

## Temperature and Pressure Dependent Equilibrium Studies of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane Nickel(II) in Coordinating Solvents

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### Abstract

In coordinating solvents, the complex 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane nickel(II) bisperchlorate exists as an equilibrium mixture involving four coordinate  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> and five coordinate  $R,S,R,S$ -[Ni(tmc)(solvent)]<sup>2+</sup> species. Spectrophotometric measurements of this equilibrium in a number of solvents have been conducted over a range of temperatures and pressures. The stability order for the five coordinate complex in the solvents investigated is CH<sub>3</sub>CN > DMF > DMSO > C<sub>6</sub>H<sub>5</sub>CN > H<sub>2</sub>O > ClCH<sub>2</sub>CN at 25 °C. Differences in stability are considered in terms of the measured thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$ . Both steric and electronic factors were found to influence solvent coordination with the macrocyclic complex.

For the equilibrium in CH<sub>3</sub>CN, C<sub>6</sub>H<sub>5</sub>CN, DMF and H<sub>2</sub>O, reaction volumes,  $\Delta V^\circ$ , of  $-3.2 \pm 0.5$ ,  $-4.2 \pm 0.5$ ,  $-0.2 \pm 0.5$  and  $-0.5 \pm 0.5$  cm<sup>3</sup> mol<sup>-1</sup> respectively have been determined. Each is significantly smaller than the corresponding solvent molar volume. The  $\Delta V^\circ$  for the equilibrium in CH<sub>3</sub>CN is comparable with the previously determined activation volume for exchange of this solvent on  $R,S,R,S$ -[Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup>. The equilibrium and measured volume parameters are discussed in relation to the mechanism for solvent exchange.

### Introduction

Nickel(II) complexes of the macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc) have been a subject of interest for some time [1–8]. Particular attention has been focussed on these complexes because of the wide range of stereochemistries exhibited. Of the five possible complex configurations (Fig. 1), the  $R,R,S,S$  and  $R,S,R,S$  isomers have been isolated and are the most widely studied [1, 2, 9]. The  $R,S,R,R$  isomer has been identified in nitromethane solution using <sup>13</sup>C NMR [10].

Barefield and Wagner [1] have shown that direct combination of the tmc ligand with Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> yields the isomer in which all four methyl groups lie on the same side of the NiN<sub>4</sub> plane ( $R,S,R,S$ ). The  $R,R,S,S$  species, which has two methyl groups on either side of the ligand plane, may be synthesized by methylation of the parent complex, Ni(cyclam)<sup>2+</sup> (cyclam = 1,4,8,11-tetraazacyclotetradecane) [2]. Although it was previously believed that isomeric forms of [Ni(tmc)]<sup>2+</sup> were non-interconvertible [9], isomerization processes involving these species have recently been observed. Moore *et al.* [11] have demonstrated that under suitable conditions, interconversion of  $R,S,R,S$  and  $R,R,S,S$  complexes may occur to attain an equilibrium involving these species. The conversion of  $R,S,R,R$  to  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> has also been reported [10].

In the presence of coordinating solvents [Ni(tmc)]<sup>2+</sup> complexes have been shown to participate in spin-state equilibria involving a diamagnetic square planar complex and a paramagnetic five or six coordinate species [6, 9]. For  $R,R,S,S$ -[Ni(tmc)]<sup>2+</sup> an octahedral solvento species is formed by axial coordination of two solvent molecules. Because of the different ligand stereochemistry, a pentacoordi-

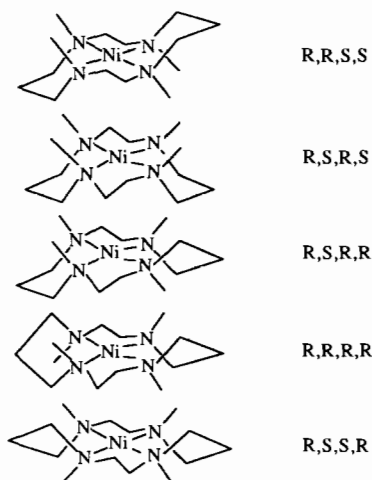


Fig. 1. Stereoisomers of [Ni(tmc)]<sup>2+</sup>.

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nate paramagnetic solvent adduct is formed from the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> complex. The metal geometry of the five coordinate species in solution remains uncertain; fluxional trigonal bipyramidal and square pyramidal structures have been proposed [9]. Solid state structure determinations of the five coordinate complexes indicate a square pyramidal configuration with the solvent molecule in the apical position [12, 13].

A number of solvation equilibrium studies involving macrocyclic complexes have been conducted. The vast majority of these concern equilibria between four and six coordinate nickel macrocycles, investigating the influence of ligand structure and of 'in-plane' field strength in particular, on solvent adduct stability [14–16]. Considerably less attention has been directed towards the equilibria between four and five coordinate species.

