Proton Nuclear Magnetic Resonance Study of Ligand Exchange on the Pentakis(*N*-methylacetamide)dioxouranium(VI) Ion

By **Geoffrey J. Honan, Stephen F. Lincoln,*** and **Evan H. Williams,** Department of Physical and Inorganic Chemistry, University of Adelaide, S.A.5001, Australia
Thomas M. Spotswood, Department of Organic Chemistry, University of Adelaide, G.P.O. Box 498, Adelaide, S.A. 5001, Australia

Pentakis(*N*-methylacetamide)dioxouranium(VI) ion, $[UO_2(nma)_5]^{2+}$, is shown to be the predominant species in solutions of $[UO_2]^{2+}$ and nma in CD_2Cl_2 or CD_3CN. The virtual constancy of the rate of nma exchange on $[UO_2(nma)_5]^{2+}$ over a 56.9-fold range of free-nma concentration in CD_3CN is interpreted in terms of a dissociative mechanism. A typical set of kinetic data for this process is $k_{ex}(273\ K) = 336 \pm 16\ s^{-1}$, $\Delta H^{\ddagger} = 54.4 \pm 0.6\ kJ\ mol^{-1}$, and $\Delta S^{\ddagger} = 3.3 \pm 2.3\ J\ K^{-1}\ mol^{-1}$ for a solution in which $[UO_2(nma)_5{}^{2+}]$, [nma], and $[CD_3CN]$ are 0.162 4, 0.661 3, and 15.92 mol dm^{-3} respectively. In CD_2Cl_2 higher values are observed for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, but both data sets lie on an isokinetic plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ for $[UO_2L_5]^{2+}$ systems for which the rate of exchange of L is independent of [L]. The significance of this isokinetic relationship is discussed.

RECENT dynamic n.m.r. spectral studies have established that the dioxouranium(VI) ion often assumes a ground-state stoicheiometry $[UO_2L_5]^{2+}$ when L is a unidentate oxygen-donor ligand, and further that the mechanism of ligand exchange on such species is predominantly dissociative in nature.[1-4] Nevertheless, there remains a paucity of information concerning the dynamics of the dioxouranium(VI) ion in solution by comparison with the relative wealth of data available for lighter metal-ion species.[5,6] This is surprising in view of the unusual nature of the dioxouranium(VI) species in which the axial oxide ligands are inert [7,8] whereas the equatorial ligands are labile,[1-4] quite apart from the fact that uranium is the heaviest, abundant, naturally occurring element and therefore of considerable interest on that basis alone. As a consequence of these observations the present work with the pentakis(*N*-methylacetamide)-dioxouranium(VI) species, $[UO_2(nma)_5]^{2+}$, has been undertaken to extend the present knowledge of the solution dynamics of $[UO_2L_5]^{2+}$ species.

EXPERIMENTAL

Preparation of the Dioxouranium(VI) *Complex.*—Hydrated dioxouranium(VI) perchlorate (G. Frederick Smith) (2.5 g) was stirred with triethyl orthoformate [9,10] (10 g) at 320 K for 1 h. Dry *N*-methylacetamide (1.4 g) was added at room temperature and the resulting yellow crystals of $[UO_2(nma)_5][ClO_4]_2$ were filtered off, washed with dry diethyl ether, and pumped down on a vacuum line for several hours. All preparative and handling procedures were performed under dry nitrogen, unless otherwise stated, and the exposure of $[UO_2(nma)_5][ClO_4]_2$ to light was kept to a minimum to avoid the possibility of photochemically induced redox processes. The product yield was 90% {Found: C, 21.55; H, 4.20; N, 8.50; $[UO_2]^{2+}$, 28.6. Calc. for $[UO_2(nma)_5][ClO_4]_2$: C, 21.6; H, 4.25; N, 8.80; $[UO_2]^{2+}$, 28.55%}. The $[UO_2(nmf)_5][ClO_4]_2$ complex (nmf = *N*-methylformamide) was prepared in a similar manner {Found: C, 15.45; H, 3.40; N, 9.25; $[UO_2]^{2+}$, 35.4. Calc. for $[UO_2(nmf)_5][ClO_4]_2$: C, 15.7; H, 3.30; N, 9.15; $[UO_2]^{2+}$, 35.3%}. The $[UO_2]^{2+}$ analyses were carried out using an ion-exchange technique and the C, N, and H analyses were performed by the Australian Microanalytical Service, Melbourne.

