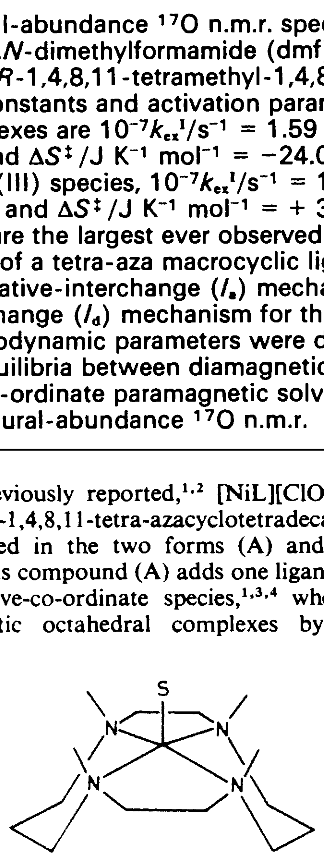
Equilibrium Studies and Kinetics of Solvent Exchange with Five- and Six-co-ordinate Mono- and Bis-(solvent)(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Perchlorate by Oxygen-17 Nuclear Magnetic Resonance Spectroscopy

Peter Moore,* John Sachinidis, and Gerald R. Willey
Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Natural-abundance ^{17}O n.m.r. spectroscopy at 54.24 MHz has been used to measure the rates of D_2O and *N,N*-dimethylformamide (dmf) exchange with $[NiLS_n]^{2+}$ ions (S = solvent: L = *R,S,R,S*- and *R,S,S,R*-1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane with n = 1 and 2 respectively). The rate constants and activation parameters for D_2O and dmf exchange with the five-co-ordinate *trans*-(I) complexes are $10^{-7}k_{ex}^{I}/s^{-1} = 1.59 \pm 0.11$ and 1.51 ± 0.08, $\Delta H^{\ddagger}/kJ\ mol^{-1} = 24.7 \pm 1.4$ and 30.1 ± 0.7, and $\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1} = -24.0 \pm 5.2$ and -6.4 ± 2.9 respectively; for the six-co-ordinate *trans*-(III) species, $10^{-7}k_{ex}^{I}/s^{-1} = 15.8 \pm 1.8$ and 32.8 ± 4.1, $\Delta H^{\ddagger}/kJ\ mol^{-1} = 37.4 \pm 2.4$ and 38.3 ± 1.4, and $\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1} = +37.6 \pm 9.0$ and $+46.7 \pm 5.6$ for D_2O and dmf respectively. These rates are the largest ever observed for solvent exchange at Ni^{2+}, and show the pronounced labilising effect of a tetra-aza macrocyclic ligand. The activation parameters are interpreted in terms of an associative-interchange (I_a) mechanism for the five-co-ordinate species, and a dissociative-interchange (I_d) mechanism for the six-co-ordinate complexes. Equilibrium constants and associated thermodynamic parameters were determined, either by spectrophotometry or by ^1H or ^{17}O n.m.r. shifts, for equilibria between diamagnetic four-co-ordinate $[NiL]^{2+}$ and the corresponding five- or six-co-ordinate paramagnetic solvates. The rate of dmf exchange with $[Ni(dmf)_6]^{2+}$ was redetermined by natural-abundance ^{17}O n.m.r.

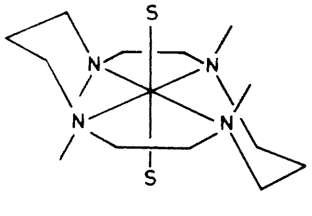
As previously reported,[1,2] $[NiL][ClO_4]_2$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) can readily be prepared in the two forms (A) and (B). In co-ordinating solvents compound (A) adds one ligand on axis to give a high-spin five-co-ordinate species,[1,3,4] whereas (B) forms paramagnetic octahedral complexes by adding two solvent molecules.[2,5] In weakly co-ordinating solvents such as water, *N,N*-dimethylformamide (dmf) or dimethyl sulphoxide (dmso), equilibrium (1) does not go to completion and both paramagnetic solvated and diamagnetic unsolvated species coexist in solution [4,5] (S = solvent molecule).



(A)

trans-(I)

S = solvent



(B)

trans-(III)

$$[NiL]^{2+} + nS \rightleftharpoons [NiLS_n]^{2+} \quad (1)$$

In a previous study [6] of acetonitrile exchange with the two isomers, an associative mechanism was proposed for solvent exchange with the five-co-ordinate complex, and a dissociative mechanism for the six-co-ordinate complex, on the basis of differences in activation parameters for the two systems. A large negative value of $\Delta S^{\ddagger}$ and a small value of $\Delta H^{\ddagger}$ was observed for the five-co-ordinate complex, and a positive value of $\Delta S^{\ddagger}$ and larger $\Delta H^{\ddagger}$ for the six-co-ordinate complex.

