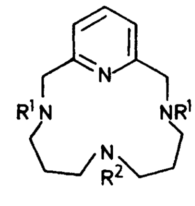
Variable-temperature and -pressure Proton Nuclear Magnetic Resonance Studies of the Rates and Mechanisms of *N,N*-Dimethylformamide and Acetonitrile Exchange with the Square-pyramidal Complexes Mono(solvento)-{3,7,11-tribenzyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene}nickel(II)

Lee Fielding and Peter Moore *
Department of Chemistry, University of Warwick, Coventry CV4 7AL

Rates and activation parameters have been determined for solvent (solv) exchange with square-pyramidal complexes $[Ni(L^1)(solv)]^{2+}$ [L^1 is the pyridine-containing tetra-aza macrocycle, 3,7,11-tribenzyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene; solv = *N,N*-dimethylformamide or acetonitrile] using variable-temperature and -pressure ^1H n.m.r. spectroscopy. At 298.2 K, $10^{-2}k_{ex}/s^{-1} = 32.7 \pm 1.9$ and 3.82 ± 0.29, $\Delta H^{\ddagger}/kJ\ mol^{-1} = 36.3 \pm 1.1$ and 68.9 ± 3.8, $\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1} = -55.8 \pm 3.3$ and $+35.6 \pm 12.3$, and at 323 K, $\Delta V^{\ddagger}/cm^3\ mol^{-1} = +10.6 \pm 0.8$ and -3.5 ± 0.9 for solv = *N,N*-dimethylformamide and acetonitrile respectively. The mechanistic significance of these data is discussed.

Recently we isolated the tetra-aza macrocycle L^1, and its five-co-ordinate complexes $[M(L^1)(solv)]^{2+}$ (M = Ni or Zn; solv = dimethyl sulphoxide, dmso).[1] The nickel(II) complex is very similar to those of the related macrocycles L^2 and L^3, and is assumed to have the same uncommon square-pyramidal geometry [Figure 1, (**A**)] found in the crystal structures of $[Ni(L^2)Cl]^+$ and $[Ni(L^3)X]^{n+}$ ($X = Cl^-$, $n = 1$; X = dmso or H_2O, $n = 2$).[2,3] In this unusual geometry, the unidentate ligand (X or solv) is in the basal plane of the square pyramid, and in a *trans* position to the pyridine N atom. The same folded ligand conformation has also been found recently in a related six-co-ordinate complex, *cis*-$[Ir(L^4)Cl(H)][PF_6]$.[4]

Previous studies have shown how tetra-aza macrocycles,[5,6] and other amine ligands,[7,8] can have a pronounced labilising effect upon nickel(II) solvates. For example, in complexes of the type $[Ni(L)(solv)_n]^{2+}$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, tmc; n = 1 or 2; solv = *N,N*-dimethylformamide, acetonitrile, or water) the strong in-plane ligand field from the four macrocyclic N atoms markedly labilises the axially bound solvent molecules in five- and six-co-ordinate complexes of types (**B**) and (**C**) (Figure 1).[5,6] Since the nickel(II) complex of L^1 has a strong affinity for a single solvent molecule (a square-planar unsolvated complex could not be isolated[1]), and because the geometry of this five-co-ordinate complex [Figure 1, (**A**)] is very different to that studied previously, we have investigated the lability of the unique solvent site in $[Ni(L^1)(solv)]^{2+}$ (solv = *N,N*-dimethylformamide and acetonitrile) for comparison with previous results.[5,6] Attempts to study the analogous, but less hindered, complexes of L^3 were thwarted by isomerisation reactions involving Me–N inversions, to give mixtures of isomers described peviously.[2] The benzyl-substituted macrocyclic complexes were not observed to isomerise in this way.