Preparation of Solutions.—*N*-Methylacetamide, nmf, CD_2Cl_2, and CD_3CN (99.4 and 99.6% respectively, CEA, France) were redistilled and stored over Linde 4A molecular sieves. Solutions of the dioxouranium(VI) species and nma or nmf, in CD_2Cl_2 or CD_3CN, were prepared in volumetric flasks (5 cm^3) in a dry nitrogen atmosphere. The relative concentrations of bound and free nma and nmf were kept approximately constant since such solutions produce the ^1H n.m.r. spectra best suited to derivations of site lifetimes through complete lineshape analyses. This requirement precluded the study of the nma system in CD_2Cl_2 below [nma] $\simeq$ 0.3 mol dm^{-3} since below this concentration $[UO_2(nma)_5][ClO_4]_2$ precipitated.

RESULTS AND DISCUSSION

In CD_2Cl_2 solution the 90 MHz ^1H n.m.r. spectrum of $[UO_2(nma)_5]^{2+}$ consists of a *N*-methyl doublet [*J*(Me–NH) 3.5 Hz] 75.5 Hz downfield from the acetyl methyl singlet at 235 K [solution (i) in the Table]. In the same solution free nma exhibits doublet [*J*(Me–NH) 4.7 Hz] and singlet resonances respectively 37.8 and 31.0 Hz upfield (235 K) from the analogous resonances of bound nma. In CD_3CN solution similar spectra are observed for bound and free nma in the temperature range 230—245 K except that resolution of the bound nma doublet is less, probably as a consequence of a greater degree of viscosity broadening in CD_3CN. Under conditions of slow exchange of nma between the bound and free sites a comparison of the integrated areas of the resonances of bound and free nma indicates that, within experimental error, five nma ligands (see Table) are bound to dioxouranium(VI) in both CD_2Cl_2 and CD_3CN diluents consistent with $[UO_2(nma)_5]^{2+}$ being the predominant dioxouranium(VI) species in solutions (i)—(ix). These determinations are based upon the spectra observed for bound and free nma which arise from the nma isomer in which the *N*-methyl group is *trans* to the acetyl methyl group.[11] In contrast, 8% of nmf exists as the *cis* isomer [11] and in CD_2Cl_2 solutions of $[UO_2(nmf)_5][ClO_4]_2$ and nmf at 200 K resonances arising from bound and free *cis*- and *trans*-nmf are observed. Unfortunately, precipitation of $[UO_2(nmf)_5][ClO_4]_2$ prevented a reliable determination of the stoicheiometry of the dioxoura-