During the course of our investigation of the solvent exchange kinetics for  $R,S,R,S$ -[Co(tmc)-(CH<sub>3</sub>CN)]<sup>2+</sup> and  $R,S,R,S$ -[Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup> in CH<sub>3</sub>CN [17], a spin-state equilibrium involving four and five coordinate [Ni(tmc)]<sup>2+</sup> complexes was identified. Our observations of an unsolvated species, together with a slightly positive activation volume for the exchange of coordinated solvent, were taken as evidence of a dissociative mechanism for the exchange process. Other workers [18, 19] have concluded, on the basis of the large negative activation entropy, that  $R,S,R,S$ -[Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup> undergoes solvent exchange via an associative interchange (I<sub>a</sub>) pathway. However, we believe the labile spin-state equilibrium provides an important pathway by which a dissociative solvent exchange process may occur. An understanding of this equilibrium is thus considered central to any mechanistic studies of solvent exchange on  $R,S,R,S$ -[Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup>.

Observation of a spin-state equilibrium in CH<sub>3</sub>CN is contrary to a previous report which suggested complete formation of  $R,S,R,S$ -[Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup> in this solvent [9]. It had been proposed that formation of the monosolvento adduct is dependent upon steric considerations which arise from interaction of the solvent molecule with the tmc ligand and thus, 'rod-like' molecules such as CH<sub>3</sub>CN form stable solvento species [9]. However, other factors may also contribute to complex stability. We have therefore conducted a thermodynamic investigation of the spin-state equilibrium involving  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> in CH<sub>3</sub>CN and extended this to include a range of solvents with different structural characteristics in an attempt to highlight important factors which might influence these equilibria.

In addition, we have measured the reaction volumes,  $\Delta V^\circ$ , for the spin-state equilibrium involving the title complex in some solvents. It was anticipated that measurement of  $\Delta V^\circ$  would provide a

valuable adjunct to our solvent exchange activation volume studies and enable a more definitive interpretation of the mechanism for this process.

## Experimental

The ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Strem Chemicals, U.S.A.) was used as supplied. Purity was checked by <sup>1</sup>H NMR and mass spectroscopy.

The complex  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> was prepared using the method described by Barefield and Wagner [1] and then refluxed in dry nitromethane for 24 h in an attempt to attain complete conversion of any  $R,S,R,R$  isomeric impurity to the  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> product [10]. Our crystallographic studies of the unsolvated [Ni(tmc)]<sup>2+</sup> complex [21] and the acetonitrile solvent adduct [Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup> [12] obtained from the same product are consistent with the  $R,S,R,S$  stereochemical assignment. The [Ni(tmc)(DMF)]<sup>2+</sup> structure has also been reported [13] with the same  $R,S,R,S$  configuration.

Solvents used were of analytical grade and were further purified as follows. Acetonitrile, chloroacetonitrile and nitromethane were dried by reflux over CaH<sub>2</sub> and distilled under an atmosphere of nitrogen. DMF, DMSO and C<sub>6</sub>H<sub>5</sub>CN were stored over freshly regenerated Linde 4 Å molecular sieves for 5–7 days, then distilled under vacuum.

Aqueous solutions of the complex were prepared using twice distilled, once deionized water. Solutions of  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> in non-aqueous solvents were prepared for spectroscopic study and transferred to air-tight quartz cells in a glove box under dry nitrogen. Complex concentrations between  $8 \times 10^{-3}$  M and  $1.4 \times 10^{-2}$  M were chosen to ensure measurable absorbance changes with temperature. No additional electrolytes were used to adjust ionic strengths which were thus between 0.027 and 0.04 M.

Freshly prepared solutions of  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> in the non-aqueous solvents DMF, DMSO, CH<sub>3</sub>CN, C<sub>6</sub>H<sub>5</sub>CN and ClCH<sub>2</sub>CN were found to have visible absorbance spectra which varied with time. These changes may be attributed to the presence of small amounts of other [Ni(tmc)]<sup>2+</sup> complex configurations in the prepared product, which undergo conversion to the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> species. Such isomerization processes are the topic of further investigation and will be discussed elsewhere. It is noteworthy that similar behaviour has been established for other macrocyclic complexes [10, 11, 20].

Although the procedure to obtain an isomerically pure product by recrystallization in nitromethane [10] appears to have been unsuccessful, our experimental results suggest that ageing of the solution serves to establish a single spin-state equilibrium involving four coordinate  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> and

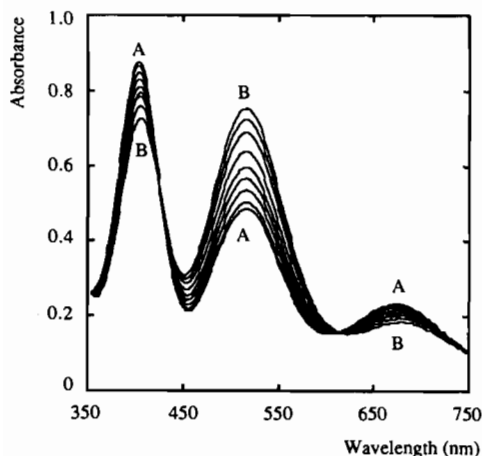


Fig. 2. Variable temperature visible spectra of  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> ( $1.087 \times 10^{-2}$  M) in DMSO. Temperatures increase from 20.1 °C (A) to 80.5 °C (B).

the five coordinate solvent adduct  $R,S,R,S$ -[Ni(tmc)(S)]<sup>2+</sup> (S = solvent). Thermodynamic and pressure studies based on the assumption of this equilibrium were therefore conducted on solutions of the complex which had previously been maintained at elevated temperature until absorbance spectra remained constant with time, indicating that all isomerisation processes were complete. These solutions yielded temperature dependent spectra with clean isosbestic points as shown in Fig. 2.

