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Proton Magnetic Resonance Study of Rotation about Carbon–Nitrogen Bonds in Pentakis(1,1-dimethylurea)dioxouranium(VI) and its 1,3-dimethylurea Analogue

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Abstract

In CD_3CN solutions the kinetic parameters characterising rotation about the C–NMe_2 and C–NH_2 bonds in $[UO_2(1,1\text{-DMU})_5]^{2+}$ (1,1-DMU = 1,1-dimethylurea) were determined as: k(265 K) = 39.1 ± 0.4 and 2960 ± 60 s^{-1}, $\Delta H^{\ddagger}$ = 49.1 ±0.76 and 61.1 ±0.5 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −28.3 ±2.7 and 53.1 ±2.2 J K^{-1} mol^{-1} respectively from ^{1}H NMR studies. Resonances arising from the three isomeric 1,3-DMU (= 1,3-dimethylurea) ligands were observed for $[UO_2(1,3\text{-DMU})_5]^{2+}$ in CD_3CN solution and the kinetic parameters characterising their isomerisations were also determined. The three isomers of 1,3-DMU have not previously been detected in solution and it appears that coordination of 1,3-DMU to UO_2^{2+} increases the barrier to rotation about the carbon nitrogen bond, as is also shown to be the case for 1,1-DMU.

Introduction

Dioxouranium(VI) complexes of stoichiometry $[UO_2L_4]^{2+}$ [1, 2] and $[UO_2L_5]^{2+}$ [3–7], where L is a monodentate oxygen donor ligand, have been well characterised in the solid state and in solution. In several of these complexes L has been a formamide [5], an acetamide [6], or a urea [7]. It is known that coordination of formamides and acetamides through oxygen can substantially decrease the rate of rotation about the carbon–nitrogen bond in these ligands [8, 9]. This effect had not been well characterised for a urea, until the recent observation that rotation about the carbon–nitrogen bond in 1,1,3,3-tetramethylurea (TMU) was markedly decreased in dioxouranium(VI) complexes [7]. This observation is of considerable interest as TMU, in common with several other ureas, has a particularly low barrier to rotation about the carbon–nitrogen bond in comparison with formamides and acetamides [10] Accordingly the efficacy of dioxouranium(VI) in decreasing the rate of rotation about carbon–nitrogen bonds in hitherto unreported complexes with these ligands has been studied to test the generality of this effect. It has been speculated [11] that 1,3-DMU exists predominantly as isomer A (Fig. 1) in the free state, and in consequence data obtained for the three possible isomers (A, B and C, Fig. 1) of this ligand in the dioxouranium(VI) complex are of particular interest.

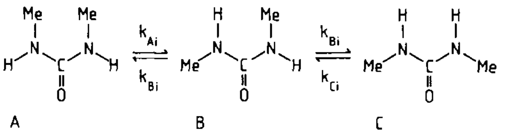

Fig. 1. The three isomers of 1,3-dimethylurea.

Experimental

In the preparation of $[UO_2(1,1\text{-DMU})_5](ClO_4)_2$ hydrated dioxouranium(VI) perchlorate (2.5 g) was dissolved in a triethylorthoformate/ethanol mixture (20 cm^3/7 cm^3) (the ethanol appeared to assist in the dissolution of the poorly soluble 1,1-DMU added later in the preparation) and heated at 323 K for 90 min with stirring in a round-bottomed flask fitted with a reflux condenser and a silica gel guard tube; after which finely divided 1,1-DMU (2.0 g) was added. Heating was continued for a further 90 min. On cooling to room temperature undissolved 1,1-DMU was filtered off and anhydrous ether (30 cm^3) was added to the filtrant with stirring, whereupon an oil precipitated. This oil crystallised after a few days under ether. The yellow crystals were filtered off, washed with anhydrous ether and dried under dry nitrogen (Yield = 85%). {Found: C, 19.58; H, 4.16; N, 15.32; UO_2^{2+}, 30.1. $[UO_2(1,1\text{-DMU})_5](ClO_4)_2$ requires C, 19.81; H, 4.43; N, 15.4; UO_2^{2+}, 29.7%}.

