

properties of the quadridentate chelate group (Schiff bases, porphyrins, and macrocycles). The results support the hypothesis that the oxygen carrying ability of metal complexes depends on their ease of oxidation.

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Lability of Coordinated Acetonitrile in Nickel(II) Complexes. A Nitrogen-14 Magnetic Resonance Study

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Abstract: The parameters characterizing acetonitrile exchange (where k_{ex} (25°) refers to a single site) in Ni(triol)-(CH₃CN)₃²⁺ and Ni(triam)(CH₃CN)₃²⁺ (all three CH₃CN equivalent in both species) are respectively $k_{\text{ex}} = (1.0 \pm 0.2) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 15.9 \pm 0.8 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = 8.7 \pm 2.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ and $k_{\text{ex}} = (555 \pm 60) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 9.3 \pm 1.0 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -0.9 \pm 3.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$. For Ni(diamol)(CH₃CN)₃²⁺ $k_{\text{ex}} = (180 \pm 20) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 12.0 \pm 1.1 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = 5.4 \pm 3.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ calculated on the assumption that the single observed exchange process pertains to the two equivalent acetonitrile ligands only. The rate parameters for the faster site in Ni(trenol)(CH₃CN)₂²⁺ are $k_{\text{ex}} = (40 \pm 6) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 12.0 \pm 1.2 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = 2.8 \pm 4.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$. These data, in conjunction with those for Ni(CH₃CN)₆²⁺ and Ni(tren)(CH₃CN)₂²⁺, indicate that CH₃CN is labilized in six-coordinate Ni(II) species by the groups -NH₂ > N< > -OH ~ CH₃CN in the order of decreasing effectiveness shown. The exchange parameters are discussed in terms of a dissociative mechanism.

The lability of solvent in the first coordination sphere of nickel(II) exhibits a variable but systematic dependence upon the nature of a second ligand in that coordination sphere.¹ This dependence, in conjunction with the recently reported observations of different labilities for the two solvent molecules in Ni(tren)-(solvent)₂²⁺ (where tren = 2,2',2''-triaminotriethylamine and solvent = H₂O² or CH₃CN³), comes tantalizingly close to revealing at least some of the major factors determining solvent lability on nickel(II). It appears that the variation in coordinated solvent lability induced by chelating ligands of similar geometry, but bonding to nickel(II) through different donor atoms, may lead to a better understanding of some of the factors controlling solvent exchange processes. Accordingly CH₃CN exchange studies on the four species, Ni(triol)-(CH₃CN)₃²⁺ (A), Ni(triam)(CH₃CN)₃²⁺ (B), Ni(diamol)(CH₃CN)₃²⁺ (C), and Ni(trenol)(CH₃CN)₂²⁺ (D) (where triol = 2,2-di(hydroxymethyl)-1-propanol, triam = 2,2-di(aminomethyl)-1-propylamine, diamol = 2,2-di(aminomethyl)-1-propanol and trenol = 2,2',2''-trihydroxytriethylamine) shown diagrammatically in Figure 1, are reported. These species were selected on the basis that in both A and B the three CH₃CN ligands are equivalent, and consequently the effect of the oxygen and primary nitrogen chelate donor atoms on the lability of single solvent molecules may be separately discerned, whereas in C the effect of oxygen and primary nitrogen donor atoms may be assessed. Species D

facilitates a comparison of the labilizing effects of oxygen and tertiary nitrogen donor atoms and also bears an obvious geometric similarity to Ni(tren)(CH₃CN)₂²⁺ (E) in which the labilizing effects of primary and tertiary nitrogen atoms may be compared.