In this study we have attempted to confirm these results by extension to two other solvents, namely D_2O and dmf in acetone solution, using natural-abundance ^{17}O n.m.r. paramagnetic line broadening. The equilibrium constants and thermodynamic parameters for equilibria (1) have also been determined, either by spectrophotometry or by using ^1H n.m.r.[5] or ^{17}O n.m.r. paramagnetic shifts. We also report a redetermination of the rate of dmf exchange with $[Ni(dmf)_6]^{2+}$. Previous studies by ^1H n.m.r.[7,8] and continuous-wave (c.w.) ^{17}O n.m.r.[9] line broadening gave widely divergent values for the activation parameters. We have repeated the study by natural-abundance Fourier-transform (F.t.) ^{17}O n.m.r. spectroscopy.

The reactions were studied in mixed solvents (D_2O–acetone) primarily to extend to lower temperatures, since solvent-exchange rates are extremely rapid in these systems. Acetone was also used as an internal reference marker. In the study of dmf exchange with $[Ni(dmf)_6]^{2+}$ in mixed solvents Frankel [7] found that the activation parameters and exchange rates are independent of solvent composition in non-co-ordinating diluents.

Experimental

The two isomers of $[NiL][ClO_4]_2$ were prepared by standard methods,[1,2] recrystallised from nitromethane–diethyl ether, and dried *in vacuo* at 100 °C for several hours. Purity was checked by comparison of visible and ^1H n.m.r. spectra in dry nitromethane. The complex $[Ni(dmf)_6][ClO_4]_2$ was prepared following Drago's method,[10] recrystallised from acetone-ethanol, and dried *in vacuo*.

Solvents used were Analytical or spectroscopic grade and were stored over pre-dried 4A molecular sieves prior to use. Samples were prepared in a dry-box under a nitrogen atmosphere.

Visible Spectra.—Variable-temperature spectra were recorded in stoppered, thermostatted 1-cm cells with a Shimadzu UV-365 spectrophotometer. Temperatures were measured with a calibrated platinum-resistance thermometer inserted into the sample cell.

N.M.R. Spectra.—Variable-temperature 90-MHz ^{1}H n.m.r. spectra were recorded with a Bruker WH 90 Fourier-transform spectrometer equipped with a temperature-control unit. Oxygen-17 n.m.r. spectra at natural abundance were recorded with a Bruker WH 400 Fourier-transform spectrometer (at 54.24 MHz) equipped with a B-VT-1000 temperature-control unit. Full linewidths at half-height ($\Delta\nu_{\frac{1}{2}}$) were determined by an iterative least-squares Lorentzian lineshape-fitting procedure, and T_2 values calculated from the relationship $T_2 = 1/\pi\Delta\nu_{\frac{1}{2}}$. Chemical shifts were measured relative to the resonance of the internal standard [^{2}H$_6$]acetone, but are referenced to pure D_2O or dmf.

Computation.—A Hewlett-Packard 9845B desktop computer was used for the data analyses.[11]

Equilibrium Measurements.—(*a*) *By visible spectrophotometry.* For both isomers of $[NiL][ClO_4]_2$ in dmf–acetone the thermodynamic parameters for the paramagnetic–diamagnetic equilibria (1) were determined by conventional spectral methods. Absorbances (A) at a single wavelength as a function of temperature were fitted with equations (2) and (3) by a non-linear least-squares program;[11] $[Ni]_0$ is the total nickel-ion

$$A = \{K[Ni]_0(\varepsilon_p - \varepsilon_d)/(1 + K)\} + \varepsilon_d[Ni]_0 \qquad (2)$$

$$K = \exp(-\Delta H^{\ominus}/RT + \Delta S^{\ominus}/R) \qquad (3)$$

concentration, K is the ratio of the concentrations of paramagnetic and diamagnetic species, and ε_p and ε_d are the respective molar absorption coefficients. For the *trans*-(I) isomer data were analysed at eight temperatures in the range 285.5—349.8 K at 510 nm. For the *trans*-(III) isomer, eleven spectra were analysed at 500 nm from 283.7 to 351.7 K.

