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Five Coordinate Tetramethylcyclam Complexes of Co(II) and Ni(II); Associative Interchange and Dissociative Mechanisms for Solvent Exchange in Acetonitrile

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Variable temperature and pressure ^{13}C NMR measurements have been used to study the kinetics of solvent exchange of the five coordinate complexes of Co(II) and Ni(II) with 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane in acetonitrile. While the activation volume value of -9.6 ± 0.5 ml mol^{-1} supports the proposal of an associative interchange, I_a, mechanism for the Co(II) system, the value of $+2.3 \pm 1.3$ ml mol^{-1} for the Ni(II) system suggests a dissociative, D, mechanism.

UV–visible spectral measurements of the Ni(II) complex in acetonitrile over a range of temperatures are consistent with the presence of an equilibrium involving the five coordinate and a square planar form of the complex. It is proposed that the solvent exchange on the five coordinate Ni(II) complex takes place via this four coordinate species.

Introduction

Complexes of the quadridentate ligands 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tetramethylcyclam, TMC) have been of interest for a number of reasons. There have been a number of studies concerned with the kinetic and thermodynamic aspects of the complexation of metal ions by such ligands, which have concentrated on the differences in behaviour between cyclic ligands and comparable linear polydentate ligands [1, 2]. The ligands have been shown to have the ability to stabilise metal ions in unusual oxidation states [3]. Complexes may form which are involved in spin state equilibria and associated coordination number changes in a number of solvents [4, 5].

A number of geometries and conformations have been observed or proposed for complexes of TMC with metal ions. It has been shown [6] that the complex formed by the direct reaction of TMC with metal ions in solution has a structure in which the four methyl groups are on the same side of the complex. For Ni(II)–TMC complexes of this type in a number of solvents an equilibrium exists between a diamagnetic square planar complex and a paramagnetic pentacoordinate species [4, 5]. The evidence suggests that the five coordinate species in solution has a fluxional trigonal bipyramidal structure [4, 7]; crystallographic studies on a number of complexes precipitated from solution have shown the species to be square pyramidal with a unidentate ligand in the axial position [7]. Where there are substantial proportions of the four and five coordinate species in solution, such as in water, the solvent is apparently easily removed and the isolated solid is the diamagnetic square planar species [6].

Barefield [8] has shown that the TMC complex in which the ligand adopts the more thermodynamically stable conformation, where the four methyl groups are arranged with two on each side of the ligand plane, can only be formed by direct methylation of the previously formed cyclam complex. In suitable solvents, the octahedral Ni(II)–TMC complex based on this conformation, with solvent in the two axial positions, may also be involved in a spin state equilibrium with the diamagnetic square planar species [4].

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In two recent publications, Moore [9, 10] reported studies on the kinetics and mechanism of solvent exchange on the octahedral Ni(II)–TMC complex in acetonitrile and the five coordinate TMC complexes of Co(II) and Ni(II) in acetonitrile [10]. It was reported [4] that in the reaction with the 'rod like' solvent molecule, CH_3CN, the five coordinate complex was entirely in the pentacoordinate form so that no complications due to spin state equilibria needed to be considered. On the basis of the dramatic difference in activation entropy, Moore proposed that while the mechanism for acetonitrile exchange was a dissociative interchange for the six coordinate Ni(II) ion, it was an associative interchange for the five coordinate Ni(II) and Co(II) cases. It was also noted [10] for the five coordinate complexes that while the solvent lability for the Ni(II) species was around 10^3 times that of the hexasolvated metal ion, complexation by the quadridentate macrocycle only increased the solvent exchange rate by less than a factor of two for the Co(II) case.

High-pressure kinetic studies leading to the measurement of the volume of activation have proved extremely useful in understanding the details of the reaction mechanism [11]. This has been especially so for solvent exchange processes [12], where there is not the complication of electrostrictive effects which arise in reactions involving ions. We have therefore set out to measure the temperature and pressure dependent kinetics of acetonitrile solvent exchange on the five coordinate Ni(II) and Co(II) complexes of TMC. Although there have now been a large number of studies of ligand substitution reactions of square planar and octahedral complexes, much less is known about the mechanism of reaction for five coordinate species. No activation volume studies have been reported for such systems, and it was hoped that such measurements would be of value in understanding the detailed mechanism of these reactions.

Experimental

Acetonitrile (Fluka, puriss) was refluxed over CaH_2 for two hours, then distilled. Dioxan (Fluka, pura) was shaken with $CaCl_2$ and distilled. Both solvents were stored over 4A molecular sieves (Merck). 99% enriched $CH_3\text{-}^{13}CN$ (Stohler Isotope Chemicals) contained around 20% water; this was eliminated by two successive distillations from CaH_2 on a vacuum line immediately prior to solution preparation. This enriched solvent was added to normal dry acetonitrile to a level which enabled high pressure spectra, which use a small capillary sample, to be accumulated in an acceptable time. All sample solutions were prepared in a glove box under dry nitrogen.