Experimental Section

Materials. Redistilled acetonitrile, toluene, and 2,2',2''-trihydroxytriethylamine were dried and stored over Linde 4A molecular sieves. Koch-Light 2,2-di(hydroxymethyl)-1-propanol was recrystallized from benzene and dried under vacuum, and 2,2-di(aminomethyl)-1-propylamine was prepared by a method similar to that of Stetter and Böckmann.⁴ A major by-product of this preparation, 2,2-di(aminomethyl)-1-propanol (diamol), was separated as the dihydrochloride, diamol(HCl)₂, from aqueous solution in which it has a much higher solubility than triam(HCl)₃. Diamol(HCl)₂ was purified by fractional crystallization and was converted to diamol by passing an aqueous solution over an ion-exchange resin (Deacidite FF) in the hydroxide form. Water was removed by azeotropic distillation from benzene to give a benzene solution of diamol. The benzene was removed under vacuum and the diamol, a waxy solid at 25°, was distilled under vacuum. Diamol(HCl)₂ prepared from this product exhibits (in D₂O) ¹H resonances at 4.23 (-CH₂OH), 3.70 (-CH₂NH₂), and 1.65 ppm (-CH₃) downfield from a TMS capillary. *Anal.* Calcd for CH₃C(CH₂OH)(CH₂NH₃Cl)₂: C, 31.42; H, 8.44; N, 14.66. Found: C, 29.91; H, 8.52; N, 14.24. The complex bis(2,2-di(aminomethyl)-1-propylamine)nickel(II) perchlorate was prepared by allowing stoichiometric amounts of triam and nickel(II) perchlorate to react in aqueous solution from which the sparingly soluble lilac product precipitated. The product was washed with water, ethanol, and ether and dried under vacuum. *Anal.* Calcd for Ni(CH₃C(CH₂NH₂)₂)₂(ClO₄)₂: C, 24.41; H, 6.15; N, 17.08. Found: C, 24.48; H, 6.23; N, 16.29.

Spectral Measurements. All solutions were prepared in a dry nitrogen atmosphere. Solutions of Ni(triol)(CH₃CN)₃²⁺, Ni-

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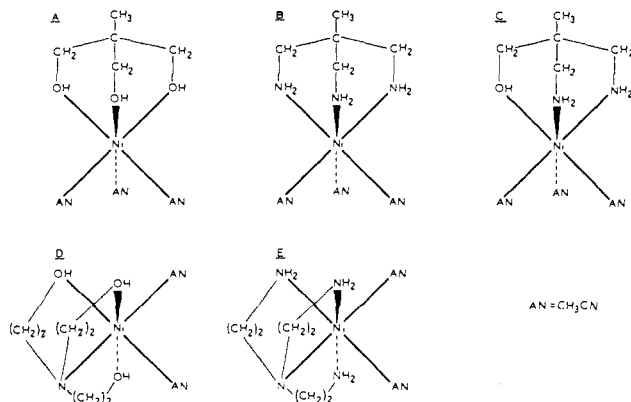


Figure 1.

(diamol)(CH₃CN)₃²⁺, and Ni(trenol)(CH₃CN)₂²⁺ were prepared by adding a 3% molar excess of the ligand to [Ni(CH₃CN)₆](ClO₄)₂, whereas the Ni(triam)(CH₃CN)₃²⁺ solutions were prepared by adding a 2% molar excess of [Ni(triam)](ClO₄)₂ to [Ni(CH₃CN)₆](ClO₄)₂.⁵ In general three solutions were prepared of each species within the concentration range 0.075–0.62 *m* (0.057–0.45 *M*). Visible spectra were determined using a Unicam SP700, and magnetic moments were determined by the method of Evans⁶ using toluene as reference.

Nitrogen-14 nmr measurements were made at 3.07 MHz on previously described equipment⁷ using the first derivative method. Line widths were corrected for modulation broadening, which never exceeded 7% of the total line width at half absorption amplitude, by the method of Wahlquist.⁸ Line width and chemical shift measurements were made at power levels below saturation, in triplicate, and were reproducible to within 0.1 and 0.2 G, respectively. No significant broadening or shift was induced in the bulk acetonitrile ¹⁴N signal in a 0.654 *m* Zn(ClO₄)₂ solution over the experimental temperature range. The ¹⁴N line broadening exhibited a linear dependence upon the concentration of the nickel(II) complex in all cases.