L^1 $R^1 = R^2 = CH_2Ph$
L^2 $R^1 = CH_2Ph, R^2 = H$
L^3 $R^1 = R^2 = Me$
L^4 $R^1 = H, R^2 = Me$

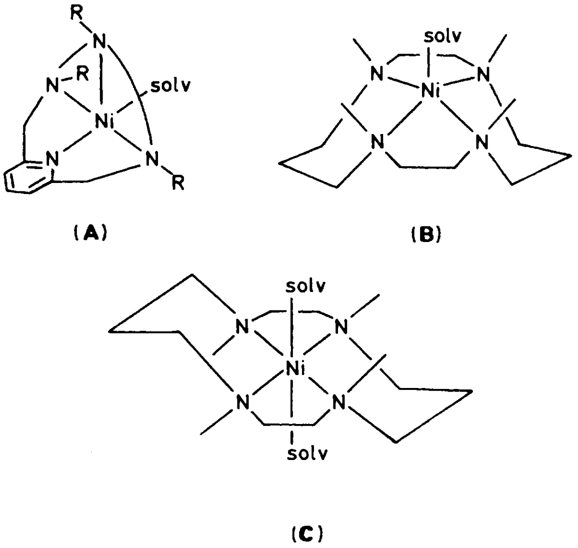


Figure 1. Structures of (**A**) $[Ni(L^1)(solv)]^{2+}$ ($R = CH_2Ph$), (**B**) *trans*-I-$[Ni(tmc)(solv)]^{2+}$, and (**C**) *trans*-III-$[Ni(tmc)(solv)_2]^{2+}$

Experimental

Materials and Methods.—The complex $[Ni(L^1)(dmso)][ClO_4]_2$ was the sample isolated previously.[1] The solvents *N,N*-dimethylformamide (dmf) and acetonitrile (MeCN) were freshly distilled, and dried over 4A molecular sieves. Solutions for ^1H n.m.r. investigation were prepared by dissolving a weighed amount of the dimethyl sulphoxide complex in the appropriate amount of weighed solvent (dmf or MeCN), and the mole fraction of bound solvent molecules (P_m) calculated assuming a solvation number of one.[1] Exchange of dmso by dmf or MeCN is complete under these conditions as shown by the visible spectra (Table 1). A small amount of $SiMe_4$ was added

Table 1. Visible spectra of $[Ni(L^1)(solv)]^{2+}$ ions (molar absorption coefficients in parentheses)

Solvent (solv)	dmso[a]	dmf[b]	MeCN[c]
$\lambda_{max.}$/nm	580 (61)	610 (47)	575 (51)
$\lambda_{max.}$/nm	756 (39)	805 (32)	740 (33)

[a] In nitromethane solution, ref. 1. [b] In dmf. [c] In MeCN.

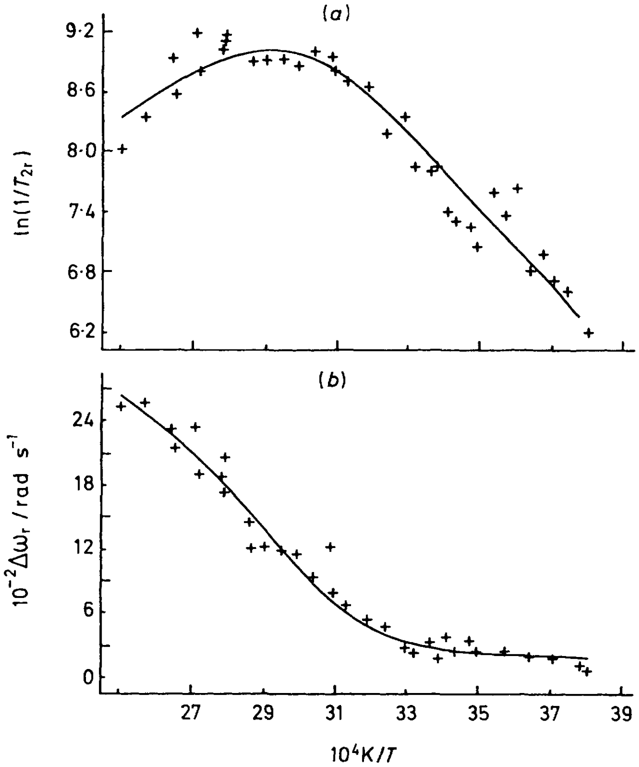


Figure 2. Variation of (*a*) $\ln(T_{2r}^{-1})$ and (*b*) 10^{-2} $\Delta\omega_r$/rad s^{-1} with 10^4 K/*T* for $[Ni(L^1)(dmf)]^{2+}$ ion. Crosses represent observed points, and the continuous curves are those calculated by non-linear least-squares analysis using equations (3)—(8)