Visible spectroscopic measurements were recorded with a Varian 635D spectrophotometer equipped with a cell block which could be thermostatted between -10 and 80 °C to within  $\pm 0.1$  °C. The spectrophotometer was interfaced to a DEC PDP 11/10S minicomputer which was used to record the signal output and control scanning of each spectrum.

High pressure spectra were recorded using a thermostatted stainless steel bomb [22] mounted in the cell compartment of the spectrophotometer. A quartz optical cell located within the bomb is fitted with a silicone rubber membrane which serves to transmit the applied pressure to the solution. The high pressures are generated with a manual pump (Blackhawk Enerpac P-288) using Shell Ondina hydrocarbon oil as the pressurizing medium. Pressure measurements were recorded with a Budenberg pressure gauge (0-40000 PSI).

#### Data Treatment

The total absorbance for each spectrum was resolved into individual Gaussian component bands [23]. Each spectral band was defined in terms of three variables: wavelength of absorbance maximum  $\lambda_{\max}$ , peak absorbance at  $\lambda_{\max}$  and peak width at half height at  $\lambda_{\max}$ . Refinement of these variables was carried out using the non-linear least-squares

program ITERAT [17]. By assigning the band centred near 516 nm to the four coordinate  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup>, the concentration of this species could be calculated using eqn. (1).

$$[4] = \text{Abs}_{4\lambda} / (\epsilon_{4\lambda} l) \quad (1)$$

where [4] = concentration of four coordinate  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> complex;  $\text{Abs}_{4\lambda}$  = resolved absorbance for  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> at four coordinate peak maximum ( $4\lambda$ );  $\epsilon_{4\lambda}$  = extinction coefficient for  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> at  $4\lambda$ ;  $l$  = cell path length (cm).

The extinction coefficient  $\epsilon_{4\lambda}$  was obtained from a nitromethane solution of the [Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> product in which only the unsolvated complex is present. In all solvents except ClCH<sub>2</sub>CN, the concentration of the  $R,S,R,S$ -[Ni(tmc)(S)]<sup>2+</sup> complex and extinction coefficients associated with this species were determined from mass balance calculations after appropriate corrections were made to account for changes in solution volume with temperature (eqns. (2) and (3)).

$$[5] = [C_t] - [4] \quad (2)$$

$$\epsilon_{5\lambda} = \text{Abs}_{5\lambda} / ([5]l) \quad (3)$$

where [5] = concentration of five coordinate  $R,S,R,S$ -[Ni(tmc)(S)]<sup>2+</sup> complex;  $[C_t]$  = analytical concentration;  $\text{Abs}_{5\lambda}$  = resolved absorbance for  $R,S,R,S$ -[Ni(tmc)(S)]<sup>2+</sup> at five coordinate peak maximum ( $5\lambda$ );  $\epsilon_{5\lambda}$  = extinction coefficient for  $R,S,R,S$ -[Ni(tmc)(S)]<sup>2+</sup> at  $5\lambda$ .

Visible spectra were successfully resolved by proposing that absorbance bands were associated with the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> and  $R,S,R,S$ -[Ni(tmc)(S)]<sup>2+</sup> complexes only. Spectral data obtained from this Gaussian analysis are listed in Table I. The results of this analysis of a visible spectrum of  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> in DMSO are illustrated in Fig. 3.

For aged ClCH<sub>2</sub>CN solutions of  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup>, in addition to the bands associated with the previously identified complexes, an absorbance band at 429 nm was observed, indicative of another nickel(II) macrocyclic species in solution. The intensity of this peak was not temperature dependent and thus participation of this complex in spin-state equilibria was discounted. The existence of the third species in ClCH<sub>2</sub>CN solution precluded evaluation of the spin-state equilibrium constant using the mass balance equations described for the other solvents. However, by noting that the extinction coefficients for the five coordinate CH<sub>3</sub>CN and C<sub>6</sub>H<sub>5</sub>CN adducts for the absorbance band near 380 nm were almost identical ( $153$  and  $152$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> respectively) and assuming the same extinction coefficient to characterize the solvent adduct in ClCH<sub>2</sub>CN, concentrations of both the four and five

TABLE I. Gaussian Analysis of Visible Spectral Data<sup>a, b</sup> for  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> in Various Solvents

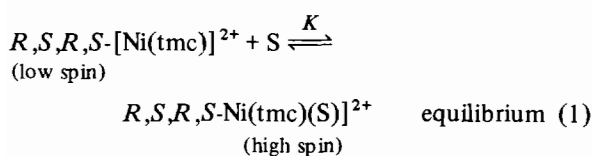
Solvent	$\lambda_{\max}$ (nm) ( $\epsilon$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )) <sup>c</sup>		
CH <sub>3</sub> CN	382(153)	516(208)	611(40)
C <sub>6</sub> H <sub>5</sub> CN	380(152)	524(203)	621(35)
CICH <sub>2</sub> CN	377(153) <sup>d</sup>	521(207)	625 <sup>e</sup>
DMF	400(149)	512(206)	663(40)
DMSO	403(102)	515(208)	675(27)
H <sub>2</sub> O	395(112)	508(202)	655(33)
CH <sub>3</sub> NO <sub>2</sub>		516(208)	