Results and Data Treatment

Visible Spectra. The visible absorption spectra (Figure 2) of all four complexes studied are typical of six-coordinate nickel(II) in which the bands may be assigned,⁹ in order of decreasing energy, to the transitions ³A_{2g} → ³T_{1g}(P), ³A_{2g} → ³T_{1g}(F), and ³A_{2g} → ³T_{2g}. The band maxima frequencies (cm⁻¹) and extinction coefficients (ε) are Ni(triam)(CH₃CN)₃²⁺ 29,100 (15.4), 18,500 (12.8), 11,400 (11.0); Ni(triol)(CH₃CN)₃²⁺ 26,700 (9.0), 16,600 (5.3), 9900 (4.9); Ni(diamol)(CH₃CN)₃²⁺ 28,500 (12.7), 17,900 (9.5), 11,200 (8.5); Ni(trenol)(CH₃CN)₂²⁺ 26,400 (13.4), 16,800 (6.6), 10,400 (8.8); Ni(CH₃CN)₆²⁺ 27,500 (8.0), 17,200 (5.9), 10,400 (6.3). The variation of the band frequencies is qualitatively consistent with positions of the coordinating groups in the spectrochemical series.⁹

¹⁴N Magnetic Resonance Data. The relationship of bulk solvent nuclear relaxation and the associated chemical shift to solvent exchange processes on paramagnetic metal ions in dilute solutions have been previously discussed in detail,^{1,10,11} and hence only those aspects of this relationship pertinent to the systems under study are considered here. The ¹⁴N nuclear

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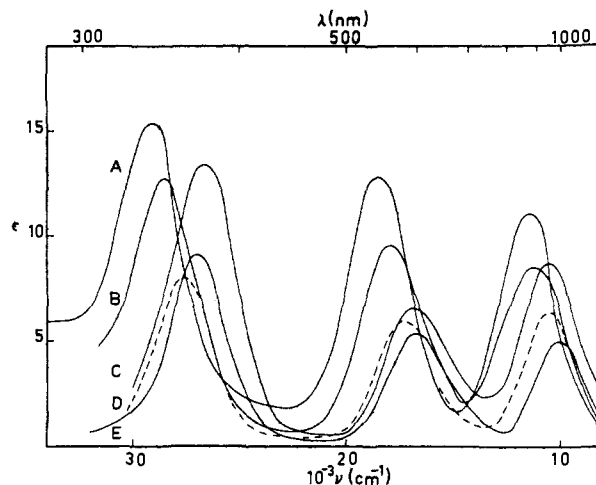


Figure 2. Absorption spectra in acetonitrile solution: A, Ni(triam)(CH₃CN)₃²⁺; B, Ni(diamol)(CH₃CN)₃²⁺; C, Ni(trenol)(CH₃CN)₂²⁺; D, Ni(CH₃CN)₆²⁺; E, Ni(triol)(CH₃CN)₃²⁺.

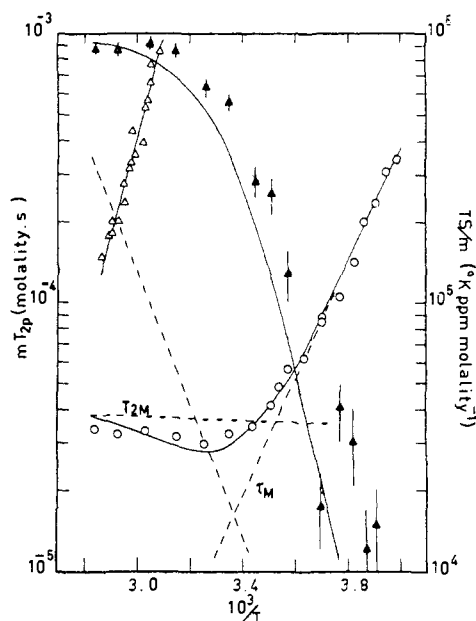


Figure 3. Nitrogen-14 relaxation and shift data for bulk acetonitrile. The relaxation data (open triangles) fit for the Ni(triol)(CH₃CN)₃²⁺ system is shown as a solid curve. The Ni(triam)(CH₃CN)₃²⁺ shift data (closed triangles) and relaxation data (open circles) fits are shown as solid curves, and the components of the relaxation curve are shown as labeled broken curves.