$[UO_2(1,3\text{-DMU})_5](ClO_4)_2$ was prepared as follows. Hydrated dioxouranium(VI) perchlorate (4.0 g)

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was dissolved in triethylorthoformate (26 cm^3) and heated with stirring at 323 K for 90 min. Finely divided 1,3-DMU (3.5 g) was added and an oil precipitated. Heating at 323 K was continued for a further 90 min. The supernatent liquid was decanted off at room temperature and anhydrous ether (30 cm^3) was added with stirring, whereupon yellow crystals formed. The filtered crystals were washed with anhydrous ether and dried under dry nitrogen. (Yield = 90%) {Found: C, 20.08; H, 4.49; N, 15.70; UO_2^{2+}, 30.1. $[UO_2(1,3\text{-DMU})_5](ClO_4)_2$ requires C, 19.81; H, 4.43; N, 15.40; UO_2^{2+}, 29.7%}. Analyses for UO_2^{2+} as a bipositive ion were carried out using an ion-exchange technique and C, H and N analyses were performed by the Australian Microanalytical Service, Melbourne. **CAUTION**: No explosion hazard was encountered with these complexes but it should be noted that perchlorate salts are sometimes explosive.

Infrared spectra were run in nujol mulls between sodium chloride plates using a Perkin-Elmer 683 spectrophotometer. Proton NMR spectra were run at 300.13 MHz on a Bruker CXP300 spectrometer locked on the deuterium frequency of CD_3CN. Spectra were stored as 8 K data blocks and were subjected to complete lineshape analyses similar to those described previously [2, 5–7], using Nicolet BNC-12 and Cyber 173 computers for the $[UO_2(1,1\text{-DMU})_5]^{2+}$ and $[UO_2(1,3\text{-DMU})_5]^{2+}$ systems respectively. Spectrometer temperature control was monitored by a platinum resistance thermometer and was better than ±0.3 K at each temperature studied at approximately three degree intervals in the range 227–300 K. Chemical shifts were measured directly from the proton impurity resonance of CD_3CN and were then recalculated on the basis of the known shift of this resonance from that of TMS.

Solutions of the dioxouranium(VI) complexes in CD_3CN (Aldrich 99% – distilled and dried over Linde 4A molecular sieves) were prepared by weight under dry nitrogen, and were then degassed and sealed in 5 mm NMR tubes under vacuum.

Results

Perchlorate infrared absorptions were observed at 1090 ($\nu 1$, s), 915 ($\nu 2$, w) and 618 ($\nu 3$, m) cm^{-1} for $[UO_2(1,1\text{-DMU})_5](ClO_4)_2$ and 1090 ($\nu 1$, s), 912 ($\nu 2$, w) and 522 ($\nu 3$, m) for $[UO_2(1,3\text{-DMU})_5](ClO_4)_2$ in nujol mulls, consistent with perchlorate retaining its T_d symmetry. Thus the equatorial planes of both dioxouranium(VI) complexes are occupied solely by five, 1,1- or 1,3-DMU ligands. Absorptions arising from the carbonyl group were observed at 1635 and 1595 cm^{-1} for $[UO_2(1,1\text{-DMU})_5](ClO_4)_2$; 1660 and 1610 cm^{-1} for 1,1-DMU; 1605 cm^{-1} for $[UO_2(1,3\text{-DMU})_5](ClO_4)_2$; and 1615 cm^{-1} for 1,3-DMU (these absorptions for the latter two species are broad.) The shift of the carbonyl frequencies to lower values on coordination of the ureas is consistent with a decrease in the carbonyl bond order, and is usually accompanied by an increase in the carbon–nitrogen bond order [7, 8]. This should be evidenced by an increase in the frequency of the carbon–nitrogen absorbance of the coordinated ureas but the overlapping nature of the absorbances in the range 1400–1530 cm^{-1} precluded the drawing of definite frequency correlations. To make comparisons of rates of rotation about carbon–nitrogen bonds it is desirable to carry out the proton NMR kinetic studies in the same solvent for each system. Propylene carbonate, CD_2Cl_2, CD_3NO_2 and CD_3CN, none of which displace the coordinated ureas, were tested as solvents and only CD_3CN was found to dissolve both dioxouranium(VI) complexes and 1,3-DMU (1,1-DMU was insoluble in all four solvents) and accordingly was the chosen solvent.