<sup>a</sup>Absorbance peak maxima obtained from resolution of spectra into Gaussian component bands. <sup>b</sup>Extinction coefficients for peaks near 516 nm determined from nitromethane solution as described in text. <sup>c</sup>Errors typically;  $\lambda$ ,  $\pm 1$  nm;  $\epsilon$ ,  $\pm 1$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. <sup>d</sup>Average of  $\epsilon$  values for complex in CH<sub>3</sub>CN and C<sub>6</sub>H<sub>5</sub>CN at this wavelength. <sup>e</sup>Weak absorbance.

coordinate complexes were calculated directly from the individual absorbance contributions and hence the equilibrium constant in this solvent was determined.

## Results and Discussion

Visible spectra of aged solutions of the title complex in the solvents DMF, DMSO, CH<sub>3</sub>CN, C<sub>6</sub>H<sub>5</sub>CN, CICH<sub>2</sub>CN and H<sub>2</sub>O contain optical bands consistent with the presence of a diamagnetic-paramagnetic equilibrium of the form:



where  $K = [R,S,R,S\text{-[Ni(tmc)(S)]}^{2+}] / [R,S,R,S\text{-[Ni(tmc)]}^{2+}]$ .

### Variable Temperature Equilibrium Studies

Equilibrium constants for the spin-state equilibrium were evaluated over a range of temperatures in each solvent. Plots of  $\ln K$  versus  $1000/T$  are presented in Fig. 4. The linearity of these plots further supports the assumption of a single equilibrium. Spectral data obtained from fresh solutions of the complex in non-aqueous solvents at various temperatures gave rise to deviations from linearity in the  $\ln K$  versus  $1000/T$  plot, a feature which has recently been attributed to the presence of other isomeric species in solution [20].

Values of  $\Delta H^\circ$  and  $\Delta S^\circ$  derived from the data in Fig. 4 are listed in Table II. For comparison, relevant data from independent studies are also included. The thermodynamic parameters for the  $R,S,R,S$ -

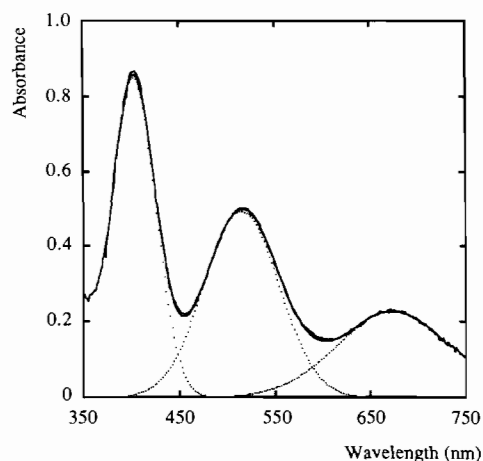


Fig. 3. Gaussian resolution of a visible spectrum of  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> in DMSO at 25 °C showing the experimental and total calculated spectra. Dotted lines represent individual peak components.

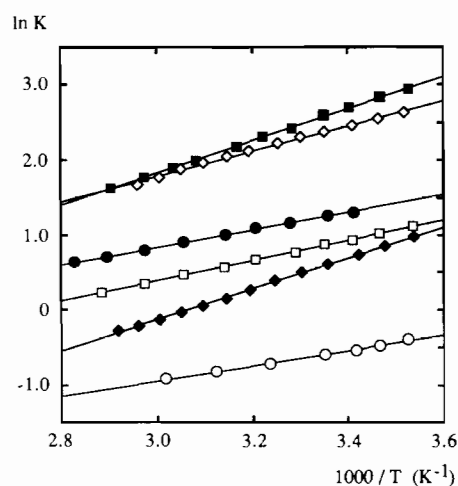


Fig. 4. Temperature dependence of the equilibrium constant,  $K$ . Plots of  $\ln K$  vs.  $1000/T$  for  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> in the solvents; (■) CH<sub>3</sub>CN, (◇) DMF, (●) DMSO, (□) C<sub>6</sub>H<sub>5</sub>CN, (●) H<sub>2</sub>O and (○) CICH<sub>2</sub>CN.

[Ni(tmc)]<sup>2+</sup> complex in DMF are in excellent agreement with those reported elsewhere [13]. Reasonable agreement with our earlier determination of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the equilibrium in CH<sub>3</sub>CN was obtained considering the previous study was carried out on solutions aged for less than 24 h [17]. The values from a similar investigation in H<sub>2</sub>O [9] are not concordant with those presented here, however, these differences may be due to the different values of the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> extinction coefficient used in the calculation of the spin-state equilibrium constant.