Table 2. Parameters determined for the exchange of solvents (solv) with $[Ni(L^1)(solv)]^{2+}$ ions, from T_{2r} and $\Delta\omega_r$ data determined as a function of temperature and pressure and fitted by equations (3)—(10) (errors quoted are the standard deviations)

Solvent	MeCN[a]	dmf[b]
10^{-2} k_{ex}/s^{-1}	3.82 ± 0.29	32.7 ± 1.9
$\Delta H^‡$/kJ mol^{-1}	68.9 ± 3.8	36.3 ± 1.1
$\Delta S^‡$/J K^{-1} mol^{-1}	+35.6 ± 12.3	−55.8 ± 3.3
$\Delta V^‡$/cm^3 mol^{-1}	−3.5 ± 0.9 (323 K) −4.9 ± 0.7 (329 K)	+11.8 ± 1.1 (304 K) +10.6 ± 0.8 (323 K)
10^{-3} B_0/Hz	−9.50 ± 0.83	11.81 ± 0.54
10^{-6} B_1/Hz K	2.98 ± 0.29	−3.12 ± 0.19

[a] A_m/s^{-1} = 1 000; E_m/J mol^{-1} = 4 000; A_{os}/s^{-1} = 0; corr/rad s^{-1} = 179 ± 69. [b] A_m/s^{-1} = 630; E_m/J mol^{-1} = 500; A_{os} = 1.1; corr/rad s^{-1} = 1 900.

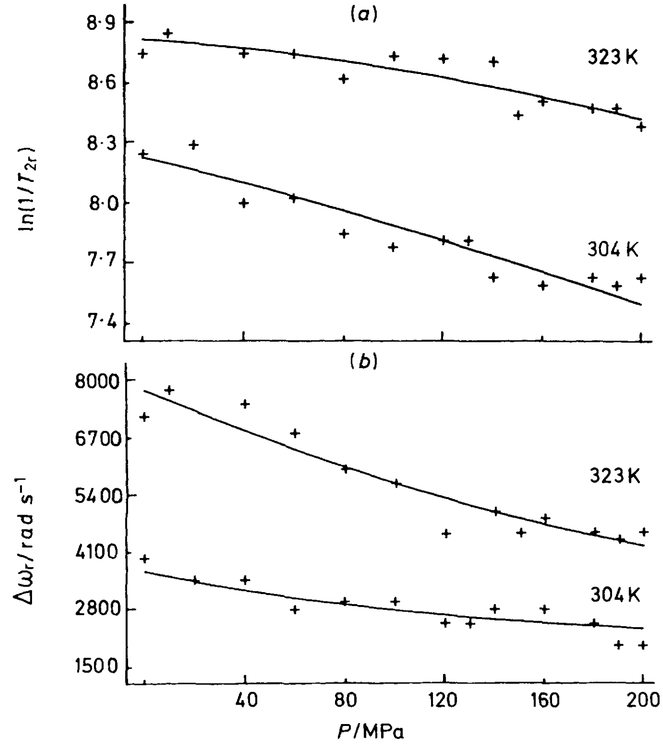


Figure 3. Variation of (*a*) $\ln(T_{2r}^{-1})$ and (*b*) $\Delta\omega_r$/rad s^{-1} with pressure/MPa for $[Ni(L^1)(dmf)]^{2+}$ ion. Crosses represent the observed points and the continuous curves are those calculated by non-linear least-squares analysis using equations (3)—(10)

to each solution as an internal shift marker, and as a measure of field inhomogeneity. Proton n.m.r. spectra were recorded with a Bruker WH90 Fourier-transform spectrometer fitted with a temperature-control unit (±0.2 K). Shifts and linewidths were measured for the formyl proton of dmf, and the methyl proton of MeCN, referenced to those of the corresponding neat solvents. Digitised Fourier-transformed data from the WH90 were downloaded to an IBM PC-AT microcomputer, and linewidths calculated by non-linear least-squares fitting of these data to the equation for a Lorentzian curve.[9] Values of T_{2r}^{-1} and $\Delta\omega_r$ were calculated from equations (1) and (2), and in variable-temperature experiments were fitted to the modified Swift–Connick equations (3)—(8), with suitable weighting of the linewidth and shift data as described in our previous studies (definitions of terms are as previously described[5,10]). In variable-pressure experiments, equation (5) was replaced by equations (9) and (10).[9] For studies in *N*,*N*-dimethylformamide,