In CD_3CN solution at 233 K $[UO_2(1,1\text{-DMU})_5]^{2+}$ exhibits ^1H doublet resonances for the $-NH_2$ (δ = 6.14, 5.79 ppm) and $-NMe_2$ (δ = 3.21, 3.11 ppm) groups of 1,1-DMU consistent with rotation about both carbon–nitrogen bonds (or $-NH_2$ proton site exchange) occurring slowly on the NMR time scale. As the temperature was increased over the temperature range 233–261 K for $-NH_2$ and 247–276 K for $-NMe_2$ these doublets coalesced to singlets, consistent with rotation about the carbon–nitrogen bonds occurring with increasing rapidity. Analysis of these coalescences using site-exchange complete lineshape analysis methods [7, 12] yielded the kinetic parameters for rotation about the carbon–nitrogen bonds given in Table I. The freezing points (*ca.* 231 K) of the solutions precluded the extrapolation into the coalescence temperature range of the non-exchange modified linewidths ($W_{1/2}$) and chemical shifts (δ) of the coalescing $-NH_2$ doublet components from a substantial slow-exchange temperature range.

These extrapolations are necessary for reliable lineshape analyses [12], and accordingly were obtained by the following alternative method. At the lowest temperature examined (233 K) the $-NH_2$ doublet components still showed a small chemical exchange-induced broadening, but the δ values were not affected at this slow exchange rate. Above 261 K exchange is in the fast exchange limit, such that the temperature variation of the singlet resonance $W_{1/2}$ is the environmental average of the coalesced doublet components. By assuming this temperature variation to apply to the non-exchange modified $-NH_2$ doublet component $W_{1/2}$ values in the coalescence temperature range are obtained to a reasonable approximation. The non-exchange modified δ values

TABLE 1. Kinetic Parameters for Rotation about Carbon–Nitrogen Bonds.[a]

Species	Solvent	Bond	k (265 K) s^{-1}	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	Ref.
1,1-DMU	$(CD_3)_2CO$	$C-NMe_2$	4465			[13]
1,1-DMU	$(CD_3)_2CO$	$C-NMe_2$	115 ±1 (220 K)	36.8 ±0.4	−35.2 ±1.6	[13]
1,1-DMU	$(CD_3)_2CO$	$C-NMe_2$	49.5 (211 K)			[13]
1,1-DMU	$(CD_3)_2CO$	$C-NMe_2$	42.3 (211 K)			[11]
1,1-DMU	$(CD_3)_2CO$	$C-NH_2$	330 (211 K)			[11]
$[UO_2(1,1\text{-DMU})_5]^{2+}$	CD_3CN	$C-NMe_2$	39.1 ±0.4	49.1 ±0.7	−28.3 ±2.7	this work
$[UO_2(1,1\text{-DMU})_5]^{2+}$	CD_3CN	$C-NMe_2$	0.10 (211 K)			this work
$[UO_2(1,1\text{-DMU})_5]^{2+}$	CD_3CN	$C-NH_2$	2960 ±60	61.1 ±0.5	53.1 ±2.2	this work
$[UO_2(1,1\text{-DMU})_5]^{2+}$	CD_3CN	$C-NH_2$	1.95 (211 K)			this work
$[UO_2(1,3\text{-DMU})_5]^{2+}$	CD_3CN	C–NHMe (isomer A)	77.8 ±2.6	53.2 ±0.7	−1.7 ±3.0	this work
$[UO_2(1,3\text{-DMU})_5]^{2+}$	CD_3CN	C–NHMe (isomer B)	317 ±5	47.6 ±0.7	−16.3 ±2.6	this work
$[UO_2(1,3\text{-DMU})_5]^{2+}$	CD_3CN	C–NHMe (isomer C)	96.0 ±3.0	58.8 ±0.7	3.8 ±2.4	this work
$[UO_2(1,1\text{-TMU})_5]^{2+}$	CD_2Cl_2	$C-NMe_2$	20400			[7]
$[UO_2(1,1\text{-TMU})_5]^{2+}$	CD_2Cl_2	$C-NMe_2$	126 ±7 (195 K)	29.0 ±0.5	−52 ±3	[7]
$[UO_2(1,1\text{-TMU})_5]^{2+}$		$C-NMe_2$	8×10^{-3} (153 K)			[7]
TMU	$CDCl_3/(CD_3)_2CO/$ $CHFCl_2$	$C-NMe_2$	$6.16 \times 10^{+3}$ (153 K)			[11]