$Co(CH_3CN)_6(ClO_4)_2$ was prepared from the hexaaquo salt using the method described by van Leeuwen [13]. $Co(TMC)CH_3CN(ClO_4)_2$ was prepared by direct reaction of the ligand (Strem Chemicals) with a solution of $Co(CH_3CN)_6(ClO_4)_2$ in dry acetonitrile. Purple crystals of the compound were precipitated with ether, then recrystallised from dry acetonitrile, and dried on a vacuum line for 1 hour. Elemental analyses confirmed the composition of the compound as $Co(TMC)CH_3CN(ClO_4)_2$ (Calculated: Co 10.61%, C 34.61%, H 6.35%, N 12.61%, Cl 12.77%. Found: Co 10.52%, C 33.79%, H 6.61%, N 12.27%, Cl 12.19%). UV–visible spectra show bands at 445 nm (ϵ = 53 cm^{-1}), 525 nm (ϵ = 39 cm^{-1}), and 670 (ϵ = 16 cm^{-1}) which is analogous with those reported by Kaden [5] for $Co(TMC)(ClO_4)_2$ in a number of solvents, where the complex is proposed to be five coordinate.

For the temperature dependent kinetic study of the solvent exchange reaction on this complex, solutions of $Co(TMC)CH_3CN(ClO_4)_2$ were prepared in dry acetonitrile containing 9% dry dioxan as a linewidth and frequency shift reference: P_m was 1.88×10^{-3}. ^{13}C spectra were obtained on a Bruker WP60 spectrometer equipped with a multinuclear probe tuned to 15.08 MHz, using broad-band decoupling and an external ^{19}F lock. The shift of the broadened bulk solvent nitrile carbon was measured using the spectrometer cursor; the linewidths of the solvent nitrile peak and the dioxan signal, which was used to correct the data for field inhomogeneity and to determine the excess exchange broadening, were evaluated by computer-fitting a Lorenzian function to the stored data.

Solutions for the pressure dependent kinetic study of the Co(II) system were prepared in acetonitrile with around 70% ^{13}C enrichment; P_m was 1.74×10^{-3}. Spectra were run on a Bruker WP60 spectrometer fitted with a special high pressure probe head [14]; the system was operated with an external ^{19}F lock, with broad band decoupling.

The direct reaction between $Ni(CH_3CN)_6^{2+}$ and TMC in acetonitrile is complicated and is the topic of a further study. The five coordinate Ni(II) system was studied by preparing the unsolvated $Ni(TMC)(ClO_4)_2$ by the reported method [6] and dissolving in dry acetonitrile. Microanalysis and UV–visible spectra in dry nitromethane, water, and acetonitrile were in agreement with those reported in the literature [4–6].

From the results of Moore on the Ni(II) system [10], it is clear that a higher field, and consequently greater shift than is provided by the WP-60 spectrometer, would extend the region of broadening dominated directly by the rate constant for solvent exchange within the accessible temperature range of the solvent. Therefore, temperature- and pressure-dependent ^{13}C spectra were obtained on a

Bruker CXP-200 spectrometer operating at 50.31 MHz. For the pressure dependent spectra a special probe head, described previously for ^{1}H spectra [17] but used for the first time here for ^{13}C work was fitted. The magnetic field was sufficiently stable that no lock was used; broad band decoupling was employed for the temperature-dependent study but not for the pressure dependence. The acetonitrile solvent for these experiments had a ^{13}C enrichment of 7%; 0.01% ^{13}C benzene was used as a shift and linewidth reference; P_m for all Ni(II) runs was 1.92×10^{-3}.

For all pressure dependent spectra 28.1 Hz due to the linewidth of pure proton coupled solvent ($^{2}J_{CH} \simeq 7$ Hz) was subtracted from the measured linewidth to obtain the excess broadening due to chemical exchange [14]. Temperature measurements were carried out using a Pt resistance thermometer placed inside the bomb for variable pressure work [15], and with a substitution technique for variable temperature work [16].

UV-visible spectra were recorded on a Perkin Elmer 340 spectrophotometer in 10 mm cells with an integral thermostat jacket.

Data Treatment

Functions describing the effects of solvent exchange on the linewidth and chemical shift of the bulk solvent peak were similar to those presented previously [14]:

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left\{\frac{1}{T_2} - \frac{1}{T_2^0}\right\}$$

$$= \frac{1}{\tau_m}\left\{\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2}\right\} + \frac{1}{T_{2os}} \qquad (1)$$

$$\Delta\omega_r' = \Delta\omega'/P_m = \frac{\Delta\omega_m}{(\tau_m/T_{2m}^2 + 1)^2 + \tau_m^2\Delta\omega_m^2} + \frac{\Delta\omega_{ref}}{P_m} \qquad (2)$$

T_2 is the observed relaxation time, T_2^0 is the relaxation time of pure solvent, and P_m is the mol fraction of coordinated solvent; τ_m is the chemical relaxation time for exchange of solvent in the first coordination sphere of the metal ion, T_{2m} is the transverse relaxation time of bound solvent in the absence of chemical exchange, $\Delta\omega_m$ is the chemical shift between coordinated and free solvent, and $1/T_{2os}$ is the contribution to the relaxation rate of solvent in the outer coordination sphere. $\Delta\omega'$ is the observed shift with respect to the reference peak, which, in the case of the Co(II) system is dioxan, and for the Ni(II) system is benzene; $\Delta\omega_{ref}$ is the shift of the reference peak with respect to the pure solvent.