(*b*) *By* ^{1}H *n.m.r. shifts.* Equilibrium parameters were determined from the variable-temperature ^{1}H n.m.r. shifts of the three furthest downfield ligand (L) resonances as previously described.[5] The data were simultaneously fitted by non-linear least squares with equations (3)—(6); $\nu_{obs.}$ is the

$$\nu_{obs.} = \nu_p\alpha + \nu_d(1 - \alpha) \qquad (4)$$

$$K = \alpha/(1 - \alpha) \qquad (5)$$

$$\nu_p = C/T + \nu_d \qquad (6)$$

measured shift and ν_p and ν_d are the shifts of the paramagnetic and diamagnetic species respectively, C is the Curie constant, and α is the mole fraction of paramagnetic complex.

Kinetic Studies.—The ^{17}O n.m.r. linewidths and shifts were fitted with modified Swift–Connick equations (7)—(13);[11]

$$1/T_{2p} \equiv 1/T_2 - 1/T_{2A}{}^0 = \frac{P_m}{\tau_m} \cdot \frac{T_{2m}{}^{-2} + T_{2m}{}^{-1}\tau_m{}^{-1} + \Delta\omega_m{}^2}{(T_{2m}{}^{-1} + \tau_m{}^{-1})^2 + \Delta\omega_m{}^2} + \frac{P_m}{T_{2os}} \qquad (7)$$

$$1/T_{2m} = A_m \exp(E_m/RT) \qquad (8)$$

$$1/T_{2os} = A_{os} \exp(E_{os}/RT) \qquad (9)$$

$$\Delta\omega_m = B_1/T \qquad (10)$$

$$\Delta\omega = P_m\Delta\omega_m/[(\tau_m T_{2m}{}^{-1} + 1)^2 + \tau_m{}^2\Delta\omega_m{}^2] \qquad (11)$$

$$k_{ex}{}^{I} \equiv \tau_m{}^{-1} = (k_B T/h)\exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R) \qquad (12)$$

$$P_m = nK[Ni]_0/[S](1 + K) \qquad (13)$$

n is the number of bound solvent molecules, [S] is the solvent concentration, T_2 is the observed relaxation time, $T_{2A}{}^0$ is the relaxation time of the pure solvent, T_{2m} is the relaxation time of the bound solvent, T_{2os} is the outer-sphere contribution, τ_m is the residence time of a bound solvent molecule and is related to the pseudo-first-order rate constant for exchange of a single solvent molecule ($k_{ex}{}^{I}$), P_m is the mole fraction of bound solvent and is related to the equilibrium constant (K) whose temperature dependence is given by equation (3), $\Delta\omega$ is the observed chemical shift relative to that in the pure solvent, and $\Delta\omega_m$ is the chemical shift between free and bound solvent molecules in the absence of exchange and is assumed to have a normal $1/T$ temperature dependence. Data fitting was performed by a non-linear least-squares program with automatic weighting of each data set.[11] In all cases the values of E_m and E_{os} were fixed at 4 kJ mol^{-1}, since it was found that iterated values had large errors associated with them and that this had a minimal effect on the other parameters. Data were fitted as $\ln(1/T_{2p})$ and $\Delta\omega$ as functions of inverse temperature, taking $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, B_1, A_m, A_{os}, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$ as unknowns to be optimised as appropriate in each case.

Results and Discussion

Equilibrium Studies.—The results of equilibrium studies of $[NiL]^{2+}$ in D_2O and dmf by spectrophotometry or by ^{1}H n.m.r. shifts are summarised in Table 1. Also included are the corresponding values for the *trans*-(III) isomer (B) derived from fitting the ^{17}O n.m.r. T_{2p} and shift data alone. An attempt to derive equilibrium parameters from such a fit for the *trans*-(I) isomer (A) failed to converge to meaningful values. This is due to the greater proportion of paramagnetic species in these systems (*i.e.* K is larger) giving too small a deviation of the shift from simple Curie-law behaviour.

In fitting the data for the *trans*-(I) isomer (A) in dmf by the spectral method, the value of the molar absorption coefficient of the diamagnetic species, ε_d, was fixed at that obtained in dry nitromethane (190 dm^3 mol^{-1} cm^{-1}). Variation of this value between 180 and 200 dm^3 mol^{-1} cm^{-1} had no significant effect on the other parameters. For the *trans*-(III) isomer (B), ε_p was fixed at zero since iteration of this parameter converged at a small negative value. The iterated value of ε_d (68.2 ± 1.1 dm^3 mol^{-1} cm^{-1}) compares reasonably with the corresponding value in nitromethane (83 dm^3 mol^{-1} cm^{-1}).

The equilibrium constants and thermodynamic parameters in Table 1 derived by the different methods are in very good agreement and well within experimental error. For the *trans*-(III) isomer (B) in D_2O–acetone the results are also concordant with previous values obtained in neat D_2O by the ^{1}H n.m.r. shift method[5] ($K = 1.0$, $\Delta H^{\ominus} = -39.7 \pm 0.3$ kJ mol^{-1}, $\Delta S^{\ominus} = -133 \pm 1$ J K^{-1} mol^{-1}, and $[Ni]_0 = 0.0659$ mol dm^{-3}). The higher nickel concentration used there may account for the smaller K value since the equilibrium constant decreases with increasing ionic strength. Hence the added solvent diluent has minimal effect on the equilibrium.