relaxation of bulk acetonitrile induced by the nickel(II) complexes may be expressed as

$$T_{2p} = 2\gamma^{-1}(W_{\text{obsd}} - W_0)^{-1} \text{ (sec)} \quad (1)$$

where γ is the ¹⁴N gyromagnetic ratio (1934 G⁻¹ sec⁻¹) and W_{obsd} and W_0 are the full line widths (in G) of the bulk acetonitrile ¹⁴N resonance at half-maximum amplitude in the acetonitrile solution of the nickel complex and the acetonitrile reference solution, respectively. The variation of mT_{2p} , where m is the molality of the complex, with $1/T$ for Ni(triol)(CH₃CN)₃²⁺ (Figure 3) is consistent with the expression

$$mT_{2p} = \tau_M C/3 \quad (2)$$

where $C = 1000(\text{molecular weight of acetonitrile})^{-1}$ and τ_M is the mean lifetime of an acetonitrile molecule in the

Table I

Complex	No. of equiv sites for CH ₃ CN	10 ⁻³ k _{ex} (25°), sec ⁻¹	ΔH‡, kcal mol ⁻¹	ΔS‡, cal mol ⁻¹ deg ⁻¹	A/h, Hz	μ _{eff} , BM
Ni(CH ₃ CN) ₆ ²⁺ ^a	6	2.0 ± 0.3	16.4 ± 0.5	12.0 ± 2.0		3.15
Ni(triol)(CH ₃ CN) ₃ ²⁺	3	1.0 ± 0.2	15.9 ± 0.8	8.7 ± 2.5		
Ni(triam)(CH ₃ CN) ₃ ²⁺	3	555 ± 60	9.3 ± 1.0	-0.9 ± 3.5	24.3 × 10 ⁶	3.08
Ni(diamol)(CH ₃ CN) ₃ ²⁺	2	180 ± 20	12.0 ± 1.1	5.4 ± 3.5	26.0 × 10 ⁶	3.09
Ni(diamol)(CH ₃ CN) ₃ ²⁺	1	<1				3.09
Ni(tren)(CH ₃ CN) ₂ ²⁺ ^b	1	165 ± 35	10.8 ± 1.1	1.4 ± 5.0	15.1 × 10 ⁶	3.00
Ni(tren)(CH ₃ CN) ₂ ²⁺	1	>2000			15.1 × 10 ⁶	3.00
Ni(trenol)(CH ₃ CN) ₂ ²⁺	1	40 ± 6	12.0 ± 1.2	2.8 ± 4.0	16.0 × 10 ⁶	3.10
Ni(trenol)(CH ₃ CN) ₂ ²⁺	1	~2				3.10

^a Reference 12. ^b Reference 3.

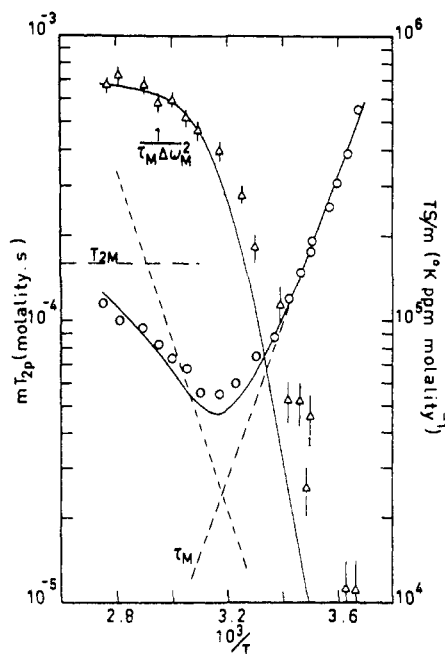


Figure 4. Nitrogen-14 shift and relaxation data for bulk acetonitrile in the Ni(diamol)(CH₃CN)₃²⁺ system. The shift data (open triangles) and relaxation data (open circles) fits are shown as solid curves, and the components of the relaxation curve are shown as labeled broken curves.

first coordination sphere of nickel(II). The temperature dependence of τ_M is given by

$$\tau_M^{-1} = k_{\text{ex}} = r/3[\text{Ni}(\text{triam})(\text{CH}_3\text{CN})_3^{2+}]^{-1} = (kT/h) \times \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R) \quad (3)$$

where k_{ex} and r are the rate constant and rate for acetonitrile exchange and the other symbols have their usual meaning. The derived kinetic parameters are listed in Table I.