There is no evidence in any of the data here of an effect due to T_{2os}, and this term was set to zero.

The temperature dependence of τ_m will be given by equation (3), where k_{ex} is the rate constant, ΔH^* is the activation enthalpy, and ΔS^* is the activation entropy for solvent exchange:

$$\tau_m^{-1} = k_{ex} = \frac{kT}{h} \cdot \exp(-\Delta H^*/RT)\cdot\exp(\Delta S^*/R) \qquad (3)$$

As in the study of the acetonitrile exchange on $Co(CH_3CN)_6^{2+}$ [14], the temperature dependence of $\Delta\omega_m$ in the Co(II)/(TMC) system was adequately described by Bloembergen's equation to give $\Delta\omega_m = 18.44\ (A/h)/T$, where A/h is the scalar coupling constant; for the Ni(II)/(TMC) system, as was found for the solvent exchange on $Ni(CH_3CN)_6^{2+}$ [18], it was necessary to include a quadratic term to give $\Delta\omega_m = A'/T + B'/T^2$.

At higher temperatures, the curvature observed in the plots of $\ln(T_{2r}^{-1})$ *vs.* 1000/T for both the Co(II)/(TMC) and Ni(II)/(TMC) systems seems to indicate a contribution of T_{2m} to the relaxation rate; an initial treatment of the data included this term. However, rough estimates can be made of the value of T_{2m} for ^{13}C nitrile coordinated to a Co(II) or Ni(II) centre; these, together with comparable data, are given in Table I. The fitted values of the term attributed to T_{2m} are far too high to be reasonable. While there is no question that the curvature at high temperatures is real, we must conclude that this is due to other factors operating in the systems at these temperatures. For the analysis of the results reported in the next section, the data at temperatures above which this curvature is important were removed, and the terms containing T_{2m}^{-1} set to zero, so that Equation (1) becomes:

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m}\left\{\frac{\Delta\omega_m^2}{\tau_m^{-2} + \Delta\omega_m^2}\right\} \qquad (4)$$

All experimental data was analysed using a general-purpose non-linear least squares fitting program, ITERAT [19], in which the user defined required function, together with the required unknown parameters, were separately set up in an easily modified subroutine. Sets of data for different functions involving the same unknown parameters could be simultaneously fitted if desired. Reported errors are standard deviations.

The linewidth data, $\ln(T_{2r}^{-1})$ *vs.* 1000/T, and shift data, $\Delta\omega_m'$ vs. 1000/T, were simultaneously fitted to give the least squares best fit values of the parameters ΔH^*, ΔS^*, A (or A′ and B′), and $\Delta\omega_{ref}$. We note that Moore [8, 9] has not reported data above these temperatures and has ignored any contribution due to T_{2m} in his temperature dependent kinetic study of these systems. It should be noted that our reasons for neglecting this contribution are based entirely on the apparently unrealistic values of T_{2m}.

TABLE I. Estimates of T_{2m} for Coordinated Solvent.

System	A_m (s^{-1})	E_m (kJ mol^{-1})	$1/T_{2m}$ (298 K) (s^{-1})	Reference
$CH_3CN/Co(TMC)(CH_3CN)^{2+}$	657	12420	98800	a
$CH_3CN/Co(TMC)(CH_3CN)^{2+}$	–	–	1500	b
$CH_3CN/Co(CH_3CN)_6^{2+}$	38	3400	150	c
$CH_3CN/Ni(TMC)(CH_3CN)^{2+}$	326	12000	41400	a
$CH_3CN/Ni(TMC)(CH_3CN)^{2+}$	–	–	1300	b
$CH_3CN/Ni(CH_3CN)_6^{2+}$	103	4100	540	d

[a] This work, using the full linewidth expression. [b] Rough estimates taking into account dipolar and scalar relaxation contributions (see ref. e for equations). The correlation time τ_2 was assumed as 1 ps (ref. f) and the relaxation time T_{2e} was taken as 1 ps for both Co^{2+} and Ni^{2+} (ref. g). [c] F. K. Meyer, K. E. Newman and A. E. Merbach, *Inorg. Chem., 18,* 2142 (1979). [d] K. E. Newman, F. K. Meyer and A. E. Merbach, *J. Am. Chem. Soc., 101,* 1470 (1979). [e] A. R. Monnerat, K. E. Newman and A. E. Merbach, *Mol. Phys., 45,* 373 (1982). [f] H. G. Hertz, 'Progress in NMR Spectroscopy', *3,* 159 (1967). [g] Y. Ducommun, K. E. Newman and A. E. Merbach, *Inorg. Chem., 19,* 3696 (1980).

If the T_{2m} terms are included in the fitting functions, the kinetic parameters derived for the solvent exchange processes for both the Co(II) and Ni(II) systems studied, while slightly different, would not affect any mechanistic argument about the exchange process.

The pressure dependence of the solvent exchange rate constant at a temperature T will be given by:

$$k_{ex(P,T)} = \tau_m^{-1} = k_{ex(O,T)} \cdot \exp(-\Delta V^*/RT) \qquad (5)$$

where $k_{ex(O,T)}$ refers to the exchange constant at 1 atm and temperature T, and ΔV^* is the volume of activation. Equations (4) and (5) can therefore be combined to describe the pressure dependence of the observed linewidth. In other systems [14], $\Delta\omega_m$ has been shown to be pressure independent; that independence was assumed for all the studies reported here, and in addition two of the three series of experiments were made in the slow exchange region where the rate constants are practically independent of $\Delta\omega_m$.