$$T_{2r}^{-1} = \pi(\nu_{\frac{1}{2}}^{obs.} - \nu_{\frac{1}{2}}^{0})/P_m \quad (1)$$

$$\Delta\omega_r = 2\pi(\omega^{obs.} - \omega^0)/P_m \quad (2)$$

$$T_{2r}^{-1} = [T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2]/\tau_m[(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2] + T_{2os}^{-1} \quad (3)$$

$$\Delta\omega_r = \Delta\omega_m/[(\tau_m/T_{2m} + 1)^2 + \tau_m^2\Delta\omega_m^2] + \text{corr} \quad (4)$$

$$\tau_m^{-1} = (kT/h)\exp(\Delta S^‡/R)\exp(-\Delta H^‡/RT) \quad (5)$$

$$T_{2m}^{-1} = A_m \exp(E_m/RT) \quad (6)$$

$$T_{2os}^{-1} = A_{os} \exp(E_{os}/RT) \quad (7)$$

$$\Delta\omega_m = 2\pi(B_0 + B_1/T) \quad (8)$$

$$\tau_m^{-1} = \exp[\ln(k_0) - (\Delta V^‡/RT)P + (\Delta\beta^‡/2RT)P^2] \quad (9)$$

$$\ln(k_0) = \ln(kT/h) + \Delta S^‡/R - \Delta H^‡/RT \quad (10)$$

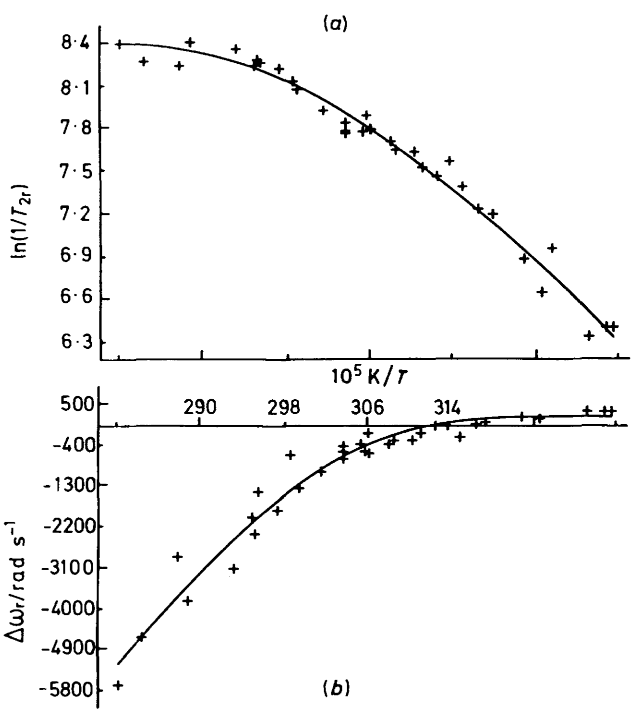


Figure 4. Variation of (a) ln (T_{2r}^{-1}) and (b) $\Delta\omega_r$(rad s^{-1}) with 10^5 K/T for $[Ni(L^1)(MeCN)]^{2+}$ ion. Details as in Figure 2