[a] These rate constants are determined at the quoted temperature in the midst of the coalescence temperature range and hence are more reliable than those calculated for other temperatures.

for the $-NH_2$ doublet components were only observed below 235 K and accordingly, anchored on these data, δ was allowed to vary systematically in the coalescence temperature range during the lineshape analyses to optimise the fits of the calculated lineshapes and the experimental spectra. The coalescence of the $-NH_2$ doublet occurred over a smaller temperature range (247–276 K), as a consequence of the smaller difference in δ between the doublet components. The slow exchange limit occurred at a higher temperature (242 K) and hence the temperature variations of the non-exchange modified $-NH_2$ $W_{1/2}$ and δ values were observed over a larger temperature range, which in conjunction with the approach used for the $-NH_2$ doublet provided good estimates of the variation of $W_{1/2}$ and δ in the $-NH_2$ coalescence temperature range.

The three possible isomers of 1,3-DMU (Fig. 1) present four chemical sites for the $-N\underline{H}Me$ and $-NH\underline{Me}$ protons. In CD_3CN solution at 300 K however the spectrum of 1,3-DMU consists of a broadened $-N\underline{H}Me$ quartet (δ 5.33 ppm) and a sharp $-NH\underline{Me}$ doublet (δ 2.63 ppm, J(H–H) 4.9 Hz) which (apart from systematic variations in δ) persisted down to 233 K, consistent with a single isomer predominating, or two or more isomers being in the fast exchange limit of the NMR time scale. In contrast the spectrum of $[UO_2(1,3\text{-DMU})_5]^{2+}$ at 230 K exhibits a $-N\underline{H}Me$ triplet (δ 6.32, 6.18, 5.88 ppm; no spin–spin splitting resolved) as seen in Fig. 2 and a $-NH\underline{Me}$ quartet (δ 3.00, 2.80, 2.78, 2.74 ppm – no spin–spin splitting resolved) consistent with rotation about the carbon-nitrogen bonds of the three coordinated isomers of 1,3-DMU (Fig. 1) being slow on the NMR time scale.

Intermolecular exchange of 1,3-DMU between the coordinated and free states is also slow at 233 K as new $-N\underline{H}Me$ (δ 5.50 ppm) and $-NH\underline{Me}$ (δ 2.63 ppm) resonances appear on addition of 1,3-DMU to a CD_3CN solution of $[UO_2(1,3\text{-DMU})_5]^{2+}$. These resonances may be used as aids to assign the resonances of $[UO_2(1,3\text{-DMU})_5]^{2+}$ if it is assumed that the magnetic environments of H and Me most distant from the uranium(VI) centre in the coordinated 1,3-DMU isomers most closely resemble those of free 1,3-DMU. On this basis $[UO_2(1,3\text{-DMU})_5]^{2+}$

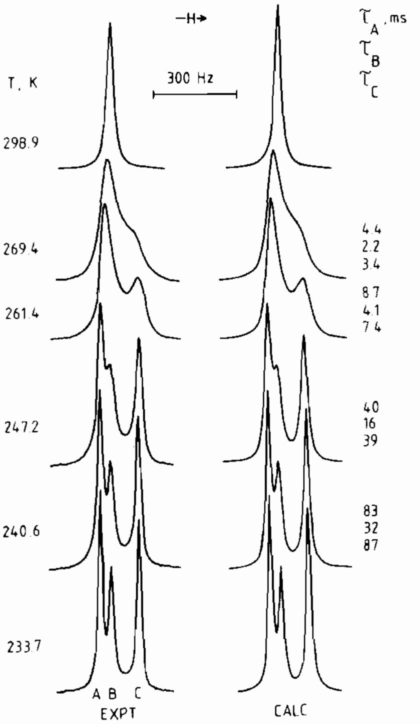

Fig. 2. Coalescence of the ^1H–N$\underline{H}$Me resonances characterising the A, B and C isomers of 1,3-dimethylurea in $[UO_2(1,3\text{-}DMU)_5]^{2+}$ in CD_3CN solution. The experimental spectra and temperatures are at the left and the best-fit lineshapes and the corresponding isomer lifetimes (τ_A, τ_B and τ_C) derived through complete lineshape analyses are to the right of the Figure respectively.