Table 1. Results of equilibrium studies of $[NiL]^{2+}$ in D_2O [a] and dmf [b]

Compound	Solvent	$-\Delta H^{\ominus}$/ kJ mol^{-1}	$-\Delta S^{\ominus}$ [c]/ J K^{-1} mol^{-1}	K at [c]/ 298.2 K	$-\Delta S^{\ominus}$ [d]/ J K^{-1} mol^{-1}	K at 298.2 K [d]/ dm^3 mol^{-1}	$[Ni]_0$/ mol dm^{-3}	Method
trans-(I), (A)	D_2O	19.9 ± 1.0	46.0 ± 1.4	12.1	75.5 ± 3	0.349	0.0214	^1H N.m.r. [e]
	dmf	19.6 ± 1.3	40.9 ± 3.4	19.8	62.2 ± 5	1.53	0.009 15	Spectral [f]
	MeCN	16.8 ± 0.8	32.0 ± 2	18.7	56.5 ± 4	0.977	0.0016	Spectral [g]
trans-(III), (B)	D_2O	37.6 ± 0.8	111.7 ± 2.6	5.65	170.7 ± 4	0.004 70	0.0208	^1H N.m.r. [h]
	D_2O	37.9 ± 1.3	114.6 ± 4	4.50	173.6 ± 6	0.003 74	0.0204	^{17}O N.m.r.
	dmf	27.7 ± 0.4	83.7 ± 1.6	3.04	126.2 ± 2	0.0182	0.005 38	Spectral [i]
	dmf	29.3 ± 3.9	89.3 ± 12	2.95	131.8 ± 15	0.0177	0.005 30	^{17}O N.m.r.

[a] Measured in 50% (v/v) D_2O–[$^2H_6$]acetone. [b] Measured in 90% (v/v) dmf–[$^2H_6$]acetone. [c] Based on $K = [NiLS_n]/[NiL]\alpha_S^n$ where $\alpha_{D_2O} = 0.80$ and $\alpha_{dmf} = 0.90$, calculated from $\alpha_S = \gamma x_S$ where the activity coefficient, γ, is assumed to be unity and x_S is the mole fraction of solvent, S. [d] Based on a stoicheiometric equilibrium constant $K = [NiLS_n]/([NiL][S]^n)$ where $[D_2O] = 27.8$ mol dm^{-3} and [dmf] = 11.6 mo dm^{-3} in 50% D_2O and 90% dmf. [e] ν_d/Hz = −9 025, −2 635, and −1 722 and $10^{-6}C$/Hz K = 10.75, 3.305, and 2.448 for the three resonances used. [f] $\varepsilon_p = 8.6 \pm 1.1$ dm^3 mol^{-1} cm^{-1} at 510 nm. [g] Ref. 15. [h] ν_d/Hz = 1 552, 517, and 626 and $10^{-6}C$/Hz K = 6.13, 2.85, and 2.49 for the three resonances used. [i] $\varepsilon_d = 68.2 \pm 1.1$ dm^3 mol^{-1} cm^{-1} at 500 nm.

Table 2. Results of the solvent-exchange studies on various nickel(II) species; cyclam = 1,4,8,11-tetra-azacyclotetradecane

Complex	k_{ex}^1/s^{-1} at 298.2 K	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	Ref.
trans-(I)-$[NiL(D_2O)]^{2+}$	$(1.59 \pm 0.11) \times 10^7$	24.7 ± 1.4	−24.0 ± 5.2	This work [a]
trans-(I)-$[NiL(dmf)]^{2+}$	$(1.51 \pm 0.08) \times 10^7$	30.1 ± 0.7	−6.4 ± 2.9	This work [b]
trans-(I)-$[NiL(MeCN)]^{2+}$	$(0.56 \pm 0.04) \times 10^7$	20.3 ± 0.5	−47.8 ± 2.2	6
trans-(III)-$[NiL(D_2O)_2]^{2+}$	$(1.58 \pm 0.18) \times 10^8$	37.4 ± 2.4	37.6 ± 9.0	This work [c]
trans-(III)-$[NiL(dmf)_2]^{2+}$	$(3.28 \pm 0.41) \times 10^8$	38.3 ± 1.4	46.7 ± 5.6	This work [d]
trans-(III)-$[NiL(MeCN)_2]^{2+}$	$(0.15 \pm 0.02) \times 10^8$	41.5 ± 1.1	31.6 ± 4.7	6
trans-(III)-$[Ni(cyclam)(H_2O)_2]^{2+}$	$(0.21 \pm 0.07) \times 10^8$	40.1 ± 6.7	30.5 ± 2.9	12
$[Ni(H_2O)_6]^{2+}$	$(3.20 \pm 0.09) \times 10^4$	56.9 ± 0.8	32.0 ± 3.0	*e*
$[Ni(dmf)_6]^{2+}$	$(0.87 \pm 0.06) \times 10^4$	64.4 ± 2.9	46.4 ± 9.4	This work [f]
$[Ni(MeCN)_6]^{2+}$	$(0.28 \pm 0.01) \times 10^4$	64.3 ± 0.9	37 ± 3	*g*