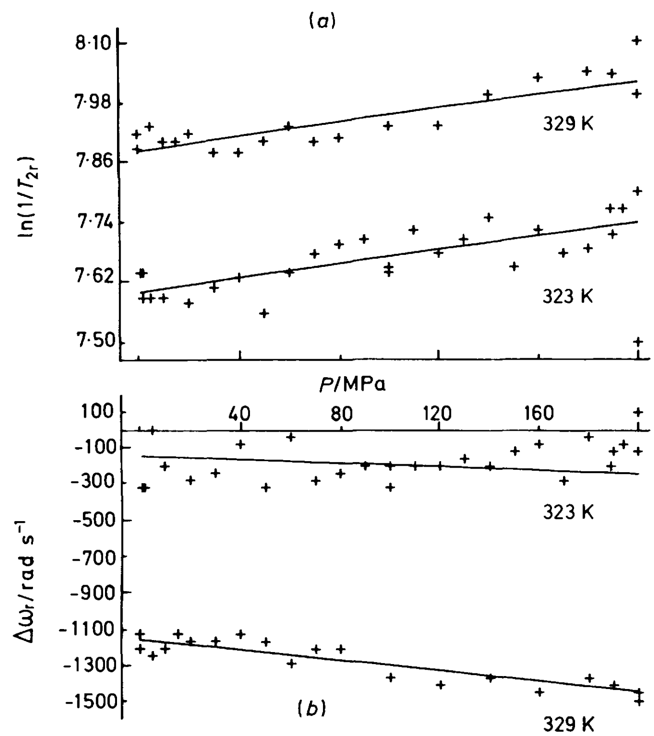


Figure 5. Variation of (a) ln (T_{2r}^{-1}) and (b) $\Delta\omega_r$ with pressure/MPa for $[Ni(L^1)(MeCN)]^{2+}$ ion. Details as in Figure 3

values of the entropy of activation ($\Delta S^‡$), and enthalpy of activation ($\Delta H^‡$), were obtained from the variable-temperature studies along with the parameters B_0 and B_1. In initial fits of the data, only $\Delta H^‡$, $\Delta S^‡$, B_0, and B_1 were refined, using estimated values of the other parameters. Once reasonable values had been found for these four parameters, they were held constant to determine better estimates for the parameters A_m, E_m, A_{os}, and E_{os}. A final refinement of $\Delta H^‡$, $\Delta S^‡$, B_0, and B_1 was then carried out with the best estimates of the other four parameters. There were insufficient data, and the available data were not of sufficiently good quality, to refine all eight parameters simultaneously. In variable-pressure studies at a fixed temperature the parameters obtained from the variable-temperature studies were held constant to obtain the volume of activation, $\Delta V^‡$, from the pressure dependence of T_{2r} and $\Delta\omega_r$. It was found necessary to allow the temperature to be refined as one of the unknown parameters to obtain the most accurate fit to the observed pressure data. The estimated temperature was within 2—3 K of the measured value. The term involving $\Delta\beta^‡$ in equation (9) was found to be negligible within experimental error, and was set to zero in the refinement of the variable-pressure data.

For studies in *N*,*N*-dimethylformamide, a P_m of 0.003 81 was used, with measurements taken at 46 temperatures over the range 223 to 399 K. Most of the data are in the slow-exchange region of the Swift–Connick curve as shown in Figure 2. Variable-pressure studies were carried out at 10- or 20-MPa intervals over the range 0.1 to 200.0 MPa, using a high-pressure probe for a Bruker WH90 built to the design of Merbach and co-workers.[11] Measurements were made at 323 and 304 K and the results are summarised in Figure 3 and Table 2.

Variable-temperature studies in acetonitrile were carried out at P_m values of 0.007 84 and 0.0156 at 33 temperatures over the range 303 to 354 K. All of the data are in the slow-exchange region of the Swift–Connick curve, up to the boiling point of the solvent. Data were also recorded at temperatures down to 250 K, but at the P_m used negligible line broadening was observed below 303 K, so the low-temperature data were excluded from the data analysis. Data were fitted with $A_{os} = 0$, and with estimated values of A_m and E_m (Table 2). Variable-pressure studies were carried out at $P_m = 0.0156$ and at 323 and 329 K. At 329 K, both the linewidths and shifts are pressure dependent, whereas at 323 K only the linewidths are pressure sensitive. The results from the variable-temperature and -pressure experiments are in Table 2. The fits of these data by equations (3)—(10) are shown in Figures 4 and 5 respectively.