Solution compositions and kinetic parameters for the $[UO_2(nma)_5]^{2+}$ system

	$[UO_2(nma)_5{}^{2+}]$ [a]	[nma] [b]	[diluent]		k_{ex} (273 K) [d]	$\Delta H^\ddagger$ [e]	$\Delta S^\ddagger$ [e]
	mol dm^{-3}				s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
Solution			CD_3CN	C.N. [c]			
i	0.341 7	1.798	13.04	4.9 ± 0.1	323 ± 24	59.2 ± 0.9	20.8 ± 3.6
ii	0.162 4	0.661 3	15.92	5.0 ± 0.1	336 ± 16	54.4 ± 0.6	3.3 ± 2.3
iii	0.070 70	0.372 0	17.75	4.9 ± 0.1	351 ± 17	55.6 ± 0.6	8.0 ± 2.3
iv	0.033 11	0.134 8	17.86	5.0 ± 0.1	336 ± 16	55.5 ± 0.6	7.3 ± 2.2
v	0.015 64	0.082 31	18.19	4.9 ± 0.1	340 ± 24	52.5 ± 0.9	−3.3 ± 3.4
vi	0.008 672	0.035 31	18.25	5.0 ± 0.1	326 ± 12	55.2 ± 0.5	6.1 ± 1.8
			CD_2Cl_2				
vii	0.287 7	1.581	11.95	4.9 ± 0.2	166 ± 9	68 ± 1	48 ± 5
viii	0.159 1	0.964 2	12.39	4.9 ± 0.2	173 ± 10	67 ± 1	44 ± 4
ix	0.040 41	0.296 8	14.67	4.9 ± 0.2	190 ± 20	67 ± 1	45 ± 6

[a] Added as $[UO_2(nma)_5][ClO_4]_2$. [b] Added as nma liquid. [c] The number of nma molecules co-ordinated per $[UO_2]^{2+}$ ion as determined from a comparison of the integrated areas of the co-ordinated and free signals in the temperature ranges 230—245 and 225—250 K respectively in CD_3CN and CD_2Cl_2. [d] k_{ex} (273 K) values occur in the middle of the coalescence phenomena and are taken from the linear regression line. The errors are one standard deviation. [e] The errors quoted are one standard deviation.

nium(VI) species in CD_2Cl_2 solution, and at the lowest temperatures achievable in CD_3CN solution (235 K) the resonances of bound and free nmf were still coalesced.

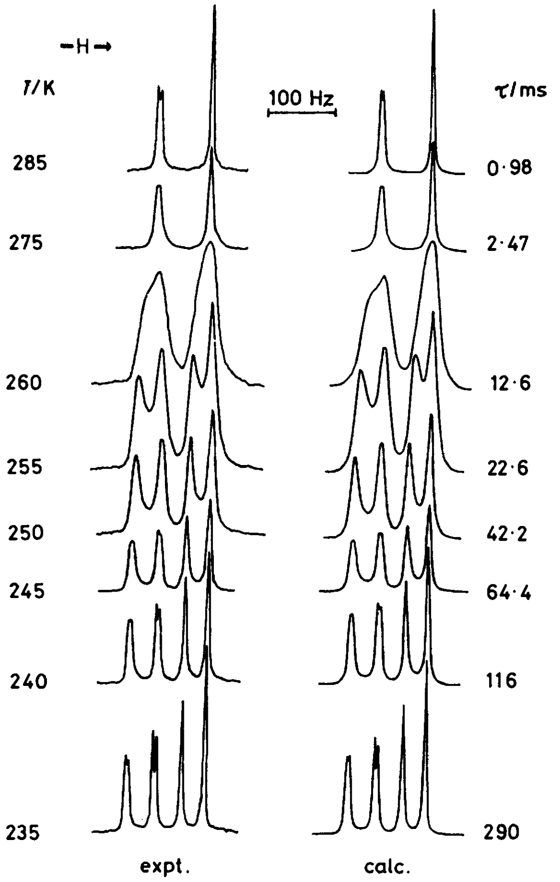

FIGURE 1 Experimental (left-hand side) and best-fit calculated ^1H n.m.r. lineshapes of a solution containing $[UO_2(nma)_5]^{2+}$ (0.3417), nma (1.798), and CD_3CN (13.04 mol dm^{-3}). Experimental temperatures and best-fit τ values appear to the left and right of the Figure respectively