The relative stabilities of the  $R,S,R,S$ -[Ni(tmc)(S)]<sup>2+</sup> complexes in the solvents investigated follow

TABLE II. Thermodynamic Data for Solvent Coordination with  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup>

Solvent	$GN^a$	$\Delta H^\circ$ <sup>b</sup> (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ <sup>c</sup> (J K <sup>-1</sup> mol <sup>-1</sup> )	$T\Delta S^\circ$ <sup>d</sup> (kJ mol <sup>-1</sup> )	$K^d$	Reference
CH <sub>3</sub> CN	14.1	-17.9	-38.4	-11.4	13.4	this work
		-16.8	-32.0	-9.5	18.6	17
C <sub>6</sub> H <sub>5</sub> CN	11.9	-11.3	-30.8	-9.2	2.4	this work
ClCH <sub>2</sub> CN	NA <sup>e</sup>	-8.4	-33.1	-9.8	0.5	this work
DMF	26.6	-13.9	-26.9	-8.0	10.8	this work
		-12.8	-24.1	-7.2	10.0	13
DMSO	29.8	-9.8	-22.3	-6.6	3.5	this work
H <sub>2</sub> O	33.0	-17.3	-52.9	-15.8	1.8	this work
		-12.2	-41.0	-12.2	1.0	9

<sup>a</sup>Gutmann donor number from ref. 25. <sup>b</sup>Errors in  $\Delta H^\circ$  typically  $\pm 1$  kJ mol<sup>-1</sup>. <sup>c</sup>Errors in  $\Delta S^\circ$  typically  $\pm 1.5$  J K<sup>-1</sup> mol<sup>-1</sup>. <sup>d</sup>At  $T = 25^\circ\text{C}$ . <sup>e</sup>NA, not available.

the order CH<sub>3</sub>CN > DMF > DMSO > C<sub>6</sub>H<sub>5</sub>CN > H<sub>2</sub>O > ClCH<sub>2</sub>CN throughout the temperature range studied and the proportion of five coordinate species increases with decreasing temperature. In each case, solvent adduct formation arises as a consequence of a favourable enthalpic contribution to the overall free energy change (Table II). As has been confirmed from crystallographic studies [12, 13, 21], solvent coordination by  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> according to equilibrium (1), involving a metal spin-state change to a larger high-spin centre, gives rise to an increase in the nickel(II)-ligand nitrogen bond lengths. The negative enthalpies of reaction obtained in this study indicate that this endothermic process is more than compensated by formation of the metal-solvent bond.

The negative values of  $\Delta S^\circ$  observed in all cases are consistent with the decrease in translational entropy which is expected upon coordination of a solvent molecule during adduct formation. However, the entropy change arising from steric restrictions imposed on the coordinated solvent molecule by the macrocyclic ligand may also be significant. These factors, along with the degree of disorder of the bulk solvent from which this molecule is removed and the electronic entropy contribution associated with the increase of the metal spin-state, must be considered in any detailed interpretation of  $\Delta S^\circ$ .

For the entire range of solvents, no correlation of either  $\Delta H^\circ$  or  $\Delta S^\circ$  with the observed stability order is obvious. Prediction of stability on the basis of either parameter is thus inadequate and due consideration must be given to factors which influence both enthalpy and entropy changes before stability trends may be understood.

The findings of this study highlight two major factors which influence solvent adduct formation. It has been suggested [9] that the title complex forms stronger adducts with solvent molecules

whose structures enable coordination free of steric hindrance imposed by the macrocyclic ligand. Our thermodynamic data for CH<sub>3</sub>CN and H<sub>2</sub>O complexes are consistent with this proposal. The enthalpic contributions to the five coordinate complex stability in each case are very similar and the reduced stability of the aquo species is a consequence of a more negative  $\Delta S^\circ$  (Table II). The differences in  $\Delta S^\circ$  for the aquo and CH<sub>3</sub>CN complexes may be rationalized on the basis of a greater degree of steric interaction between the tmc and H<sub>2</sub>O ligands. The greater negative entropy change associated with formation of the aquo complex implies a more ordered coordination environment for the water case. Indeed, since water is a more highly structured solvent than CH<sub>3</sub>CN [24], it is evident that the order imposed on the H<sub>2</sub>O ligand compared with a CH<sub>3</sub>CN molecule when coordinated is considerable. By contrast, the 'rod-like' CH<sub>3</sub>CN molecule may enter the coordination cavity offered by the macrocyclic complex without appreciable obstruction from the ligand alkyl backbone or the methyl substituent groups.

Whereas differences in stability between CH<sub>3</sub>CN and H<sub>2</sub>O complexes can be attributed to steric effects, the trend in stability for the nitrile complexes cannot be similarly explained. It is obvious from thermodynamic data (Table II) that the relative stabilities of the nitrile adducts are determined by enthalpic rather than entropic factors. Whilst the  $\Delta H^\circ$  values reflect the trend in stability of the three solvated species, little variation of  $\Delta S^\circ$  is shown. Examination of molecular models indicates that, regardless of the size of the substituent group on the coordinating nitrile (CH<sub>3</sub>-, C<sub>6</sub>H<sub>5</sub>-, or Cl-CH<sub>2</sub>-), steric interactions of the coordinated solvent molecule with the macrocyclic complex are negligible and thus it is not surprising that  $\Delta S^\circ$  values are comparable. Assuming that the endothermic

