalesce to a doublet at 250 K (Figure 1) and above, consistent with the intermolecular exchange of DMF between the bound and free sites. The formyl singlets coalesce to a singlet as the temperature is increased also consistent with the intermolecular exchange of DMF. The coalescence phenomena seen in Figure 1 may be analysed according to two schemes, the first of which is one in which the chemical shifts of both methyl groups of bound DMF become identical probably as a consequence, in part at least, of the magnetic anisotropy of the dioxouranium(VI) ion [14, 15]. Intermolecular exchange of DMF now becomes a four site exchange problem [16] (equation 1) in which exchange occurs between sites 1 and 2, and site 3 and 4 only, as rotation about the C–N bond in bound DMF is assumed to be slow on the NMR time scale



(1)

in the temperature range 190–250 K as is known to be the case for free DMF [17]. Computer calculated best fit line shapes [16] for this scheme (equation 1) are shown in Figure 1 and are seen to reproduce the experimental spectra. The mean lifetimes of DMF bound in $UO_2(DMF)_5^{2+}$, τ_B, derived from the best fit line shapes are at the right of Figure 1. Computer calculation of these best fit lineshapes requires the relative chemical shifts between the exchanging sites and their line widths at half resonance amplitude in the absence of exchange induced modifications as input parameters. The input values for the chemical shift differences between the bound DMF methyl resonance and the upfield and downfield methyl resonances of free DMF, which varied as 1/T, were 50.3 and 41.4 Hz (190 K) and 48.7 and 37.6 Hz (296 K). The bound, and upfield and downfield free DMF line widths which also varied as 1/T were 3.36, 2.50, and 2.70 Hz (190 K), and 2.18, 1.81 and 1.60 Hz (290 K). (In a solution of DMF alone at 170 K the high field and low field DMF methyl resonances exhibit a coupling of 0.65 and 0.25 Hz with the formyl proton. This coupling was not observed in the $UO_2(DMF)_5^{2+}$/DMF solutions and hence is not included in the line shape calculations. In any event the inclusion of this coupling would have a negligible effect on the derived τ_B values as a consequence of the much greater magnitude of the frequency difference between the bound and free DMF resonances.)

An alternative explanation for the singlet resonance of the bound DMF methyl groups is that the rotation about the C–N bond in bound DMF is in the fast exchange limit over the entire experimental temperature range. Intermolecular exchange of DMF is now reduced to a three site exchange problem in which the bound methyl groups become effectively one site, as a consequence of the postulated fast rotation about the C–N bond, as shown in equation (2). According to this scheme exchange now occurs between sites 1 and 2, and sites 1 and 3, and indirectly between sites 2 and 3. This



(2)

scheme leads to a singlet line shape being observed (Figure 1) in the fast intermolecular exchange limit. Lineshapes calculated, using the Kubo–Sack method [16], for this three site scheme using the τ_B values (and also the same chemical shift and line width input values) obtained from the four site scheme, are shown at the right hand side of Figure 1. It is clear from Figure 1 that it is the four site exchange scheme (equation 1) which is operative. It appears that the magnetic anisotropy of the dioxouranium(VI) entity is a contributing factor to the magnetic equivalence of the methyl groups in $UO_2(DMF)_5^{2+}$ as in the magnetically isotropic species [18–20] $Be(DMF)_4^{2+}$, $Al(DMF)_6^{3+}$ and $Ga(DMF)_6^{3+}$ the chemically non-equivalent methyl groups are also magnetically non-equivalent. An approximate estimate of the change in the chemical shift, $\Delta\delta$, of the DMF methyl groups caused by the anisotropic field may be gained through [15, 21] equation (3)

$$\Delta\delta = \frac{\Delta\chi(1 - 3\cos^2\gamma)}{3r^3} \tag{3}$$

in which $\Delta\chi = \chi(\text{parallel}) - \chi(\text{perpendicular})$

where χ is the magnetic susceptibility [14] of the dioxouranium(VI) ion parallel and perpendicular to the principle magnetic axis which is considered coincident with the O=U=O axis, γ is the angle between this axis and a line passing through the uranium centre and the mean methyl proton position, and r is the mean distance of that proton from the uranium centre. If it is assumed that free rotation occurs about the U–O bond formed between the uranium atom and the donor carbonyl oxygen atom of the DMF ligand then the effects of the anisotropic field averaged over a complete rotation converts equation (3) to equation (4)

$$\Delta\delta = \Delta\chi\frac{(1 - 3/2\sin^2\theta)}{3r^3} \tag{4}$$

where $\theta = 90 - \gamma$. Using a value [14] of $\Delta\chi = -2.74 \times 10^{-28}$ and $\theta = 7.08$ and r = 5.14 Å for the methyl group *trans* to the formyl proton (which gives rise to the upfield signal in DMF [22, 23]), $\Delta\delta$ is calculated to be −0.657 ppm, whereas $\Delta\delta = -0.334$ when θ = 25.78° and r = 5.81 Å for the *cis* methyl group. These compare with experimental values (190 K) of