For the exchange of acetonitrile on the Ni(II)/TMC complex system in acetonitrile, the non-linear least squares fitting procedure was used to optimise $k_{ex(O,T)}$ and ΔV^* so as to best describe the pressure dependence of the observed linewidth.

The sample for high pressure spectra for the Co(II)/(TMC) system was prepared in a capillary which had a total volume around 0.25 ml. Solubility of the compound made it necessary for these samples to be prepared directly by weight, involving milligram quantities of solid with a number of dry box transfers preceding the final solution preparation, rather than dilution of a concentrated stock solution. Because of the uncertainty in the final concentration using this procedure, a factor relating the assumed P_m and true P_m was included as a variable parameter in the fitting function, and was implicit in T_{2r} for these experiments. For these calculations, the rate constant $k_{ex(O,T)}$ was calculated using the activation parameters from the temperature dependent study and held as a fixed parameter, and ΔV^* and the concentration correction factor determined from the pressure dependence of the observed linewidth.

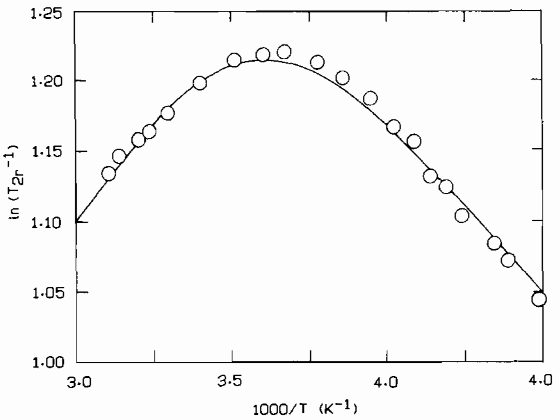

Fig. 1. Variable temperature ^{13}C NMR (15.08 MHz) for the nitrile resonance of $Co(TMC)(CH_3CN)(ClO_4)_2$ in acetonitrile. Solvent transverse relaxation rates, $\ln(T_{2r}^{-1})$, *vs.* 1000/T (K^{-1}).

Results and Discussion

Experimental data obtained for the temperature-dependent study of the Co(II)/TMC system, and for all other data presented as figures in this work, are available from the authors. For reasons given in the

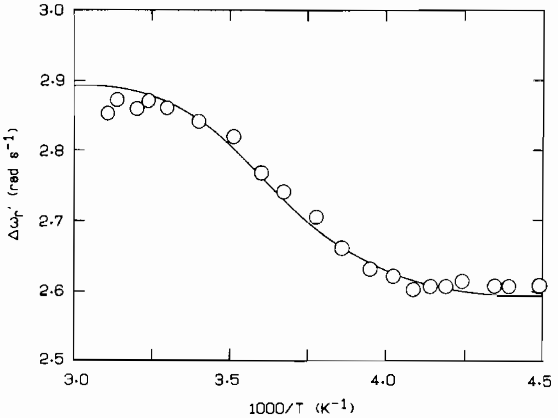

Fig. 2. Variable temperature ^{13}C NMR (15.08 MHz) for the nitrile resonance of $Co(TMC)(CH_3CN)(ClO_4)_2$ in acetonitrile. Solvent chemical shifts, $\Delta\omega_r'$ (rad s^{-1}), *vs.* 1000/T (K^{-1}).

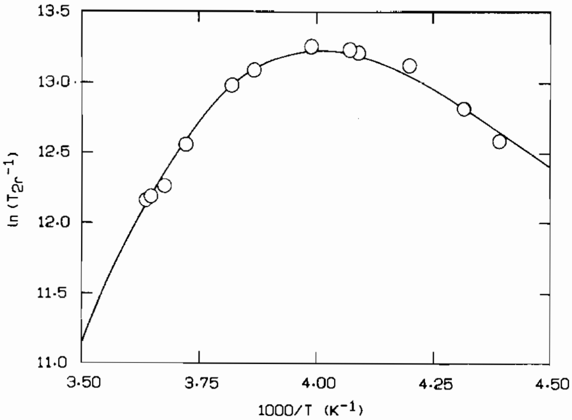

Fig. 4. Variable temperature ^{13}C NMR (50.31 MHz) for the nitrile resonance of $Ni(TMC)(ClO_4)_2$ in acetonitrile. Solvent transverse relaxation rates, ln(T_{2r}^{-1}), *vs.* 1000/T (K^{-1}).