All of the $[UO_2(nma)_5]^{2+}$ solutions (i)—(ix) in the Table exhibit ^1H n.m.r. coalescence phenomena consistent with an increase in the rate of nma exchange between the bound and free sites as the temperature increases (Figure 1) until in the fast-exchange limit the environmentally averaged lineshape consists of a doublet downfield from a singlet. The mean site lifetime of bound nma, τ_B, at each temperature was obtained through a complete lineshape analysis using a program based on the Bloch equations modified for site exchange.[12] The iteratively obtained best-fit τ_B values and the corresponding computer-calculated lineshapes obtained for solution (ii) using this program are in Figure 1. This program requires as input the frequency differences between the coalescing resonances and their widths at half-amplitude, in the absence of chemical-exchange-induced modifications for each temperature at which τ_B is to be determined. These values are based upon those observed in the low-temperature slow-site-exchange region and typical of such values are those used for solution (i) for which the chemical shifts between the bound and free acetyl methyl singlets and *N*-methyl doublets were 31.0 and 37.8 Hz respectively over the experimental temperature range, and their respective linewidths varied (as $1/T$) from 3.0, 2.5, 3.2, and 3.0 Hz at 235 K to 2.2, 1.9, 2.2, and 2.0 Hz at 285 K.

The relationship between τ_B and other kinetic parameters is given by equation (1) where $\tau_B/x_B = \tau_F/x_F$,

$$\begin{aligned} 1/\tau_B = k_{ex} &= \text{exchange rate}/5[UO_2(nma)_5{}^{2+}] \\ &= (\boldsymbol{k}T/\boldsymbol{h})\exp(-\Delta H^\ddagger/RT)\exp(\Delta S^\ddagger/R) \qquad (1) \end{aligned}$$

and τ_F is the mean site lifetime of nma in the free state, x_B and x_F are the respective mol fractions of bound and free nma, k_{ex} is the observed first-order exchange rate constant, and all other symbols have their usual meaning. The enthalpy and entropy of activation for each solution were obtained from a semilogarithmic plot of $\tau_B T$ against $1/T$ (Figure 2) and the derived values are given in the Table. At 273 K (which is in the midst of the coalescence region where the most accurate τ_B values are obtained) the k_{ex} values for the CD_3CN solutions (i)—(vi) are all within two standard deviations of each other and therefore may not be meaningfully distinguished. This indicates that over the 56.9-fold range of [nma] encompassed by these solutions the rate of exchange of nma on $[UO_2(nma)_5]^{2+}$ is independent of [nma]. This is consistent with the predominant exchange mechanism being either of the dissociative (*D*) type[13] in which the rate-determining step is the formation of the reactive intermediate $[UO_2(nma)_4]^{2+}$, or of the dissociative interchange (I_D) type.[13] In the latter mechanism an nma ligand bound in the first co-ordination sphere of $[UO_2(nma)_5]^{2+}$ can only exchange with another nma molecule residing in the second co-ordination sphere as a consequence of $[UO_2(nma)_4]^{2+}$ being too reactive to have an independent existence. Thus, whilst the dissociation of the leaving nma ligand from $[UO_2(nma)_5]^{2+}$ makes the major contribution to the activation energetics, the rate of exchange will only become independent of [nma] when each $[UO_2(nma)_5]^{2+}$ species has one or more nma molecules residing in the second co-ordination sphere. A high degree of preferential occupancy of the second co-ordination sphere of $[UO_2(nma)_5]^{2+}$ would be necessary for this condition to be met in all of the solutions (i)—(vi) as a comparison of the relative [nma] and $[CD_3CN]$ values indicates (Table). In the absence of any evidence for such a preferential occupancy, and the observation of *ground-state* species of stoicheiometry $[UO_2L_4]^{2+}$ [L = H_2O,[14,15] $P(NMe_2)_3O$,[16] or tetramethylurea (tmu)[17]], the *D* mechanism and the reactive intermediate $[UO_2(nma)_4]^{2+}$ appear to offer the more plausible explanation of the observed exchange rate law.