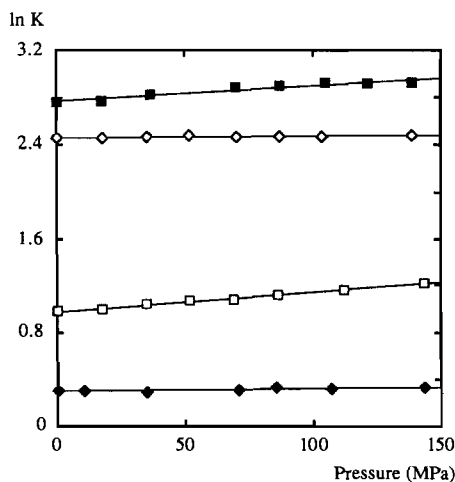


Fig. 5. Pressure dependence of the equilibrium constant,  $K$ . Plots of  $\ln K$  vs. pressure for  $R,S,R,S$ -[Ni(tmc)](ClO<sub>4</sub>)<sub>2</sub> in the solvents; (■) CH<sub>3</sub>CN, (◇) DMF, (□) C<sub>6</sub>H<sub>5</sub>CN and (●) H<sub>2</sub>O at 25 °C.

contribution to  $\Delta H^\circ$  arising from expansion of the macrocyclic ring is similar in all solvents, the observed stability trend may be explained by comparing the solvent donor strengths for CH<sub>3</sub>CN, Cl-CH<sub>2</sub>CN and C<sub>6</sub>H<sub>5</sub>CN. Gutmann donor numbers [25], which reflect solvent donor strength, are available for CH<sub>3</sub>CN and C<sub>6</sub>H<sub>5</sub>CN (Table II), but the value for ClCH<sub>2</sub>CN, to the best of our knowledge, has not been reported. However, for the series R-CN, the relative solvent donor strengths would be expected to correlate with the electron withdrawing potential of the relevant R groups, since the weakest electron withdrawing group will enable formation of the strongest metal-nitrile bond. From a comparison of  $pK_a$  values for the analogous carboxylic acids R-CO<sub>2</sub>H [26], the expected order of solvent donor strengths would be CH<sub>3</sub>CN > C<sub>6</sub>H<sub>5</sub>CN > ClCH<sub>2</sub>CN. The Gutmann numbers for CH<sub>3</sub>CN (14.1) and C<sub>6</sub>H<sub>5</sub>CN (11.9) are in accordance with this solvent ranking. The relative stabilities of the nitrile adducts of  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> follow this same trend and thus it is apparent that in the absence of any significant steric hindrance associated with the coordinated solvent and the tmc ligand, the stability constant for the five coordinate macrocyclic complex reflects the strength of the metal-solvent bond.

#### High Pressure Equilibrium Studies

The volumes of reaction ( $\Delta V^\circ$ ) for the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> spin-state equilibria in H<sub>2</sub>O, DMF, CH<sub>3</sub>CN and C<sub>6</sub>H<sub>5</sub>CN were determined by evaluating the pressure dependence of the equilibrium constant,  $K$ . Visible spectra of the complex in each solvent were recorded over a range of pressures between 0.1–140 MPa at 25 °C. Corrections to molar concentrations were made to account for changes in solu-

TABLE III. Reaction Volume Data for  $R,S,R,S$ -[Ni(tmc)]-(ClO<sub>4</sub>)<sub>2</sub> in Various Solvents at 25 °C

Solvent	$\Delta V^\circ$ <sup>a</sup> (cm <sup>3</sup> mol <sup>-1</sup> )	$V_m$ <sup>b</sup> (cm <sup>3</sup> mol <sup>-1</sup> )	$\alpha$ <sup>c</sup>
CH <sub>3</sub> CN	-3.2	52.2	-0.39
C <sub>6</sub> H <sub>5</sub> CN	-4.2	102.0	-0.21
H <sub>2</sub> O	-0.5	18.0	-0.97
DMF	-0.2	77.0	-0.22

<sup>a</sup>Reaction volume for equilibrium (1). Errors in  $\Delta V^\circ$  typically  $\pm 0.5$  cm<sup>3</sup> mol<sup>-1</sup>. <sup>b</sup>Solvent molar volume. <sup>c</sup>Calculated from eqn. (4).

tion volume due to compressibility of the solvent. Plots of  $\ln K$  versus pressure for  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> in each solvent are presented in Fig. 5. The  $\Delta V^\circ$  values derived from these plots are listed in Table III along with the solvent molar volumes ( $V_m$ ). In all solvents, coordination by the macrocyclic complex according to equilibrium (1) is characterized by a negative reaction volume indicating an increase in the proportion of five coordination species with increased pressure.

Although the solvent molar volumes range from 18 to 102 cm<sup>3</sup> mol<sup>-1</sup>, the corresponding measured reaction volumes are, by comparison, very small in magnitude (Table III). The  $\Delta V^\circ$  values are similar and do not directly reflect the variation in the size of the solvent molecule.