The temperature dependence of mT_{2p} for Ni(triam)(CH₃CN)₃²⁺ is shown in Figure 3. The datum points are fitted to eq 4 as indicated in Figure 2, in which

$$mT_{2p} = \frac{\tau_M C}{3} \left[\frac{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2}{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + \Delta\omega_M^2} \right] \quad (4)$$

components of the curve fit are also shown. The associated chemical shift S is given by

$$S = [(\omega_{\text{obsd}} - \omega_0)/\omega_0] \times 10^6 \text{ (ppm)} \quad (5)$$

where ω_{obsd} and ω_0 are the ¹⁴N frequencies (rad sec⁻¹) in the paramagnetic and reference solutions, respectively.

The shift data are plotted as TS/m in Figure 2 in which the best fit to eq 6

$$TS/m = \frac{-3 \times 10^6 \Delta\omega_M T}{C\omega_0\tau_M^2} [(1/T_{2M} + 1/\tau_M)^2 + \Delta\omega_M^2]^{-1} \quad (6)$$

where $\Delta\omega_M$ is the difference in ¹⁴N precessional frequency between coordinated and bulk acetonitrile, is shown. The best fits of the mT_{2p} and TS/m data are consistent with an A/h value of 24.3×10^6 Hz calculated from eq 7 where S_e is the electron spin of nickel(II),

$$\frac{\Delta\omega_M}{\omega_0} = \frac{-A[S_e(S_e + 1)]^{1/2} \mu_{\text{eff}} 2\pi\beta}{3hkT} \quad (7)$$

$\mu_{\text{eff}} = 3.08$ BM, and all other symbols have their usual meaning.

The temperature dependence of mT_{2p} for Ni(diamol)(CH₃CN)₃²⁺ is fitted (Figure 4) to eq 4 after multiplication of the right-hand side of that equation by 1.5 as the observed relaxation is considered to pertain to the two equivalent acetonitrile ligands in the complex only. The rationale for this assumption is, firstly, that it appears unlikely that nonequivalent acetonitrile ligands will exhibit similar labilities, particularly as in ³Ni(tren)(CH₃CN)₂²⁺ and its aqueous analog² the two solvent ligands are characterized by markedly different labilities, and, secondly, the A/h value (26×10^6 Hz) calculated from both the ¹⁴N relaxation and shift data for Ni(diamol)(CH₃CN)₃²⁺, on the basis of the exchange of two equivalent sites, is markedly similar to the A/h value for the Ni(triam)(CH₃CN)₃²⁺ system. The latter argument is somewhat equivocal, however, as the A/h values (Table I) of the Ni(tren)(CH₃CN)₂²⁺ and Ni(trenol)(CH₃CN)₂²⁺ systems are significantly less than those of the triam and diamol systems. On the basis of these limited data it appears that the magnitude of A/h may be dependent upon complex stereochemistry. The TS/m data fit to eq 6 (where the right-hand side of the equation is multiplied by 2/3) for the Ni(diamol)(CH₃CN)₃²⁺ system is shown in Figure 4. It appears that $k_{\text{ex}} < 10^3$ sec⁻¹ for the unique acetonitrile ligand in this system if the assumption that the single observed exchange process pertains to the two equivalent acetonitrile ligands is correct.

Acetonitrile solutions containing mole ratios of Ni:L = 1:2 (where L = triol, triam, or diamol) produce no significant broadening or shift of the bulk acetonitrile ¹⁴N resonance over the temperature range -10 to 80°. This is consistent with the species NiL₂²⁺, in which L is tridentate, predominating in each solution and strongly

supporting the assignment of the stoichiometry of $\text{NiL}(\text{CH}_3\text{CN})_3^{2+}$ to the predominant species in the solutions from which ^{14}N line broadening and shift data were obtained. No line broadening attributable to $\text{Ni}(\text{CH}_3\text{CN})_6^{2+}$ was observed for any system.