The observation of the nma-exchange process in CD_2Cl_2 diluent was limited to a 5.3-fold variation of [nma] as a consequence of the solubility problems alluded to in the Experimental section. Nevertheless, the k_{ex} (273 K) values observed, which are identical within two standard deviations and hence may not be meaningfully distinguished, are also consistent with exchange occurring through a *D* mechanism. The magnitudes of k_{ex} (273 K), $\Delta H^‡$, and $\Delta S^‡$ observed in the two diluents, CD_3CN and CD_2Cl_2, differ significantly and indicate a variation in the relative enthalpies and entropies of the ground state and transition state as the diluent is varied. Since there is a marked dependence of $\Delta H^‡$ and $\Delta S^‡$ upon diluent some of the variation of these quantities in CD_3CN may arise as a consequence of the relative [nma] and $[CD_3CN]$ values changing with consequent modification of the environments of the ground and transition states. These observations contrast with those made on the $[UO_2(tmu)_5]^{2+}$–tmu system for which the kinetic parameters in CD_3CN and CD_2Cl_2 were indistinguishable. In this latter system it may be concluded that either the ground-state and transition-state enthalpies and entropies are little affected by a change of environment, or that they are modified to a similar extent.

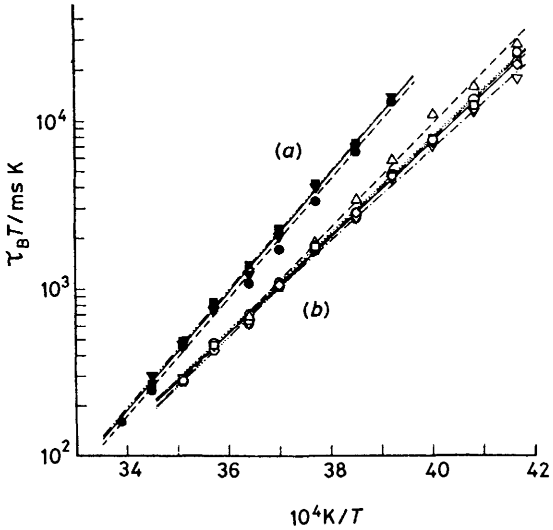

FIGURE 2 Semilogarithmic plots of $\tau_B T$ data for the $[UO_2(nma)_5]^{2+}$ system. Data for solutions (i)—(ix) appear as ▽, ○, ⬭, □, △, ◇, ■, ▼, and ● respectively, and the linear regression lines as –·–·–, ——, —····—, – – – –, —···—, —··—, – – – –, and —— respectively. Solvents: (*a*) CD_2Cl_2, (*b*) CD_3CN

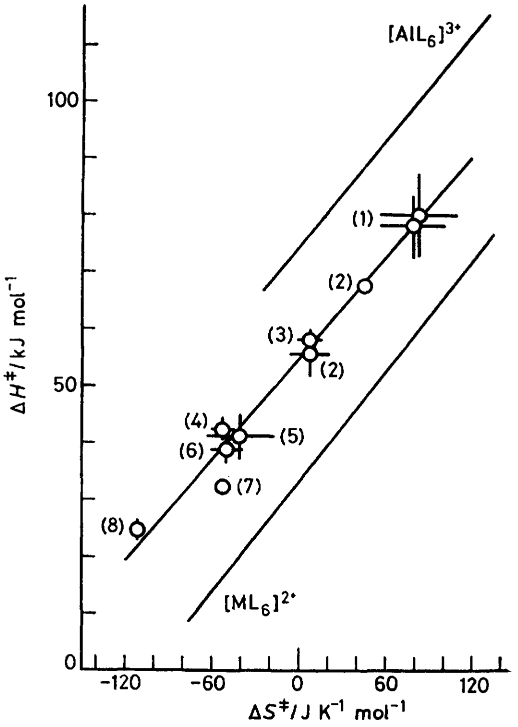

FIGURE 3 A linear free-energy plot of $\Delta H^‡$ against $\Delta S^‡$ for ligand exchange on the $[UO_2L_5]^{2+}$ species, where L = tmu (1), nma (2), dmmp (3), tep (4), dma (5), dmso (6), dmf (7), and tmp (8). The diluent was CD_2Cl_2 except systems (1) and (2) characterised by the lower $\Delta H^‡$ values in which the diluents were CD_3CN and the dmso system in which the diluent was $(CD_3)_2CO$. The solid line through the $[UO_2L_5]^{2+}$ data is a linear least-squares regression line, and the lines for $[AlL_6]^{3+}$ and $[ML_6]^{2+}$ are taken from ref. 4