Removal of a molecule from the bulk solvent into the bonding cavity of the macrocyclic complex will make a negative contribution to the overall reaction volume. However, the change from low to high-spin nickel(II) is accompanied by an increase in the Ni-N bond lengths and changes in the tmc ligand orientation which may also change the volume of the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> moiety and therefore contribute to the value of  $\Delta V^\circ$ . We propose that the reaction volume will be determined by the sum of these individual contributions and may be described by eqn. (4).

$$\Delta V^\circ = \Delta V_{ss} + \alpha V_m \quad (4)$$

where  $\Delta V^\circ$  = reaction volume;  $\Delta V_{ss}$  = change in volume of the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> moiety due to change in spin-state and increase in Ni-N bond lengths;  $V_m$  = solvent molar volume;  $\alpha$  = proportion of the solvent molecule which can be regarded as effectively transferred into the macrocyclic complex.

Previously, in the absence of structural data, the change in volume of the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> moiety associated with the transition to high-spin was calculated by taking as a model for the complex, a sphere with an open cavity allowing access of the solvent molecule to the metal centre [17]. For comparable non-cyclic tetraamine systems [27],

Ni–N bond lengths have been shown to increase 16 pm upon changing to high-spin. The increase in volume of the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> complex arising from the spin-state change was estimated by assuming an increase in sphere radius corresponding to an equivalent elongation of the Ni–N bond lengths. Using this value, a  $\Delta V_{ss}$  of +30 cm<sup>3</sup> mol<sup>-1</sup> was calculated [17]. A similar approach, using the change in effective radius of a cylinder, has been used to model volume changes for the square planar/octahedral  $R,R,S,S$ -[Ni(tmc)]<sup>2+</sup> equilibrium in H<sub>2</sub>O [3].

Our recent crystallographic studies of both the four coordinate low-spin  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> [21] and five coordinate high-spin  $R,S,R,S$ -[Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup> [12] complexes now allow us to make a better estimate of  $\Delta V_{ss}$ . A comparison of the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> moiety in each case indicates that the geometry of the macrocyclic complex is approximated more satisfactorily by a cylindrical rather than a spherical model. However, an increase in cylinder radius, due to an increase in Ni–N bond lengths, is not an appropriate description of the structural differences arising from solvent coordination. The observed increase in the average Ni–N bond length of 18 pm accompanying coordination of the CH<sub>3</sub>CN molecule is comparable with the estimate based on non-cyclic structures [27]. However, this bond length increase is accommodated by a 34 pm displacement of the nickel(II) cation from the N<sub>4</sub> tmc plane forming a square pyramidal NiN<sub>4</sub> geometry and thus no significant expansion of the macrocyclic ring is observed [12, 21]. Therefore, after taking into account van der Waals radii, each structure may be considered as a cylinder with radius 500 pm.

In the five coordinate complex the six membered rings of the tmc ligand show a greater degree of puckering and the methyl groups are orientated further from the metal centre creating a more accessible bonding cavity. These structural changes are reflected in an effective cylinder height of 620 pm for the diamagnetic species and 660 pm for the high-spin complex. The open cavity in each structure represents only a small proportion of the total molecular volume (2 and 4 cm<sup>3</sup> mol<sup>-1</sup> for the four and five coordinate complexes respectively). Using these molecular dimensions, a value of +17 cm<sup>3</sup> mol<sup>-1</sup> for  $\Delta V_{ss}$  is obtained which is significantly smaller than previous estimates.

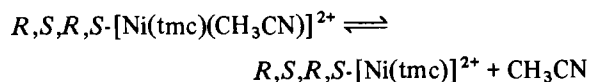
The calculated  $\Delta V_{ss}$  value of +17 cm<sup>3</sup> mol<sup>-1</sup>, together with the measured values for  $\Delta V^\circ$  may be used to evaluate from eqn. (4), the proportion,  $\alpha$ , of each coordinated solvent molecule which can be considered transferred from the bulk solvent into the bonding cavity of the macrocyclic structure. Values of  $\alpha$  for each solvent are presented in Table III. It is evident from these data that, with the ex-

ception of the H<sub>2</sub>O molecule, the bonding cavity of the  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> complex cannot completely accommodate the solvent molecule. Molecular models are consistent with this proposal. The H<sub>2</sub>O molecule, being smaller in volume than CH<sub>3</sub>CN is almost entirely incorporated into the cavity whereas only 39% of the CH<sub>3</sub>CN molecule is considered effectively transferred into the macrocyclic complex.

Few pressure dependence studies of macrocyclic complex equilibria are available for comparison. This work represents the first reported pressure investigation of spin-state equilibria involving four and five coordinate tmc complexes. Previous studies of  $R,R,S,S$ -[Ni(tmc)]<sup>2+</sup> and  $R,R,S,S$ -[Ni(cyclam)]<sup>2+</sup> in H<sub>2</sub>O have reported  $\Delta V^\circ$  values of -10.0 and -3.5 cm<sup>3</sup> mol<sup>-1</sup> respectively [3, 6]. As these equilibria involve two solvent molecules, it is not surprising that the change in volume measured here for coordination of one molecule of H<sub>2</sub>O with  $R,S,R,S$ -[Ni(tmc)]<sup>2+</sup> is somewhat smaller in magnitude.