The temperature dependence of mT_{2p} (Figure 5) for $\text{Ni}(\text{trenol})(\text{CH}_3\text{CN})_2^{2+}$ is consistent with two exchange processes occurring at different rates, and most closely conforms to eq 8. The $\tau_{M'}$ contribution to mT_{2p} is ill-

$$mT_{2p} = C[(\tau_M + (\tau_M \Delta\omega_M^2)^{-1})^{-1} + \tau_{M'}^{-1}]^{-1} \quad (8)$$

defined, but its existence is confirmed by the residual shift observed above that expected for the more rapid exchange process, characterized by τ_M , at the high temperature extreme. The shift arising from the τ_M process is calculated from the equation

$$TS/m = \frac{-10^6 \Delta\omega_M T}{C\omega_0} (1 + \tau_M^2 \Delta\omega_M^2)^{-1} \quad (9)$$

using $A/h = 16 \times 10^6$ Hz derived from the relaxation data. The absence of a well-established A/h value for the $\tau_{M'}$ process and the predominance of the $\tau_M^2 \Delta\omega_M^2$ term from eq 9 in the observed shift data for that process render a data fit to the residual shift of dubious value. The fit shown for the shift arising from the slower exchange process (broken curve) retains the temperature dependence for $\tau_{M'}$ shown in Figure 5 and $A/h = 16 \times 10^6$ Hz, but corresponds to lifetime values of $0.56 \tau_{M'}$ over the experimental temperature range. This fit demonstrates that the shift and relaxation data associated with $\tau_{M'}$ are compatible within the experimental uncertainty.

Discussion

The kinetic parameters characterizing the exchange of acetonitrile in the series of nickel(II) species studied exhibit a marked dependence upon the nature of the polydentate ligand (Table I). The 555-fold variation (at 25°) of acetonitrile lability in the stereochemically similar $\text{Ni}(\text{triol})(\text{CH}_3\text{CN})_3^{2+}$ and $\text{Ni}(\text{triam})(\text{CH}_3\text{CN})_3^{2+}$ species is explicable in terms of electron donation to, and consequent reduction of charge on, nickel(II) by the $-\text{NH}_2$ coordinating groups, which causes a considerable labilization of acetonitrile in contrast to the $-\text{OH}$ coordinating groups which appear to reduce lability if the data¹² for $\text{Ni}(\text{CH}_3\text{CN})_6^{2+}$ is taken as a reference. This rationale is similar in effect to the empirical molecular orbital model proposed by Langford¹³ according to which the greater σ donor character of the $-\text{NH}_2$ groups might be expected to produce the greater labilization of acetonitrile. The parameters characterizing the single observed exchange process in the $\text{Ni}(\text{diamol})(\text{CH}_3\text{CN})_3^{2+}$ system indicate that such labilization is a function of all of the coordinating groups of the polydentate ligand. In the case of the $\text{Ni}(\text{tren})(\text{CH}_3\text{CN})_2^{2+}$ system the two distinct exchange processes observed are indicative of a directional character in the labilization induced by the polydentate ligand, and there is substantial evidence that the acetonitrile ligand trans to the $-\text{NH}_2$ group is the more labile.³ Similarly, the two exchange processes observed in the $\text{Ni}(\text{trenol})(\text{CH}_3\text{CN})_2^{2+}$