Results and Discussion

In Table 3 a comparison is made between the activation parameters for *N*,*N*-dimethylformamide and acetonitrile exchange with $[Ni(solv)_6]^{2+}$ and $[Ni(L)(solv)_n]^{2+}$ ions [solv = solvent; L = L^1, $n = 1$; L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, tmc, n = 1 or 2; and L = L′ = the quinquedentate Schiff-base ligand derived from 2 mol of pyridine-2-carbaldehyde and bis(3-aminopropyl)-amine, n = 1]. At 298 K the rate constants for the exchange of acetonitrile and *N*,*N*-dimethylformamide with their corresponding hexakis(solvates) of Ni^{2+} are 2.8×10^3 and 8.7×10^3 s^{-1} respectively. These values are reduced to 382 and 3.3×10^3 s^{-1} respectively in the five-co-ordinate square-pyramidal complexes studied here [Figure 1, (A)], in marked contrast to the behaviour found in $[Ni(tmc)(solv)_n]^{2+}$ and $[Ni(L')(solv)]^{2+}$ where the rate constants are increased by factors of 10^2 to 10^5. The unusual geometry of $[Ni(L^1)(solv)]^{2+}$ ions must account for their relatively low rates of solvent exchange. In $[Ni(L^1)(solv)]^{2+}$ the solvent molecule is in the basal plane of the square pyramid, in a *trans* position to the pyridine N atom, whereas in the five-co-ordinate $[Ni(tmc)(solv)]^{2+}$ the solvent molecule is axial with the Ni^{2+} ion sitting above the basal plane formed by the four macrocyclic N atoms. The latter geometry, with a strong σ donation from the four

Table 3. Comparison of activation parameters at 298.2 K (unless specified) for *N,N*-dimethylformamide (dmf) and acetonitrile (MeCN) exchange with five- and six-co-ordinate complexes of nickel(II)

Complex	$\Delta G^\ddagger$/kJ mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta V^\ddagger$/cm^3 mol^{-1}
$[Ni(dmf)_6]^{2+}$	50.6 ± 5.7	64.4 ± 2.9	+46 ± 9	+9.1 ± 0.3[a]
$[Ni(MeCN)_6]^{2+}$	53.3 ± 1.8	64.3 ± 0.9	+37 ± 3	+9.6 ± 0.4[b]
$[Ni(L^1)(dmf)]^{2+}$	53.0 ± 0.2	36.3 ± 1.1	−56 ± 4	+10.6 ± 0.8[c]
$[Ni(L^1)(MeCN)]^{2+}$	58.3 ± 0.2	68.9 ± 3.8	+36 ± 12	−3.5 ± 0.9[c]
$[Ni(tmc)(dmf)]^{2+}$	32.0 ± 1.1	20.3 ± 0.5	−48 ± 2	*d*
$[Ni(tmc)(MeCN)]^{2+}$	34.6 ± 1.1	20.3 ± 0.5	−48 ± 2	+2.3 ± 1.3[e]
$[Ni(tmc)(dmf)_2]^{2+}$	24.4 ± 3.1	38.3 ± 1.4	+47 ± 6	*d*
$[Ni(tmc)(MeCN)_2]^{2+}$	32.1 ± 2.5	41.5 ± 1.1	+32 ± 5	*d*
$[Ni(L')(dmf)]^{2+}$	42.0	49.0	+23	*f*
$[Ni(L')(MeCN)]^{2+}$	36.1	49.0	+10	*f*

[a] At 294 K; F. K. Meyer, K. E. Newman, and A. E. Merbach, *Inorg. Chem.*, 1979, **18**, 2142. [b] At 297 K; K. E. Newman, F. K. Meyer, and A. E. Merbach, *J. Am. Chem. Soc.*, 1979, **101**, 1470. [c] At 323 K; this work. [d] Ref. 5. [e] Average of values at 242.7 K ($\Delta V^\ddagger$ = +1.15 cm^3 mol^{-1}) and 262.2 K ($\Delta V^\ddagger$ = 3.4 cm^3 mol^{-1}); ref. 6. [f] Ref. 8.