In Figure 3 a plot of $\Delta H^‡$ against $\Delta S^‡$ indicates that an isokinetic relationship exists for the $[UO_2L_5]^{2+}$ systems [L = nma, tmu,[17] dimethyl sulphoxide (dmso),[13] dimethylformamide (dmf),[18] *NN*-dimethylacetamide (dma),[2] trimethyl phosphate (tmp),[4] triethyl phosphate (tep),[4] and dimethyl methylphosphonate (dmmp)[3]] which are considered to undergo ligand exchange through a dissociative mechanism. The horizontal and vertical bars of the datum points indicate the *ranges* of $\Delta H^‡$ and $\Delta S^‡$ observed over the free-ligand concentration ranges for that particular system. A linear least-squares fit of the plotted data to equation (2) yields values of $T = 296 \pm 15$ K and $\Delta G^{\ddagger} = 54.2 \pm 9.4$ kJ mol^{-1}. The isokinetic

$$\Delta H^{\ddagger} = T\Delta S^{\ddagger} + \Delta G^{\ddagger} \qquad (2)$$

curves for dissociative ligand exchange on $[AlL_6]^{3+}$ ($T \approx 317$ K and $\Delta G^{\ddagger} \approx 75$ kJ mol^{-1}) and $[ML_6]^{2+}$ ($T \approx 324$ K and $\Delta G^{\ddagger} \approx 33$ kJ mol^{-1}),[4] where M is a first-row transition metal or magnesium, are also shown in Figure 3. The surface charge density of the metal centre is considered[6,19,20] to be a dominant factor determining the magnitude of $\Delta G^{\ddagger}$ characterising dissociative ligand exchange, and on this basis it may be empirically deduced that the surface charge density seen by the equatorial ligands in $[UO_2L_5]^{2+}$ lies between that in $[AlL_6]^{3+}$ (Al^{3+} radius = 0.45 Å) and $[ML_6]^{2+}$ [the extremes of the radii of the M^{2+} species characterised by the curve in Figure 3 range from 0.62 (Ni^{2+}) to 0.91 Å (Mn^{2+})].

The apparently dominant role of surface charge density in determining $\Delta G^{\ddagger}$ warrants further discussion since variation of the nature of L produces consequent variations in four other factors, *viz.*: (*i*) the basicity of the leaving group L; (*ii*) the Lewis acidity of the dioxouranium(VI) centre in the $[UO_2L_5]^{2+}$ or analogous $[ML_6]^{n+}$ species; (*iii*) the steric interactions in that species; and (*iv*) the interaction of that species with the solvent or diluent. The effect of ligand basicity upon kinetic parameters has been the subject of much debate and in some cases rate constants[21] and activation enthalpies[22,23] for ligand-dissociation processes have shown a linear dependence upon the Gutmann donor number,[24] DN, and also the Drago basicity parameters,[25] E_B and C_B. Often, as in the case of the $[UO_2L_5]^{2+}$ systems, no such simple correlation is found,[26] however. In view of the factors (*i*)—(*iv*), which vary with L, it may be rather optimistic to expect simple correlations between ligand-basicity parameters (which are usually derived through the formulation of 1 : 1 adducts) and the kinetic parameters characterising ligand substitution; indeed it is possible that some of the simple correlations which have been observed may be fortuitous.[26,27] Nevertheless, it appears that as L is varied compensatory changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ occur to produce isokinetic relationships characteristic of a given surface charge density. Bennetto and Caldin[6,28] have suggested that the origins of such isokinetic relationships lie in rearrangements of solvent or diluent outside the first coordination sphere which occur synchronously with the formation of the transition state, and which make significant contributions to $\Delta H^{\ddagger}$ and the major contribution to $\Delta S^{\ddagger}$. In an alternative model, Fischer *et al.*[29] propose that changes in the degrees of freedom for rotation and vibration occurring upon formation of the transition state produce isokinetic relationships. This model also predicts a sensitivity of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to interactions outside the first co-ordination sphere under the appropriate conditions. A clear distinction between these two models does not seem possible at this time.