–NHM$\underline{e}$ resonances at δ 2.74, 2.78, 2.80 and 3.00 ppm are assigned to isomers A, B, B and C respectively, and the –N$\underline{H}$Me resonances at δ 6.32, 6.18 and 5.88 ppm are assigned to isomers A, B and C respectively (Fig. 2). Whilst the hydrogens of the coordinated B isomer of 1,3-DMU are chemically non-equivalent they are magnetically equivalent, and the small chemical shift difference exhibited by the chemically non-equivalent methyl hydrogens indicates that the difference between their magnetic environments is small. A similar magnetic equivalence of the methyl groups in $[UO_2(DMF)_5]^{2+}$ (DMF = N,N-dimethylformamide) has been reported and the possible role of the anisotropic electric field of the UO_2^{2+} entity in producing such equivalence has been discussed [5].

The populations of the A, B and C isomers of 1,3-DMU coordinated in $[UO_2(1,3\text{-}DMU)_5]^{2+}$ involves a substantial number of permutations producing a range of isomeric complexes. Thus the –N$\underline{H}$Me (Fig. 2) and –NH$\underline{Me}$ resonances are the summation of those of the isomeric complexes which evidently exhibit very small or no chemical shift differences. As the temperature is raised from 233 K both the –N$\underline{H}$Me (Fig. 2) and –NH$\underline{Me}$ resonances coalesce to a singlet, consistent with isomerisation of the coordinated 1,3-DMU isomers becoming rapid on the NMR time scale. The coalescences of both sets of resonances are in principle amenable to complete lineshape analyses. However because of the greater chemical shift differences between the –N$\underline{H}$Me resonances of the 1,3-DMU isomers and also the consequently greater coalescence temperature range, this coalescence was selected for analysis. The slow exchange limit was only reached at 233 K and in consequence the non-exchange modified $W_{1/2}$ and δ values in the coalescence temperature range were estimated by the methods described above for $[UO_2(1,1\text{-}DMU)_5]^{2+}$. The coordinated 1,3-DMU isomer populations were determined directly from integrated resonance areas in the temperature range 234–242 K and, anchored on these values, were allowed to vary systematically in the coalescence temperature range to optimise the fit of the calculated lineshapes to the experimental spectra. This population variation did not exceed 20% for any isomer over the range 233.7–289.9 K and the variation of $W_{1/2}$ and δ was less than 10%. The lineshape analysis was carried out using an equation which encompasses the four chemically non-equivalent –N$\underline{H}$Me sites in the three 1,3-DMU isomers (Fig. 1) as described in the Appendix. A selection of experimental spectra and best-fit calculated lineshapes are shown in Fig. 2 together with the lifetimes of the coordinated 1,3-DMU isomers τ_A, τ_B and τ_C, and the appropriate temperatures.

As rotation about either of the equivalent carbon–nitrogen bonds in isomer A causes isomerisation to isomer B, $\tau_A = 1/k_{Ai} = 1/(2k_A)$ where k_{Ai} and k_A are the rate constants for isomerisation and rotation about one carbon–nitrogen bond respectively. Similarly $\tau_C = 1/k_{Ci} = 1/(2k_C)$. Rotation about either of the non-equivalent carbon–nitrogen bonds of isomer **B** (k_B and k'_B) causes isomerisation to isomer A or C and as a consequence k_B and k'_B cannot be separately determined. They were therefore set equal in the lineshape analysis, as described in the Appendix. As a consequence of this and the nature of the four site lineshape analysis $\tau_B = 1/k_{Bi} = 1/k_B = 1/k'_B$. The τ values derived at ten temperatures in the range 240.6–272.1 K (where the chemical exchange induced modification of the –N$\underline{H}$Me resonances are substantial) are plotted in Fig. 3 and associated rate constants (quoted for 265 K the midst of the coalescence temperature range where the most accurate rate data are obtained) $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ appear in Table I. The errors quoted in Table I represent one standard deviation for the linear regression fit of the τ data to the Eyring equation and do not include the possible systematic errors arising from the estimation of the non-exchange modified $W_{1/2}$ and δ values used in the lineshape analyses or the effect of the $k_B = k'_B$ assumption discussed above.