in-plane N atoms, results in a marked weakening of the axial nickel–solvent bond, as shown by the much lower enthalpies and free energies of activation. It appears that in $[Ni(L^1)(MeCN)]^{2+}$ the acetonitrile molecule is bonded somewhat more strongly than in $[Ni(MeCN)_6]^{2+}$, as shown by the slightly larger enthalpy and free energy of activation for solvent exchange. However, this is not the case in $[Ni(L^1)(dmf)]^{2+}$, where the enthalpy of activation is significantly smaller than the value found for $[Ni(dmf)_6]^{2+}$. The free energy of activation for solvent exchange with $[Ni(L^1)(dmf)]^{2+}$ is still slightly larger than the value found in $[Ni(dmf)_6]^{2+}$ due to the large negative entropy of activation. Steric effects are undoubtedly more important for solvent exchange with bulky dmf molecules compared with the rod-like MeCN, and in $[Ni(L^1)(dmf)]^{2+}$ where the solvent co-ordination site is crowded by the three N-benzyl groups, it is likely that steric effects contribute to the observed low enthalpy and negative entropy of activation. Attempts were made to study $[Ni(L^1)(dmtf)]^{2+}$ (dmtf = *N,N*-dimethylthioformamide), but with this bulkier solvent steric hindrance prevents the formation of the complex, even in neat dmtf. Collision theory predicts that a rate constant, *k*, for a sterically hindered reaction can be quite small because of a low probability factor (*P* factor) in the collision theory equation $k = PZe^{-E/RT}$ (Z = collision frequency). The low *PZ* factor will manifest itself in a negative entropy of activation as observed here. In a study of dmf exchange with another sterically hindered five-co-ordinate complex, $[Cu\{N(CH_2CH_2NMe_2)_3\}(dmf)]^{2+}$, a large negative entropy of activation was observed ($\Delta S^\ddagger = -47$ J K^{-1} mol^{-1}), but an associative mechanism was ruled out by the positive volume of activation ($\Delta V^\ddagger = +7.4$ cm^3 mol^{-1}).[12]

To gain a better insight into the mechanisms for solvent exchange, the volumes of activation were determined (Table 3). For $[Ni(L^1)(dmf)]^{2+}$ the value of $\Delta V^\ddagger$ is very similar to that reported for dmf exchange with $[Ni(dmf)_6]^{2+}$, and a dissociative, I_d or D mechanism is indicated. In contrast, for $[Ni(L^1)(MeCN)]^{2+}$, $\Delta V^\ddagger$ is -3.5 cm^3 mol^{-1} in line with an associative interchange (I_a) mechanism. For the smaller, rod-like, acetonitrile a *cis*-octahedral transition state {analogous to that observed in *cis*-$[Ir(L^4)Cl(H)]^+$}[4] is more easily achieved than with the bulkier *N,N*-dimethylformamide molecules. In a previous study of five-co-ordinate $[M(tmc)(MeCN)]^{2+}$ ions, $\Delta V^\ddagger$ was found to be $+2.3$ cm^3 mol^{-1} for M = Ni and -9.6 cm^3 mol^{-1} for M = Co, and it was postulated that a dissociative (D) mechanism applies to the former complex and an associative (I_a) mechanism for the latter.[6] The conclusion that $[Ni(tmc)(MeCN)]^{2+}$ undergoes solvent exchange with an extreme D mechanism is based on the postulate that a spin-state change occurs in forming a diamagnetic square-planar intermediate, which would result in a contraction in volume of the complex due to the shortening of the Ni–N bond lengths, and a consequent reduction in the volume of activation to the value observed.[6] However, this argument does not explain why the analogous cobalt(II) complex behaves so differently, and neglects any outer-sphere desolvation which can be expected to occur if a *cis*-octahedral transition state is involved in an associative process. Recent *ab initio* and Monte-Carlo calculations have shown that large numbers of solvent molecules are associated with the macrocycle in tetra-aza macrocyclic complexes,[13] and these cannot be overlooked if there are large macrocyclic conformational changes involved during solvent exchange. If $[Ni(tmc)(MeCN)]^{2+}$ were to undergo solvent exchange by an associative mechanism, formation of *cis*-$[Ni(tmc)(MeCN)_2]^{2+}$ in the transition state would require the macrocycle to fold, with probable desolvation of the complex and a small positive volume of activation as observed. In $[Ni(L^1)(MeCN)]^{2+}$, where the macrocycle is *already folded*, such conformational changes are minimised in forming a *cis*-octahedral transition state, leading to the observed small negative volume of activation.

We conclude that in $[Ni(L^1)(solv)]^{2+}$ ions, because the co-ordinated solvent molecule is in a relatively crowded position, flanked by the three bulky benzyl groups, the rates of solvent exchange are significantly reduced in comparison with other aminenickel(II) complexes, and associative solvent exchange is only possible with small molecules like acetonitrile.

Acknowledgements

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