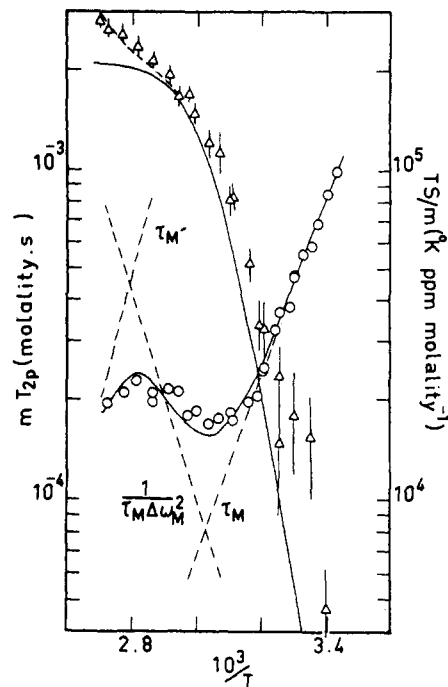


Figure 5. Nitrogen-14 shift and relaxation data for bulk acetonitrile in $\text{Ni}(\text{trenol})(\text{CH}_3\text{CN})_2^{2+}$ system. The shift data (open triangles) fit shown as a solid curve applies to the faster exchange process, while the broken curve represents the data fit for the slower exchange process. The relaxation data (open circles) fit is shown as a solid curve, and the components are shown as labeled broken curves.

system indicate a directional labilizing influence, and, as observed in the tridentate ligand systems, it is seen that the magnitudes of the exchange parameters are a function of all of the coordinating groups. On the basis of these observations, the labilizing effects of the coordinating groups (at 25°) appear to decrease in the order $-\text{NH}_2 > -\text{N} < > -\text{OH} \sim -\text{NCCH}_3$. Hunt¹ has observed a general labilizing of aquo ligands in nickel(II) species by $-\text{NH}_3$, $-\text{NH}_2$, $-\text{NCS}$, and $-\text{Cl}$ coordinating groups, but pyridyl nitrogen induces no significant labilization.

From solvent exchange and ligand substitution studies¹⁴⁻¹⁷ it appears that solvent exchange on nickel(II) species is predominantly dissociative in nature, and it is not considered necessary to reiterate the arguments for this conclusion here. The fact that ΔH^\ddagger for such processes is markedly less than the metal to ligand bond energy may be explained by assuming that either the remaining ligands, in the dissociative transition state, σ bond more strongly than in the ground state¹³ or that solvent outside the first coordination sphere participates in the transition state as has recently been considered quantitatively by Strehlow and Knoche¹⁸ or that both processes are important factors in determining the magnitude of ΔH^\ddagger . It is evident from the table that there exists an approximately linear relationship between ΔH^\ddagger and ΔS^\ddagger which persists after correction of

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ΔH^\ddagger for crystal field contributions.¹⁹ While it appears that σ bonding variation or solvation arguments may accommodate ΔH^\ddagger variations, any discussion of ΔS^\ddagger is complicated by uncertainty as to the extension of the transition state beyond the first coordination sphere. The data in the table indicate that a decrease in ΔH^\ddagger leads to increased ordering in the transition state and that an approximate linear relationship between ΔH^\ddagger and ΔS^\ddagger exists as has been observed for a considerable range of solvent exchange and ligand substitution processes on divalent metal ions.¹⁶ Bennetto and Caldin¹⁶ suggest that ΔS^\ddagger arises largely from solvent reorganization outside the first coordination sphere, and have proposed a mechanism for solvent exchange on $M(\text{solvent})_6^{2+}$, based upon the Frank and Wen²⁰ model for solvated ions, which rationalizes the approximate linear relationship between ΔH^\ddagger and ΔS^\ddagger . This mechanism envisages that if net transfer of solvent from a region of disordered solvent immediately outside the first coordination sphere to the relatively ordered bulk solvent occurs, synchronously with the bond breaking process in the first coordination sphere, then negative contributions to the observed ΔH^\ddagger and ΔS^\ddagger values (and *vice versa*) arise from these processes. If this mechanism is applied to the $\text{Ni}(\text{triam})(\text{CH}_3\text{CN})_3^{2+}$ system, it appears