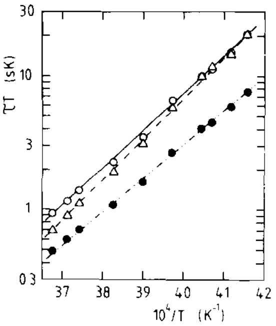

Fig. 3. The variation of τ_A (circle), τ_B (filled circle), and τ_C (triangle) with temperature. The lines drawn through each data set represent the linear regression line for the fit of the data to the Eyring equation.

When these possible error sources are considered it is probable that for [UO_2(1,1-DMU)$_5$](ClO_4)$_2$ the error in k (265 K) is three times that in Table I, with a commensurately increased error in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. For [UO_2(1,3-DMU)$_5$]$^{2+}$ the error in k (265 K) could be up to five times that quoted, with commensurately increased errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Nevertheless these errors do not significantly affect the ensuing discussion of the effects of coordination on 1,1-DMU or 1,3-DMU. Whilst the data in Table I pertain to solutions 0.0568 and 0.0755 mol dm^{-3} of [UO_2(1,1-DMU)$_5$]$^{2+}$ and its 1,3-DMU analogue respectively, other solutions yield data consistent with the quoted rate parameters.

Discussion

The rates of rotation about the carbon–nitrogen bonds in 1,1-DMU and TMU [7] in the dioxouranium(VI) complexes are substantially decreased by comparison to those observed for 1,1-DMU [11, 13] and TMU [14] in the free state, and it is reasonable to assume that a similar situation prevails for 1,3-DMU although no rate data is available for this urea in the free state. Thus the observation of the A, B and C 1,3-DMU isomers coordinated to dioxouranium(VI) (in the ratio 43.4:21.4:35.2 for A:B:C at 265 K) suggests that free 1,3-DMU could exist as all three isomers are undergoing rapid isomerisation. It is probable, however, that the isomeric ratio of 1,3-DMU changes on coordination by comparison to that existing in the free state, as is observed for the two isomers of N-methylacetamide on coordination to scandium(III) [15] and the E and Z isomers of Boc amino acid esters on coordination to europium(III) [16]. The predominant cause of the decrease in the rates of rotation about the carbon–nitrogen bonds of 1,1-DMU, 1,3-DMU and TMU in their dioxouranium(VI) complexes is probably the increase in the order of these bonds which occurs on coordination of these ureas through oxygen. A comparison of the activation parameters for rotation about the C–NMe_2 bond (Table I) in free and coordinated 1,1-DMU indicates that the *ca.* 100 fold slower rate of the latter process arises from its greater $\Delta H^{\ddagger}$. It has been observed that changes in solvent do not cause large variations in rates of rotation about carbon–nitrogen bonds [12] and this is assumed to be the case in these studies of free and coordinated 1,1-DMU.

Rotation about the C–NH_2 bond is also slowed *ca.* 100 fold in coordinated 1,1-DMU, but it is seen that the relative rotation rates for C–NMe_2 and C–NH_2 are retained in free and coordinated 1,1-DMU. Whilst the rate of rotation about the C–NMe_2 bond in coordinated TMU is slowed *ca.* 10^6 compared to that of free TMU, both of these rates are substantially greater than those characterising both states of 1,1-DMU. The rates of rotation about the C–NHMe bonds in the three coordinated isomers of 1,3-DMU differ by only a factor of four and are interposed in magnitude between those characterising the C–NH_2 and C–NMe_2 bonds in coordinated 1,1-DMU. The transition state for rotation about an urea C–NR_2 bond is envisaged to have the –NR_2 moiety perpendicular to the carbonyl plane. As the two urea carbon–nitrogen bonds are cross-conjugated steric interactions causing –NR_2 to twist out of the carbonyl plane will tend to destabilise the ground state and stabilise the transition state if the second –NR_2 simultaneously becomes more closely coplanar with the carbonyl group with a resultant increase in the order of the carbon–nitrogen bond between them. On this basis it is expected that the rate of rotation about the carbon–nitrogen bonds in TMU in both the free and coordinated states will be greater than that in the less crowded 1,1-DMU and 1,3-DMU.