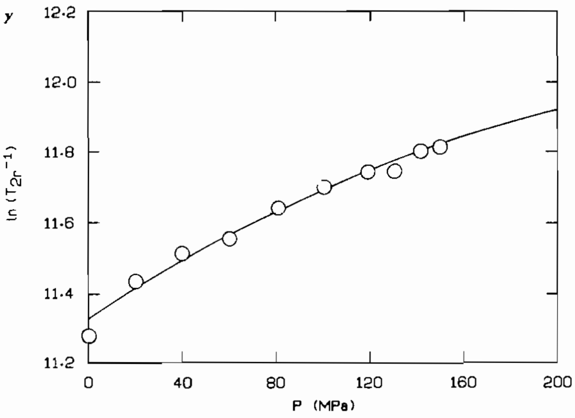

Fig. 3. Variable pressure ^{13}C NMR (15.08 MHz) for the nitrile resonance of $Co(TMC)(CH_3CN)(ClO_4)_2$ in acetonitrile at 248.6 K. Solvent transverse relaxation rates, ln(T_{2r}^{-1}) *vs.* P (MPa).

preceding section it appeared necessary to restrict the analysis of the data to temperatures below 333 K and to neglect any contribution of T_{2m} to the broadening. The data for ln(T_{2r}^{-1}) and $\Delta\omega_r'$ *vs.* 1000/T and the simultaneously-fitted functions for each are shown in Figs. 1 and 2. This fit to the data gives k_{ex} = (6.4 ± 0.2) X 10^5 s^{-1} at 298 K, and activation parameters ΔH^* = 18.7 ± 0.4 kJ mol^{-1} and ΔS^* = −71 ± 2 J K^{-1} mol^{-1}.

These results are in excellent agreement with the values of (5.6 ± 0.5) X 10^5 s^{-1}, 19.5 ± 0.8 kJ mol^{-1}, and −70 ± 4 J K^{-1} mol^{-1} obtained by Moore [9] using a similar temperature limit for treatment of the data. The other parameters obtained from the data treatment are the coupling constant, A, and the limiting shift $\Delta\omega_{ref}$; the fitted values were 5.66 ± 0.1 MHz and 4889 rad s^{-1}. While there are no strictly analogous reports for comparison, these values do compare reasonably with the values measured for the similar $Co(CH_3CN)_6^{2+}/CH_3CN$ system [14].

Data for the pressure dependent linebroadening measurements on the Co(II)/(TMC) system are shown together with the fitted function in Fig. 3. For this analysis of the data the rate constant for exchange at 1 atmosphere is 1.19 X 10^5 s^{-1}, calculated from the activation parameters obtained from the temperature dependent measurements, and is held fixed. The two least squares fitted parameters are the correction factor for P_m, and the activation volume.

The correction factor for P_m was calculated as 0.92, which we consider to be a reasonable value given the difficulties of sample preparation. The activation volume for the exchange of an acetonitrile molecule was calculated to be −9.6 ± 0.5 ml mol^{-1}. This, especially when taken together with the highly negative activation entropy for the exchange, strongly supports the suggestion [9] of an associative interchange process for the exchange.

Acetonitrile exchange on the hexasolvated Co(II) ion in acetonitrile occurs with ΔV^* of +7.7 ml mol^{-1} [14]; acetonitrile exchange on the hexasolvated Ni(II) occurs with ΔV^* of +9.6 ml mol^{-1} [18]. Both these values, and that reported for the Co(II)/TMC complex in the present study are small in magnitude compared to the molar volume of acetonitrile, 51.3 ml mol^{-1}, but the clear inference is for an interchange of dissociative character for the solvated Co(II) and Ni(II) ions, and one of associative character for the tetramethylcyclam complex. Activation volume studies have not been reported for any other 5-coordinate substitution processes, but it seems reasonable to propose that the more open access to the metal centre compared to the octahedral case makes possible the involvement of the incoming ligand in the interchange reaction and a reduction

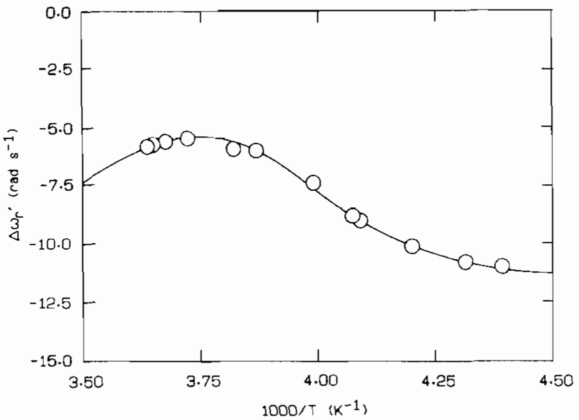

Fig. 5. Variable temperature ^{13}C NMR (50.31 MHz) for the nitrile resonance of $Ni(TMC)(ClO_4)_2$ in acetonitrile. Solvent chemical shifts, $\Delta\omega_r'$ (rad s^{-1}), *vs.* 1000/T (K^{-1}).

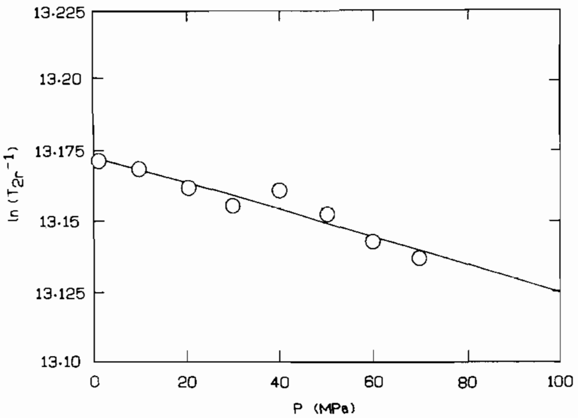

Fig. 6. Variable pressure ^{13}C NMR (50.31 MHz) for the nitrile resonance of $Ni(TMC)(ClO_4)_2$ in acetonitrile at 242.7 K. Solvent transverse relaxation rates, $\ln(T_{2r}^{-1})$, *vs.* P (MPa).

in the volume of the system in going from the reactant ground state to transition state for exchange.