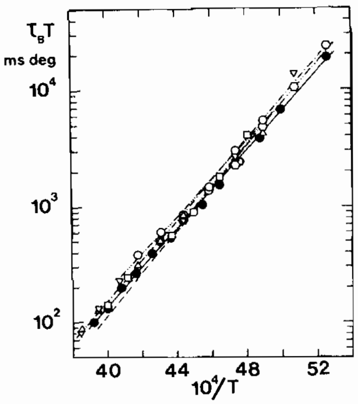


Figure 2. A semilogarithmic plot of $\tau_B T$ against $10^4/T$ for the $UO_2(DMF)_5^{2+}$ system. Individual datum points for solutions appear as (i) ●, (ii) ▫, (iii) △, (iv) ▽, (v) ○ and (vi) ○. The best fits of these data to equation (4) are shown as —— (i) ------ (ii) –·– (iv) –···– (v) and –··– (vi). The line for (iii) is omitted for clarity.

−0.558 ppm and −0.460 ppm observed for the *trans* and *cis* methyl groups of DMF in solution (i) (and similar values for the other solutions in the table). This qualitative agreement between the calculated and experimental relative chemical shifts of the DMF methyl protons demonstrates the plausibility of the argument that magnetic anisotropy is a contributing factor to the magnetic equivalence of the $UO_2(DMF)_5^{2+}$ methyl groups. The quantitative agreement is probably the best that could be expected as, quite apart from its approximate nature, equation 3, only accounts for "through space" contributions to the chemical shift whereas chemical shift modifications will also occur as a consequence of changes in the electronic distribution in DMF occurring upon coordination.

The kinetic parameters for DMF exchange on $UO_2(DMF)_5^{2+}$, which are given in the table, were derived through equation (4)

$$1/\tau_B = k_{ex} = (k_BT/h)\exp(-\Delta H^{\#}/RT)\exp(\Delta S^{\#}/R)$$

$$= \text{exchange rate}/5\,[UO_2(DMF)_5^{2+}] \qquad (4)$$

in which $\tau_B = \tau_F\chi_B/\chi_F$, and where τ_F is the mean life time of a free DMF molecule, χ_B and χ_F are the mol fractions of bound and free DMF respectively, and all other symbols have their usual significance. Semilogarithmic plots of τ_BT against 1/T are shown in Figure 2 for each of the solutions (i)–(vi) whose compositions are given in the table. Over the 20.3 fold variation of [DMF] the k_{ex} (220 K) values show only a 1.24 fold variation (the k_{ex} values for the least (vi) and second most concentrated (ii) solutions in [DMF] being identical within two standard deviations) consistent with the DMF exchange on $UO_2(DMF)_5^{2+}$ proceeding through either a dissociative (D) or dissociative interchange (I_D) mechanism [24]. In the former case the rate determining step is the formation of the reactive intermediate $UO_2(DMF)_4^{2+}$ as a consequence of the dissociation of DMF from $UO_2(DMF)_5^{2+}$. In the case of the I_D mechanism the energetics of the exchange process are still predominantly those of the dissociation of DMF from $UO_2(DMF)_5^{2+}$, but now the exchange process only proceeds through interchange of a DMF molecule in the first coordination sphere of $UO_2(DMF)_5^{2+}$ with one residing in the second coordination sphere which may be represented by the sixth DMF in the species $UO_2(DMF)_5^{2+}$...DMF. Thus the I_D exchange mechanism may be formulated as in equation 5

$$UO_2(DMF)_5^{2+} + {}^*DMF \underset{\text{fast}}{\overset{K_{assn}}{\rightleftharpoons}} UO_2(DMF)_5^{2+}\ldots{}^*DMF \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} UO_2(DMF)_4{}^*DMF\ldots DMF \qquad (5)$$

where the asterisk is a typographical distinction only and $K_{assn} = [UO_2(DMF)_5^{2+}\ldots DMF]/([UO_2(DMF)_5^{2+}][DMF])$.