The equilibrium data reported here for the coordination of CH<sub>3</sub>CN are relevant to the interpretation of the mechanism for CH<sub>3</sub>CN exchange on the  $R,S,R,S$ -[Ni(tmc)(CH<sub>3</sub>CN)]<sup>2+</sup> species. In our earlier study of this exchange process [17], a dissociative mechanism was proposed on the basis of the existence of a spin-state equilibrium and observation of a slightly positive activation volume. We believe that these equilibrium data for the macrocyclic complex in CH<sub>3</sub>CN reinforce this assignment of mechanism.

If CH<sub>3</sub>CN exchange does proceed via a dissociative pathway, the activation parameters for solvent exchange would describe the transition state for the following reaction.



The measured reaction volume,  $\Delta V^\circ$  of  $3.2 \pm 0.5$  cm<sup>3</sup> mol<sup>-1</sup> for this process, together with the previously reported activation volume,  $\Delta V^*$  of  $2.3 \pm 1.3$  cm<sup>3</sup> mol<sup>-1</sup> imply that, from a volume viewpoint, the transition state corresponds to a configuration in which the CH<sub>3</sub>CN molecule is approximately 70% dissociated from the macrocyclic structure. In terms of enthalpy, such a dissociative reaction would be expected to have  $\Delta H^\circ$  and  $\Delta H^*$  values which are similar if indeed the metal–solvent bond is completely broken in the transition state. The enthalpy of reaction for complete dissociation of the CH<sub>3</sub>CN molecule, determined in this study to be  $17.9 \pm 0.5$  kJ mol<sup>-1</sup>, is identical within experimental error, to the activation enthalpy for the exchange process previously measured as  $18.1 \pm 0.5$  kJ mol<sup>-1</sup> [17]. Thus the volume and enthalpy data support the assignment of a dissociative pathway for solvent exchange.

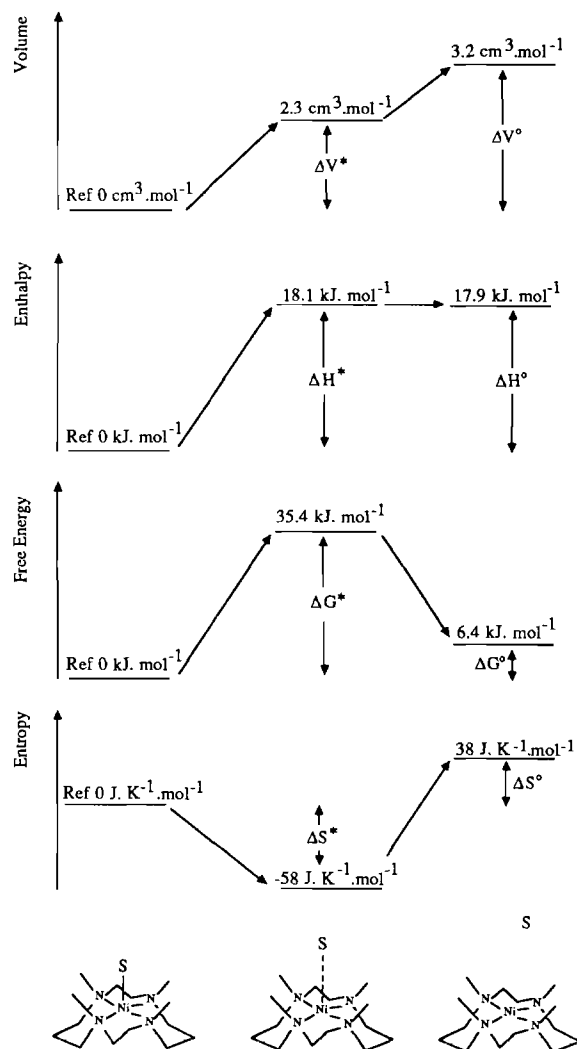


Fig. 6. Volume, enthalpy, free energy and entropy profiles for the reaction  $R,S,R,S-[Ni(tmc)(CH_3CN)]^{2+} \rightleftharpoons R,S,R,S-[Ni(tmc)]^{2+} + CH_3CN$  at 25 °C.

Volume and enthalpy profiles for the above reaction are presented in Fig. 6 together with profiles for entropy and free energy.

The negative activation entropy,  $\Delta S^*$ , of  $-58 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$  may appear contrary to the assignment of a dissociative mechanism for solvent exchange. However, interpretation of entropy changes for this reaction are complicated by a number of different factors which may contribute to the overall value of  $\Delta S^*$ . It has been demonstrated using NMR techniques that five coordinate complexes of  $R,S,R,S-[Ni(tmc)]^{2+}$  exhibit fluxional behaviour between trigonal bipyramidal and square pyramidal geometries in solution [28]. The negative activation entropy could be explained in terms of a dissociative process if, in the transition state, this fluxionality is lost. A further contribution to the decrease in

entropy would result if the change in spin-state occurs during formation of the transition state. Other studies have indicated that such a change in spin multiplicity may account for around  $-9 \text{ J K}^{-1} \text{ mol}^{-1}$  [29]. The negative solvent exchange activation entropy may thus be explained by proposing that the reaction proceeds through a low-spin, five coordinate transition state in which the ground state fluxionality has been lost.

### Supplementary Material

Experimental temperature and pressure spectrophotometric data from which figures presented in this article are derived are available from the authors on request.

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