[a] $[Ni]_0 = 0.0203$ mol dm^{-3}; $\Delta H^{\ominus} = -19.1 \pm 1.1$ kJ mol^{-1}; $\Delta S^{\ominus} = -50.7 \pm 4.2$ J K^{-1} mol^{-1}; $\nu_d = -2\,508 \pm 2\,440$ Hz; $10^{-6}C = 8.6 \pm 0.06$ Hz K; $10^{-8}B_1 = 2.096 \pm 0.039$ Hz K; and $A_m = 5\,617 \pm 1\,224$. [b] $[Ni]_0 = 0.004\,38$ mol dm^{-3}; $\Delta H^{\ominus} = -19.9 \pm 1.2$ kJ mol^{-1}; $\Delta S^{\ominus} = -42.3 \pm 3.1$ J K^{-1} mol^{-1}; $\varepsilon_p = 8.8 \pm 0.9$ dm^3 mol^{-1} cm^{-1}; $10^{-8}B_1 = 2.06 \pm 0.04$ Hz K; and $10^{-4}A_m = 2.22 \pm 0.43$. [c] $[Ni]_0 = 0.020\,44$ mol dm^{-3}; $\Delta H^{\ominus} = -41.4 \pm 1.0$ kJ mol^{-1}; $\Delta S^{\ominus} = -127.4 \pm 3.4$ J K^{-1} mol^{-1}; $\nu_d = 2\,934 \pm 302$ Hz; $10^{-6}C = 6.08 \pm 0.02$ Hz K; $10^{-8}B_1 = 2.19 \pm 0.2$ Hz K; $10^{-4}A_m = 6.97 \pm 0.29$. [d] $[Ni]_0 = 0.005\,30$ mol dm^{-3}; $\Delta H^{\ominus} = -27.8 \pm 0.3$ kJ mol^{-1}; $\Delta S^{\ominus} = -85.9 \pm 1.2$ J K^{-1} mol^{-1}; $\varepsilon_d = 67.8 \pm 0.9$ dm^3 mol^{-1} cm^{-1}; $10^{-8}B_1 = 2.01 \pm 0.02$ Hz K; $10^{-4}A_m = 4.67 \pm 0.22$. [e] Y. Ducommon, W. L. Earl, and A. E. Merbach, *Inorg. Chem.*, 1979, **18**, 2754. [f] $[Ni]_0 = 0.005\,56$—0.0642 mol dm^{-3}; $10^{-7}B_1 = 2.18 \pm 0.38$ Hz K; $A_{os} = 304 \pm 27$. [g] K. E. Newman, F. K. Meyer, and A. E. Merbach, *J. Am. Chem. Soc.*, 1979, **101**, 1470.

Comparison of $\Delta S^{\ominus}$ values shows that those for the *trans*-(III) isomer (B) are approximately twice those for the *trans*-(I) isomer (A). This is consistent with the addition of two and one solvent molecules respectively.

The value of $\Delta H^{\ominus}$ is also significantly more negative for the addition of two solvent molecules compared with one, and for the *trans*-(III) complex water is seen to be a somewhat stronger donor than dmf judging by the more negative $\Delta H^{\ominus}$ values. In the *trans*-(I) complexes the nickel sits above the plane of the four N atoms thereby relieving the steric interactions between the four adjacent N–Me groups. In this case, slight movement of the Ni atom in and out of the macrocycle cavity of the *trans*-(I) species could account for very similar $\Delta H^{\ominus}$ values observed for D_2O, dmf, and MeCN.

Kinetic Studies.—In order to fit the kinetic data the equilibrium parameters are required. Hence the ^{17}O n.m.r. line-broadening and shift data, and the corresponding equilibrium data for each system, were fitted simultaneously, with automatic weighting of each data set as described.[11] The results in Table 2 are from such fits. Also included are values for acetonitrile exchange with $[NiL]^{2+}$ and more recent values for solvent exchange on the relevant hexasolvated nickel(II) species for comparison.