Hence for the I_D mechanism the variation of k_{ex} with [DMF] is given by equation 6, from which it is seen that k_{ex} only

$$k_{ex} = kK_{assn}[DMF]/(1 + K_{assn}[DMF]) \qquad (6)$$

becomes independent of [DMF] when $K_{assn}[DMF] \gg 1$. For this limiting condition to apply in solutions (i) to (vi) a comparison of [DMF] and [d_2-methylenechloride] indicates that a very high degree of preferential solvation by DMF would be necessary, for which no experimental evidence is available. In the light of this observation and the existence of the *ground state* species [4, 7, 9, 25] $UO_2(H_2O)_4^{2+}$, $UO_2(TMU)_4^{2+}$ and $UO_2(HMPA)_4^{2+}$ in solution, the postulation of the *reactive intermediate* species $UO_2(DMF)_4^{2+}$ as required for the D exchange mechanism appears to be the more plausible mechanistic proposition. This is also consistent with observations of the exchange of trimethylphosphate, triethylphosphate, dimethylsulphoxide, N,N-dimethylacetamide, dimethylmethylphosphonate, and tetramethylurea on $UO_2L_5^{2+}$ species [3–7].

The $\Delta H^{\#}$ and $\Delta S^{\#}$ data in the table lie close to the $\Delta H^{\#}/\Delta S^{\#}$ linear free energy plot reported previously for dissociative ligand exchange on $UO_2L_5^{2+}$ species, from which it has been deduced that the effective surface charge density on the uranium(VI) centre experienced by the equatorial ligands lies between that of the aluminium(III) ion and that of the divalent first row transition metal ions in six coordinate species [3].

Acknowledgements

This work was supported by the Australian Research Grants Committee.

References

1 G. Gordon and H. Taube, *J. Inorg. Nucl. Chem., 16,* 272 (1961); *19,* 189 (1961).
2 S. W. Rabideau, *J. Phys. Chem., 71,* 2747 (1967).
3 J. Crea, R. Digiusto, S. F. Lincoln and E. H. Williams, *Inorg. Chem., 16,* 2825 (1977).
4 G. J. Honan, S. F. Lincoln and E. H. Williams, *J. Soln. Chem., 7,* 443 (1978).
5 R. P. Bowen, S. F. Lincoln and E. H. Williams, *Inorg. Chem., 15,* 2126 (1976).
6 J. Crea, S. F. Lincoln and E. H. Williams, *Aust. J. Chem., 29,* 2183 (1976).
7 G. J. Honan, S. F. Lincoln and E. H. Williams, *J. Chem. Soc. Dalton,* in press.
8 V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, Wien (1968) pp. 19–21.
9 G. J. Honan, S. F. Lincoln and E. H. Williams, *Inorg. Chem.,* in press.
10 N. M. Karayannis, C. Owens, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem., 31,* 2059 (1969).
11 P. W. N. M. van Leeuwen and W. L. Groenveld, *Inorg. Nucl. Chem. Lett., 3,* 145 (1967).
12 A. I. Vogel, "Quantitative Inorganic Analysis, 3rd ed., Longmans Green, London (1961) p. 702.
13 R. P. Bowen, S. F. Lincoln and E. H. Williams, *J. Mag. Res., 19,* 243 (1975).
14 J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc. (London), A229,* 20 (1955).
15 T. H. Siddall and C. A. Prohaska, *Inorg. Chem., 4,* 783 (1965).
16 S. F. Lincoln, *Prog. React. Kinetics, 9,* 1 (1977).
17 H. N. Cheng and H. S. Gutowsky, *J. Am. Chem. Soc., 94,* 5502 (1972).
18 N. A. Matwiyoff and W. G. Movius, *J. Am. Chem. Soc., 89,* 6077 (1967).
19 W. G. Movius and N. A. Matwiyoff, *Inorg. Chem., 6,* 847 (1967).
20 W. G. Movius and N. A. Matwiyoff, *Inorg. Chem., 8,* 925 (1969).
21 J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y. (1959) p. 178.
22 L. A. La Planche and M. T. Rogers, *J. Am. Chem. Soc., 85,* 3728 (1963).
23 J. K. Saunders and R. A. Bell, *Canad. J. Chem., 48,* 512 (1970).
24 C. H. Langford and H. B. Gray in "Ligand Substitution Processes", Benjamin, New York, N.Y. (1966).
25 A. Fratiello, U. Kubo, R. E. Lee and R. E. Schuster, *J. Phys. Chem., 74,* 3726 (1970).