(19) A. L. Companion, *J. Phys. Chem.*, **73**, 739 (1969), and references therein. Crystal field activation energies (CFAE) calculated for a square based pyramid transition state on the basis of the energies of the ${}^3T_{2g} \leftarrow {}^3A_{2g}$ transition are 5.9, 5.6, 6.4, 6.3, 6.6, and 5.9 kcal mol⁻¹, respectively, for $\text{Ni}(\text{CH}_3\text{CH})_6^{2+}$, $\text{Ni}(\text{triol})(\text{CH}_3\text{CN})_3^{2+}$, $\text{Ni}(\text{triam})(\text{CH}_3\text{CN})_3^{2+}$, $\text{Ni}(\text{diamol})(\text{CH}_3\text{CN})_3^{2+}$, $\text{Ni}(\text{tren})(\text{CH}_3\text{CN})_2^{2+}$, and $\text{Ni}(\text{trenol})(\text{CH}_3\text{CN})_2^{2+}$. These values are almost certainly the upper limits of the CFAE contribution to ΔH^\ddagger .

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that solvent reorganization outside the first coordination sphere is more highly concerted with the bond breaking process than is the case in the $\text{Ni}(\text{triol})(\text{CH}_3\text{CN})_3^{2+}$ system which has the more positive ΔS^\ddagger value. As these two species are stereochemically similar, it seems that the mechanistic differences must stem from the electron donating characteristics of the polydentate ligands, which firstly are likely to modify the bond breaking contributions²¹ to ΔH^\ddagger and secondly are likely to result in different charge densities of the first coordination sphere which in turn probably produce differing first coordination sphere-solvent interactions.

The directional characteristics of acetonitrile labilization in $\text{Ni}(\text{tren})(\text{CH}_3\text{CN})_2^{2+}$ and $\text{Ni}(\text{trenol})(\text{CH}_3\text{CN})_2^{2+}$ suggest that the contributions to ΔH^\ddagger of the bond breaking process in the nonequivalent sites vary, but unfortunately ΔH^\ddagger values were only obtained for one type of site in each species. Nevertheless support for this supposition may be adduced from the observation of different Ni-NCS distances²² in $\text{Ni}(\text{tren})(\text{NCS})_2$, which may well indicate differing Ni-NCCH₃ distances, with consequently different bond breaking contributions to ΔH^\ddagger , in the acetonitrile analog.^{3, 23}

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(21) This mode of variation of ΔH^\ddagger is contrary to the suggestion (ref 16) that ΔH^\ddagger variation arises mainly from solvent reorganization outside the first coordination sphere. It should be noted, however, that ref 16 deals with $M(\text{solvent})_6^{2+}$.

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Nuclear Magnetic Resonance Studies of Thallium(I)-205 in Aqueous Solution¹

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Abstract: The relaxation (longitudinal and transverse) of thallium(I) ions in aqueous solution is observed to be independent of the resonance frequency, isotopic substitution in the solvent (D_2O for H_2O), the resonant spin (${}^{205}\text{Tl}$ for ${}^{203}\text{Tl}$), the salt concentration, and the nature of the anions. It is, however, very sensitive to dissolved oxygen, and a linear dependence of the relaxation rate on the gas pressure up to 5 atm has been observed. It is concluded that, in oxygen-free solutions, $\text{Tl}(\text{I})$ is dominantly relaxed by the transient spin-rotation interaction and, in oxygenated solutions, by the electron-nuclear dipole-dipole interaction with considerable penetration of the hydration sphere by oxygen. No complex between the thallous ion and oxygen molecules appears to form as there is no appreciable increase in oxygen solubility in aqueous thallous solutions nor is there any appreciable shift in the $\text{Tl}(\text{I})$ resonance when the solutions are oxygenated. Solvent isotope shifts of thallium ions in light and heavy water have been determined. They are, contrary to other systems studied, rather dependent on the salt concentration and the nature of the anions. These observations are interpreted as a differential competition of various anions and solvent molecules in their interactions with the thallium ion.

Gutowsky and McGarvey^{2a} observed the large chemical and concentration shifts of the thallium

resonances in aqueous solutions. In a later study by Freeman, *et al.*,^{2b} a larger range of concentrations and solutions of thallous salts was studied. Chemical shift measurements were also made by Freeman, *et al.*,^{3a}

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