Representative simultaneous fits of the linewidths, chemical shift and spectrophotometric data for the *trans*-(III) isomer in dmf are shown in Figures 1, 2, and 3 respectively. The eight parameters used in these fits are summarised in Table 2. Due to the limited temperature range of the solvents, and the very fast exchange rates, most of the data are in the 'fast-exchange' region of the Swift–Connick curves where the $\tau_m\Delta\omega_m^2$ and T_{2m} terms dominate. Clearly, reliable kinetic information can be extracted if $\Delta\omega_m$ and T_{2m} are well defined and if the equilibrium parameters can be derived independently. In all four systems all parameters are reasonably well defined as evidenced by their small errors. The A_m value for the *trans*-(I) isomer in D_2O is ill defined and setting it to zero had no significant effect on the other parameters.

For the *trans*-(III) isomer in both D_2O and dmf the ^{17}O n.m.r. T_{2p} and shift data alone were fitted with the Swift–Connick equations allowing the equilibrium thermodynamic parameters $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ to vary. The iterated values of all parameters by this method were in very good agreement with the previous estimates, although the errors were larger (see Table 1). Hence we believe the simultaneous fit of all the data sets is a more valid approach.

For $[Ni(dmf)_6]^{2+}$ in dmf the relaxation data are in the 'slow-exchange' region with a significant contribution from the outer-sphere term T_{2os} (Figure 4). The results in Table 2 are from a fit by the full Swift–Connick equations with A_m fixed at zero. The measured shift data were not sufficiently accurate to include in the fit; however they did agree reasonably with the calculated shifts. If the data in the 'outer-sphere' region are left out and only the linear portion of the curve fitted, signifi-

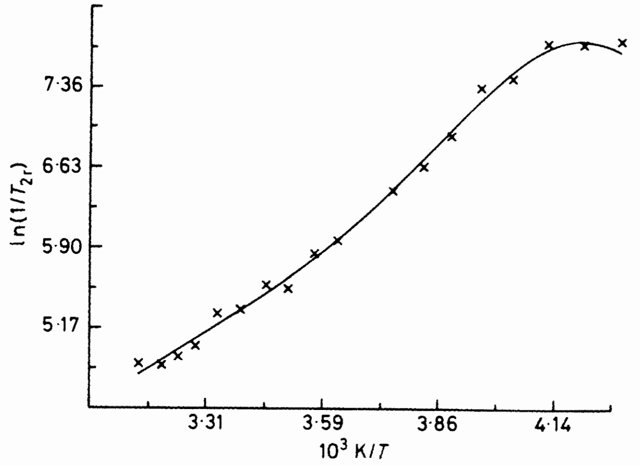


Figure 1. Plot of $\ln(1/T_{2r})$ ^{17}O n.m.r. data *versus* inverse temperature (crosses) for *trans*-(III)-[NiL(dmf)$_2$]$^{2+}$ in dmf–acetone (90% v/v). The continuous curve shows the computer fit (the data in Figures 1—3 were fitted simultaneously)

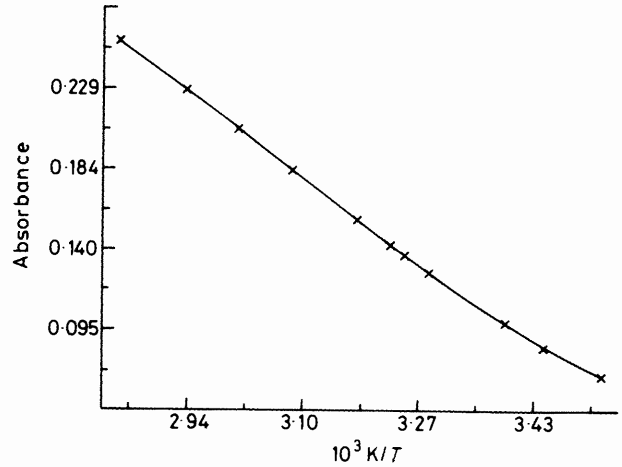


Figure 3. Plot of the observed absorbance at 500 nm (1-cm cell) *versus* inverse temperature (crosses) for *trans*-(III)-[NiL]$^{2+}$ (5.38×10^{-3} mol dm^{-3}) in dmf–acetone (90% v/v). The continuous curve shows the computer fit