This work was supported by the Australian Research Grants Committee.

[8/1806 *Received*, 16*th October*, 1978]

REFERENCES

[1] R. P. Bowen, S. F. Lincoln, and E. H. Williams, *J. Magnetic Resonance*, 1975, **19**, 243.

[2] R. P. Bowen, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, 1976, **15**, 2126.

[3] J. Crea, S. F. Lincoln, and E. H. Williams, *Austral. J. Chem.*, 1976, **29**, 2183.

[4] J. Crea, R. Diguisto, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, 1977, **16**, 2825.

[5] K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107.

[6] E. F. Caldin and H. P. Bennetto, *J. Solution Chem.*, 1973, **2**, 217.

[7] G. Gordon and H. Taube, *J. Inorg. Nuclear Chem.*, 1961, **16**, 272; **19**, 189.

[8] S. W. Rabideau, *J. Phys. Chem.*, 1967, **71**, 2747.

[9] N. M. Karayannis, C. Owens, L. L. Pytelwski, and M. M. Labes, *J. Inorg. Nuclear Chem.*, 1969, **81**, 2059.

[10] P. W. N. M. von Leeuwen and W. L. Groenveld, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 145.

[11] L. A. La Planche and M. T. Rogers, *J. Amer. Chem. Soc.*, 1963, **85**, 3728.

[12] S. F. Lincoln, *Progr. Reaction Kinetics*, 1977, **9**, 1.

[13] C. H. Langford and H. B. Gray in 'Ligand Substitution Processes,' W. A. Benjamin, New York, 1966.

[14] A. Fratiello, V. Kubo, R. E. Lee, and R. E. Schuster, *J. Phys. Chem.*, 1970, **74**, 3726.

[15] G. J. Honan, S. F. Lincoln, and E. H. Williams, *J. Solution Chem.*, 1978, **7**, 443.

[16] G. J. Honan, S. F. Lincoln, and E. H. Williams *Inorg. Chem.*, 1978, **17**, 1855.

[17] G. J. Honan, S. F. Lincoln, and E. H. Williams, *J.C.S. Dalton*, 1979, 326.

[18] R. P. Bowen, G. J. Honan, S. F. Lincoln, T. M. Spotswood, and E. H. Williams, *Inorg. Chim. Acta*, in the press.

[19] J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

[20] A. McAuley and J. Hill, *Quart. Rev.*, 1969, **24**, 18.

[21] H. Hoffman, *Pure Appl. Chem.*, 1975, **41**, 327.

[22] P. K. Chattopadhyay and B. Krotochvil, *Inorg. Chem.*, 1976, **15**, 3104.

[23] S. Funahashi and R. B. Jordan, *Inorg. Chem.*, 1977, **16**, 1301.

[24] V. Gutmann, 'Coordination Chemistry in Non-Aqueous Solutions,' Springer-Verlag, Wien, 1968, pp. 19—21.

[25] R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, 1971, **93**, 6014.

[26] L. L. Rusnak, E. S. Yang, and R. B. Jordan, *Inorg. Chem.*, 1978, **17**, 1810.

[27] J. F. Coetzee and C. G. Karakatsanis, *Inorg. Chem.*, 1976, **15**, 3112.

[28] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2191.

[29] P. Fischer, H. Hoffman, and G. Platz, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 1060.