A temperature dependent study of the solvent exchange in the Ni/TMC system was carried out. Again, neglecting any contribution of the T_{2m} term to the broadening, and now restricting the data to temperatures below 278 K, plots of $\ln(T_{2r}^{-1})$ and $\Delta\omega_r'$ *vs.* 1000/T and the fitted functions for each are given in Figs. 4 and 5. The simultaneous fit of the linewidth and shift functions to the data gives k_{ex} = $(4.0 \pm 0.2) \times 10^6$ s^{-1} at 298 K, with activation parameters ΔH^* = 18.1 ± 0.5 kJ mol^{-1}, and ΔS^* = -58 ± 2 J K^{-1} mol^{-1}. These kinetic results are again in good agreement with Moore's results of 5.6×10^6 s^{-1}, 20.3 kJ mol^{-1}, and -49 J K^{-1} mol^{-1} respectively. The fitted shift parameters A', B', and $\Delta\omega_{ref}$ have values of $-(6.4 \pm 0.6) \times 10^8$ K s^{-1}, $(2.3 \pm 0.2) \times 10^{11}$ K^2 s^{-1}, and -2281 ± 19 rad s^{-1}.

Two sets of experiments were carried to measure the pressure dependence of the linewidth, and determine the activation volume for this system. While at temperatures below 235 K the description of linewidth is dominated by the τ_m^{-1} term, and reflects changes in k_{ex} directly at temperatures above this, the linewidth is affected by changes in both τ_m (or k_{ex}^{-1}) and $\Delta\omega_m$. Although for those systems where it has been measured [14], it appears that $\Delta\omega_m$ is not pressure dependent, the experiment at lower temperatures is obviously preferred. Despite its simple interpretation however, data in the lower temperature range was restricted by the fact that the solution froze as pressure was applied. Experiments were carried out at 242.7 K and 262.2 K; even at 242.7 K the solution froze at pressures above 70 MPa. For both sets of data allowance was made for the contributions of both τ_m and $\Delta\omega_m$ to T_{2r}.

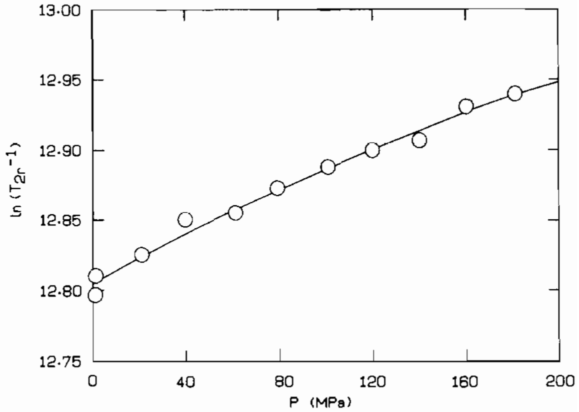

Fig. 7. Variable pressure ^{13}C NMR (50.31 MHz) for the nitrile resonace of $Ni(TMC)(ClO_4)_2$ in acetonitrile at 262.2 K. Solvent transverse relaxation rates, $\ln(T_{2r}^{-1})$, *vs.* P (MPa).

In the treatment of this data, where the sample was prepared on a larger scale than for the Co(II)/TMC high pressure experiments, P_m was assumed to be accurate and the fitting function had two variable parameters, $k_{ex(O,T)}$ and ΔV^*. The experimental data and the least squares fitted functions are shown in Figs. 6 and 7. The activation volumes for solvent exchange are calculated to be $+1.15 \pm 0.13$ ml mol^{-1} and $+3.42 \pm 0.15$ mol mol^{-1} at 242.7 K and 262.2 K. The reported computed standard deviation should be increased to 1–2 ml mol^{-1} to include possible effects due to non-random errors. The calculated exchange rate constants at 1 bar are $(6.25 \pm 0.02) \times 10^5$ s^{-1} and $(1.71 \pm 0.01) \times 10^6$ s^{-1}, which compare quite satisfactorily with 6.15×10^5 s^{-1} and 1.29×10^6 s^{-1} calculated at 242.7 K and 262.2 K using the temperature activation parameters.

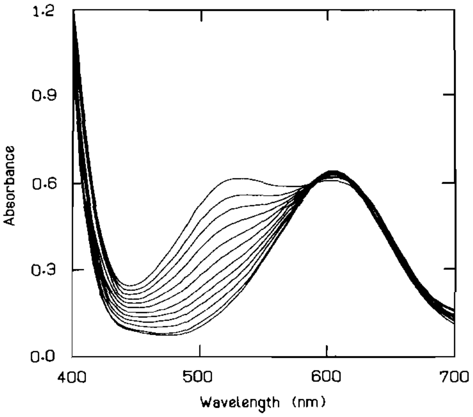

Fig. 8. Temperature dependent spectra for $Ni(TMC)(ClO_4)_2$ (1.60×10^{-3} *M*) in pure acetonitrile, from −20.5 °C to 78.0 °C.