The much greater decrease in rate exhibited by TMU upon coordination (by comparison to 1,1-DMU) may arise from the greater *intra*-ligand crowding in [UO_2(TMU)$_5$]$^{2+}$ significantly hindering rotation of –NMe_2 out of the carbonyl plane and decreasing the destabilisation and stabilisation of the ground and transition states (by comparison to those of free TMU) respectively to a greater extent than experienced by 1,1-DMU. In addition if the relative increase in carbon–nitrogen bond order on coordination is greater for TMU than 1,1-DMU then a larger decrease in rate will occur for TMU.

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References

1 L. R. Nassimbeni and A. L. Rodgers, *Cryst. Struct. Commun., 5,* 301 (1976).
2 G. J. Honan, S. F. Lincoln and E. H. Williams, *Inorg. Chem., 17,* 1855 (1978).
3 J. McB. Harrowfield, D. L. Kepert, J. M. Patrick, A. H. White and S. F. Lincoln, *J. Chem. Soc., Dalton Trans.,* 393 (1983).
4 J. Crea, R. Diguisto, S. F. Lincoln and E. H. Williams, *Inorg. Chem., 15,* 2126 (1976).
5 G. J. Honan, S. F. Lincoln, T. M. Spotswood and E. H. Williams, *Inorg. Chim. Acta, 33,* 235 (1979).
6 R. P. Bowen, S. F. Lincoln and E. H. Williams, *Inorg. Chem., 15,* 2126 (1976).
7 G. J. Honan, S. F. Lincoln and E. H. Williams, *J. Chem. Soc., Dalton Trans.,* 320 (1979).
8 K. G. Rao, E. D. Becker and C. N. R. Rao, *J. Chem. Soc., Chem. Commun.,* 350 (1977).
9 H. N. Cheng and H. S. Gutowsky, *J. Phys. Chem., 84,* 1039 (1980).
10 L. M. Jackman, in L. M. Jackman and F. A. Cotton (eds.), 'Dynamic Nuclear Magnetic Resonance Spectroscopy', Academic Press, New York, 1975, p. 203.
11 M. L. Martin, M. L. Filleux-Blanchard and G. J. Martin, *Org. Magn. Reson., 13,* 396 (1980).
12 S. F. Lincoln, *Prog. React. Kinet., 9,* 1 (1977).
13 A. M. Hounslow, private communication.
14 P. Stilbs and M. E. Moseley, *J. Magn. Reson., 31,* 55 (1978).
15 D. L. Pisaniello and S. F. Lincoln, *Inorg. Chem., 20,* 3689 (1981).
16 H. Kessler and M. Molter, *J. Am. Chem. Soc., 98,* 5969 (1976).

Appendix

The coalescence of the $[UO_2(1,3\text{-DMU})_5]^{2+}$ resonances may be simulated using the Kubo-Sack method of introducing chemical exchange effects into the classical lineshape equations [12]. If the hydrogens of the N$\underline{\text{H}}$Me groups are designated as being in site 1 for isomer A, sites 2 and 3 for isomer B, and site 4 for isomer C, the absorption mode lineshape, v, is given by eqn. (1):

$$v = \gamma B_1 M_{zeq} \mathrm{Re}(\chi_1, \chi_2, \chi_3, \chi_4) \times \begin{bmatrix} -\alpha_1 - 1/\tau_1 & 1/(2\tau_1) & 1/(2\tau_1) & 0 \\ 1/(2\tau_2) & -\alpha_2 - 1/\tau_2 & 0 & 1/(2\tau_2) \\ 1/(2\tau_3) & 0 & -\alpha_3 - 1/\tau_3 & 1/(2\tau_3) \\ 0 & 1/(2\tau_4) & 1/(2\tau_4) & -\alpha_4 - 1/\tau_4 \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \qquad (1)$$

where $\alpha_n = 1/(T_{2n}) - i(\omega_{on} - \omega)$; χ_n, $1/T_{2n}$, ω_{on}, and τ_n are respectively the population, the transverse relaxation time, the Larmor frequency, and the lifetime in site n; ω is the observed frequency; and the other symbols have their usual meaning. The site lifetimes are related through eqn. (2) where the χ_n values are obtained as described in the Results section.

$$\tau_1/\chi_1 = \tau_2/\chi_2 = \tau_3/\chi_3 = \tau_4/\chi_4 \qquad (2)$$

On this basis τ_1 and τ_4 are equal to τ_A and τ_C the lifetimes of isomers A and C respectively. The lifetime of isomer B, τ_B, is equal to τ_3 and τ_4.