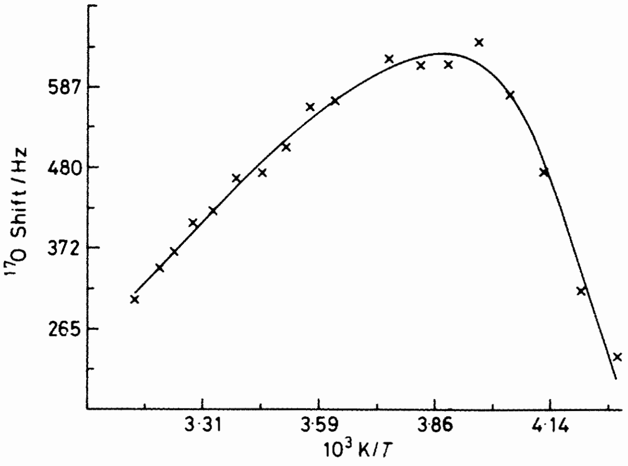


Figure 2. Plot of the observed ^{17}O n.m.r. shifts ($P_m = 9.12 \times 10^{-4}$) *versus* inverse temperature (crosses) for *trans*-(III)-[NiL(dmf)$_2$]$^{2+}$ in dmf–acetone (90% v/v). The continuous curve shows the computer fit

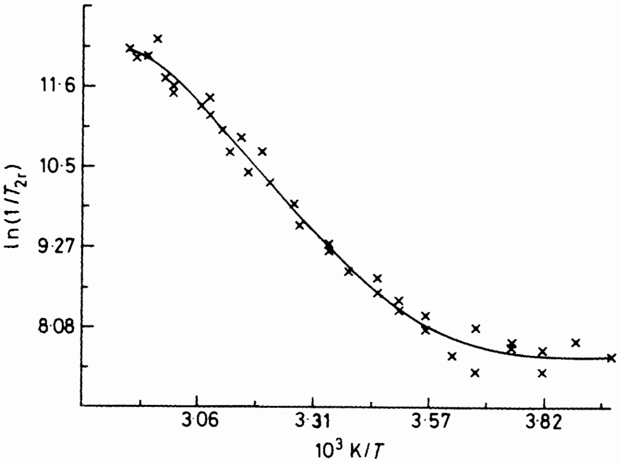


Figure 4. Plot of $\ln(1/T_{2r})$ ^{17}O n.m.r. data *versus* inverse temperature (crosses) for [Ni(dmf)$_6$]$^{2+}$ in dmf–acetone (90% v/v). The continuous curve shows the computer fit

cantly lower values of the activation parameters are obtained, although the rate constant does not change very much. Previous reports of this system (Table 3) gave divergent values for the activation parameters probably because the data were not computer fitted with the full Swift–Connick equations. The fact that the values of $k_{ex}{}^1$ are in good agreement indicate that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are strongly correlated and accurate fitting is required to resolve them.

As can be seen from Table 2, co-ordination of L to nickel(II) increases the rates of solvent exchange, compared with the hexakis(solvates), by factors of 10^3—10^4. Similar rate enhancements by N-donor ligands have been reported previously;[6,12-14] the rate constant observed here (3×10^8 s^{-1}) for dmf exchange with the six-co-ordinate *trans*-(III) isomer (B) is the largest value to date for solvent exchange at nickel(II). The use of natural-abundance ^{17}O n.m.r. to measure such large rate constants for ligand exchange is of obvious advantage in this type of study.

The remarkable accelerating effect of L on nickel(II) solvent-exchange rates arises primarily from a reduction in the enthalpies of activation by *ca.* 15—26 kJ mol^{-1} for the six-co-ordinate *trans*-(III) complexes, and by *ca.* 28—44 kJ mol^{-1} for the five-co-ordinate *trans*-(I) species. Significantly the values of $\Delta H^\ddagger$ are the lowest for the five-co-ordinate complexes, and it is manifest that for these species all of the values of $\Delta S^\ddagger$ are negative. In contrast the six-co-ordinate complexes undergo solvent exchange with positive $\Delta S^\ddagger$ values, and the values of $\Delta H^\ddagger$ are larger than for the five-co-ordinate species. We believe that the markedly different activation parameters for these five- and six-co-ordinate complexes signify different mechanisms for solvent exchange. Previously we interpreted this difference in terms of a dissociative mechanism for the six-co-ordinate complexes, and an associative mechanism for the five-co-ordinate species. However, it has recently been shown that $\Delta V^\ddagger$ for acetonitrile exchange with *trans*-(I)-[NiL(MeCN)]$^{2+}$ is $+2.3 \pm 1.3$ cm^3 mol^{-1} and the authors argue for a dissociative *D* mechanism.[15] This conclusion is reached because there would be a significant contraction in the Ni–N bond lengths, and hence a contraction in volume, on forming the diamagnetic square-planar [NiL]$^{2+}$. This volume contraction would offset the more positive $\Delta V^\ddagger$ ex-