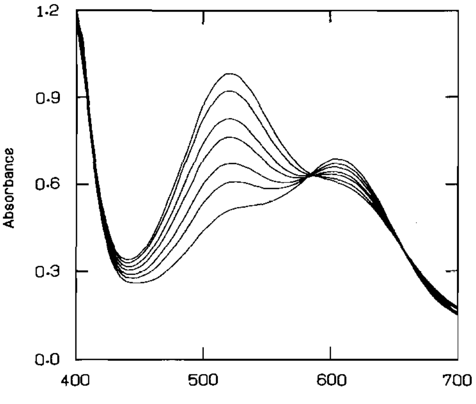

Fig. 9. Temperature dependent spectra for $Ni(TMC)(ClO_4)_2$ (1.72×10^{-3} *M*) in 1:1 mol ratio acetonitrile:nitromethane, from 14.5 °C to 74.8 °C.

Even if the maximum limits are placed on the uncertainties in the data, and a mean value of 2.3 ± 1.3 ml mol^{-1} is taken, this activation volume is clearly qualitatively and quantitatively different from that observed in the Co(II)/TMC system. The implication is that the mechanism for solvent exchange in the Ni(II)/TMC system is a dissociatively activated process rather than the associative interchange proposed by Moore.

All results reported so far on the Ni(II)/TMC system have been based on experiments at temperatures below 278 K. However it was noted that warmed solutions of the complex in acetonitrile were noticeably different in colour, and that this colour change was reversible with temperature; UV–visible spectra recorded over a range of temperatures are shown in Fig. 8.

Although it has been suggested [4] that the Ni(II)/TMC complex in acetonitrile does not participate in the coordination number equilibria that are observed in some solvent systems, the coexistence of bands around 516 nm and 604 nm is certainly not inconsistent with the presence of square planar and five coordinate forms of the complex in solution [5]. A limiting spectrum with no suggestion of the band at 516 nm is reached at around 255 K; it is not until the temperature is above 300 K that this band becomes obvious.

If the process observed in these spectra was a five coordinate/four coordinate equilibrium involving the loss of solvent, then it should be favoured by lowering the CH_3CN concentration with a non-coordinating diluent. Temperature dependent spectra in a 1:1 mol ratio of CH_3CN:CH_3NO_2 are shown in Fig. 9; the spectra are certainly qualitatively similar, with the suggested equilibrium displaced to the four coordinate side.

If the process observed here is indeed:

$$Ni(TMC)(CH_3CN)^{2+} \rightleftharpoons Ni(TMC)^{2+} + CH_3CN \qquad (6)$$

then it is straightforward to show that the data at various temperatures in pure CH_3CN and in CH_3CN/CH_3NO_2 should be consistent, and described by:

$$\ln([Ni(TMC)(CH_3CN)]/[Ni(TMC)]) - \ln(a_{CH_3CN}) = $$

$$= \Delta H^\circ/RT - \Delta S^\circ/R \qquad (7)$$

where a_{CH_3CN} is the activity of acetonitrile; we have assumed this to have a value of 1.0 for the experiments in pure acetonitrile and a value of 0.5 in 1:1 acetonitrile:nitromethane. Using as extinction coefficients for the four coordinate species those obtained in pure nitromethane (ϵ_{516} = 219 cm^{-1}, ϵ_{604} = 12.6 cm^{-1}), and for the five coordinate species those determined from the limiting spectra in pure acetonitrile at low temperature (ϵ_{516} = 10.6 cm^{-1}, ϵ_{604} = 39.4 cm^{-1}), the spectra in Figs. 8 and 9 can be analysed and the expression for equation (6) plotted as in Fig. 10.

The two sets of data are indeed consistent; not surprisingly, the experiments in CH_3CN/CH_3NO_2 where there are substantial concentrations of both coloured species are significantly more reliable. A linear least squares fit to the data in Fig. 10 gives values of ΔH° = 16.8 ± 0.8 kJ mol^{-1} and ΔS° = 32 ± 2 J K^{-1} mol^{-1}. These results compare reasonably with the results determined [4] from spectrophotometric measurements of the analogous reaction in water (ΔH° = 12.2 kJ mol^{-1}, ΔS° = 41 J K^{-1} mol^{-1}) with the differences reflecting the increased relative stability of the five coordinate species in acetonitrile.

We would therefore propose that this square planar species will be present, although in low con-

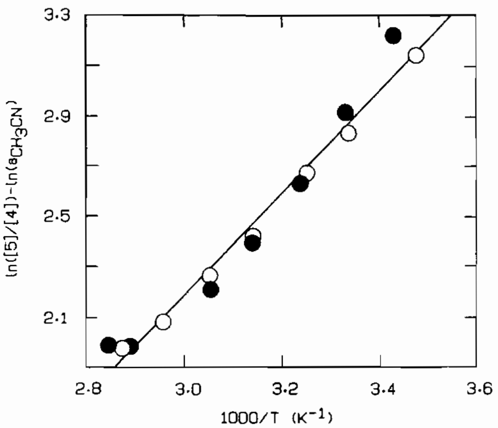

Fig. 10. Analysis of temperature dependent spectra for Ni(TMC)(ClO$_4$)$_2$ in acetonitrile solutions. ln([5]/[4]) − ln(a_{CH_3CN}) *vs.* 1000/T (K^{-1}). Closed circles are data in pure CH$_3$CN; open circles are data in 1:1 CH$_3$CN:CH$_3$NO$_2$.

centration, in the experiments measuring the exchange of acetonitrile on the five coordinate complex and further, that the presence of such a species will present a pathway for the solvent exchange which would be dissociative in character. At 278 K, the highest temperature in the kinetic study of this system, the above data indicates the amount of dissociation of the pentacoordinated complex according to reaction (6) is smaller than 3%.

Free-energy profiles for the exchange of CH$_3$CN on the five coordinate Co(II) and Ni(II) complexes are given in Fig. 11. Our concept of the transition state for the Co(II) system is straightforward; there is significant association of the incoming solvent molecule with the Co(II) centre, giving rise to a decrease in the entropy and volume of the system in achieving this state. In the Ni(II) case, however, the contributing factors to the attainment of the transition state are more difficult to resolve. Exchange via the four coordinate species involves not only bond breaking to the leaving group, but also spin state, ligand configuration, and Ni(II) to amine bond length changes which must be taken into account in describing the process.

Taking into account the van der Waals radii of the bonded atoms, we might imagine the stretching of the Ni(II)–nitrile bond to sweep out a cylinder of radius around 200 pm as the methyl group moves out into the bulk solvent; the observed activation volume, 2.3 ml mol^{-1}, could be accounted for by an increase of 30 pm in the Ni(II)–nitrile distance. A significantly larger volume increase due to dissociative loss of acetonitrile could be offset by a volume decrease due to the expected decrease in the Ni(II)–amine bond length in the proposed diamagnetic species. For non-cyclic tetra- amine systems [20], the bond length decrease has been found to be around 16 pm. By taking as a model for the Ni(II)(TMC)(CH$_3$CN)$^{2+}$ ion, a sphere of radius 500 pm, with an open cavity allowing access of the acetonitrile to the metal centre, a change of this order would lead to a contraction of around 30 ml mol^{-1}. In the more sterically-rigid macrocyclic structure the change would be expected to be smaller than 16 pm, but configurational changes of this type obviously make direct interpretation of an activation volume involving a spin state change very uncertain.

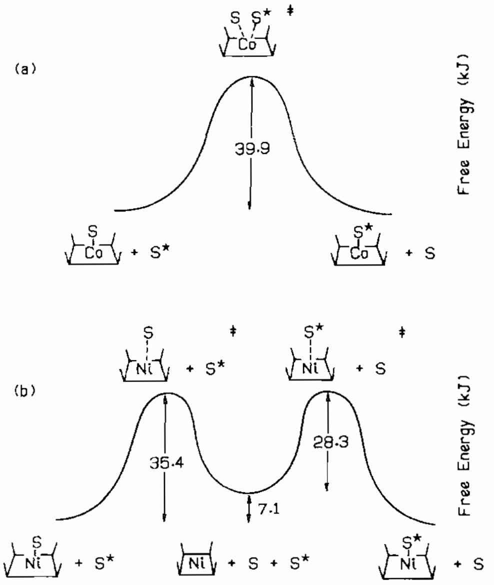

Fig. 11. Free energy profiles for the proposed mechanisms of solvent exchange for the Co(II)/TMC and Ni(II)/TMC complexes in acetonitrile at 298 K.

Again, there may be a number of contributions to the entropy change on transition state formation. Loss of the coordinated solvent would obviously be expected to lead to a positive activation entropy contribution. This would have to be offset by a large negative factor in order to achieve the −58 J K^{-1} mol^{-1} observed, although it is important to recognize that the transition state need not be the square planar configuration in which the leaving CH$_3$CN has transferred completely to the bulk solvent. The spin state change to a diamagnetic species will make a negative contribution to the electronic entropy, which can be estimated from the decrease in spin state multiplicity to be around −9 J K^{-1} mol^{-1} [21], although total entropy changes for such spin state changes may be much more negative than that calculated on the basis of electron multiplicity alone [22].

A quantitative analysis of the activation parameters for the Ni(II)(TMC)(CH$_3$CN)$^{2+}$ system is extremely difficult; however it is difficult to rationalise the positive activation volume observed and the coexistence of a species of decreased coordination with a mechanism other than dissociative D, in contrast to the associative interchange I_a apparent for the solvent exchange on the Co(II)(TMC)(CH_3-CN)$^{2+}$ ion.

In his temperature dependent study of the kinetics of acetonitrile exchange, Moore [10] comments on the difference in acceleration of solvent exchange in going from hexasolvento-Co(II) to the Co(II)/TMC complex, and that in going from the hexasolvento-Ni(II) to the Ni(II)/TMC complex. Such comparisons are difficult, given the differences in the coordination of the metal ions; however we would suggest that the over-riding factor in the disparity in these changes in rate arises from the difference in mechanism for the exchange in the five coordinate Co(II) and Ni(II) systems.

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