Table 3. Results for dmf exchange with $[Ni(dmf)_6]^{2+}$

$10^{-3}k_{ex}{}^{1}/s^{-1}$ at 298.2 K	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	N.m.r. method	Region fitted	Ref.
7.7	39.3 ± 2	−37.6 ± 8	c.w. ^{17}O	τ_m	9, *a*
3.8	62.7 ± 2	33.4 ± 8	^1H	Complete	8, *a*
6.9	58.5	25	^1H	τ_m and T_{2os}	7, *a*
6.5	54.3	12.5	^1H	τ_m and T_{2os}	7, *b*
8.7 ± 0.6	64.4 ± 2.9	46.3 ± 9.4	F.t. ^{17}O	τ_m and T_{2os}	This work, *c*
11.7	52.9 ± 1.7	10.3 ± 5.7	F.t. ^{17}O	τ_m only	This work, *c*

[a] In neat dmf. [b] 1.84 mol dm^{-3} dmf in CD_3NO_2 (14.3% v/v). [c] 90% (v/v) dmf–[$^2H_6$]acetone.

pected for loss of MeCN in a *D* mechanism, and lead to the observed small, positive $\Delta V^‡$. If a spin-state change does not occur in the transition state, then the small positive $\Delta V^‡$ observed for $[NiL(MeCN)]^{2+}$ is no proof of mechanism. In fact, for the analogous *trans*-(I)-$[CoL(MeCN)]^{2+}$, $\Delta V^‡ = -9.6 \pm 0.5$ cm^3 mol^{-1} as expected for an I_a mechanism,[15] and since $\Delta S^‡ = -71$ and -48 J K^{-1} mol^{-1} for the cobalt(II) and nickel(II) complexes respectively, it seems very unlikely that these two species undergo solvent exchange with totally different mechanisms. It could be argued that since equilibrium (1) ($n = 1$) is known to exist for good donor solvents, a *D* mechanism must be possible for the *trans*-(I) complexes. However, this does *not* preclude the associative pathway if this has a lower free energy of activation. It is known that *trans*-(I)-$[NiL]^{2-}$ forms the six-co-ordinate $[NiL(NCS)_2]$ with thiocyanate ion,[1] and although no bis-solvates of the *trans*-(I)-isomer have been detected, this does not rule out their existence in trace amounts, since they would have relatively low absorption coefficients and be difficult to detect spectrally. Even if they are unfavoured thermodynamically their existence in the transition state cannot be ruled out, and the low $\Delta H^‡$ and negative $\Delta S^‡$ values point to an associative pathway for solvent exchange. If a *D* mechanism were in operation for the *trans*-(I)-$[NiL]^{2+}$ solvates, then the transition state would closely resemble the products, and the values of $\Delta H^‡$ and $\Delta S^‡$ involved in such a process would be similar in magnitude but opposite in sign to those associated with the equilibrium data (Table 1). For example, complete loss of one acetonitrile molecule from the *trans*-(I) isomer would involve enthalpy and entropy changes close to *ca.* +17 kJ mol^{-1} and +56 J K^{-1} mol^{-1}, compared with observed activation parameters of *ca.* −20 kJ mol^{-1} and −48 J K^{-1} mol^{-1}. In contrast, for complete loss of one D_2O molecule from the six-co-ordinate *trans*-(III) isomer, $\Delta H^\ominus = 19$ kJ mol^{-1} and $\Delta S^\ominus = +85$ J K^{-1} mol^{-1} compared with observed activation parameters of +37 kJ mol^{-1} and +38 J K^{-1} mol^{-1}. In both cases, therefore, it seems very unlikely that a *D* mechanism operates, and our interpretation in terms of I_a and I_d mechanisms for the five- and six-co-ordinate species is more likely.

The small positive $\Delta V^‡$ value found for the five-co-ordinate acetonitrile complex can be explained by an interchange mechanism in which no spin-state change occurs. The changeover point for an I_a or I_d mechanism has been arbitrarily chosen as 0 cm^3 mol^{-1} for a hypothetical reaction involving spherical molecules. However, for non-aqueous solvent exchange with irregularly shaped molecules, especially where conformational changes may be involved, assignment of mechanism on this basis alone must be treated with caution. In previous studies we showed that *trans*-(I)-$[MLX]^+$ ions (M = Zn, X = Cl or NCS; M = Ni, X = Cl) are fluxional and undergo a low-energy conformational change between approximately trigonal-bipyramidal and square-pyramidal geometries.[16,17] Dynamic folding of the macrocycle could effect the $\Delta V^‡$ values, and should not be overlooked in this case.

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